# BLOCK COPOLYMERS

A THESIS

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# PREFACE

Research on the main theme of this thesis began at the University of Birmingham in 1955, under the tutelage of Sir Harry Melville F.R.S. (1)

At this stage of development, most research into block copolymers consisted of devising new methods of synthesis (2) and isolation of the small amounts of the block copolymer from large quantities of homopolymer formed with it. Block copolymers at this point in time were little more than interesting curiosities.

An important advance in block synthesis came with the advent of unterminated anionic polymerization developed by M. Szwarc. The first group of polymers made by this method in this laboratory were examined by a turbidimeter built at Adelaide. (3,4,5,30) This group of block copolymers were of polystyrene and methyl methacrylate. The polymers were characterized by viscosity, osmometry and light scattering methods. (6,7) Thermodynamic and configurational parameters were calculated from the data collected. (6,7)

It was decided at this stage to change to isoprene in place of methyl methacrylate. During this period much of the equipment was renewed, including the vacuum system, osmometer, light scattering photometer and spectrophotometers. Combined with more accurate dispensing methods for monomers, initiators and purging procedures, this resulted in polymer samples with predictable molecular weight, composition and microstructure. (8,9,10,11,25) It was clear that a full scale attack on the problem of solution behaviour could be profitable and that some indication of the type of structures present in the various solvents should emerge. (12,13,14) This work led to the conclusion that a random coil existed in good solvents for both types of segments despite the incompatibility of the homopolymers. This "pseudo-gaussian" structure also appeared plausible in poor solvents for both segment types. (15) The thermodynamic and configurational parameters strongly supported this conclusion.

More recently, some work has been done to supplement the meagre data existing on polyisoprene, (16) and to improve the accuracy of some techniques. (17)

Several years ago it was decided to attempt to elucidate the dependence of solution properties on molecular weight and composition. This work has confirmed preliminary studies and demonstrated that theories devised for homopolymers are applicable with the addition of the composition parameter. (23,24,27)

The interesting phenomenon of intra-molecular phase transition uncovered during this work (18-22) has confirmed the original assumption of the random structure occuring in good solvents. Phase separation seems to be confined to "preferential" solvents. This study has led to an interesting interpretation of the "theta" temperature of block copolymers. (24)

The importance of these materials has been discussed (28,29) and the need for an Institute for Polymer Research in Australia advocated.

Acknowledgement appropriate to the level of help received is given throughout the publications. Some earlier work on miscellaneous topics is included. (31,32,33,34)

The author claims to be the chief architect in this work, but the help received from senior colleague Dr. H.H.G.Jellinek is appreciated and acknowledged. (32,33,34) The material contained therein was presented for the degree of Doctor of Philosophy at the University of Adelaide.

The major contribution appearing in these publications represents a continuous effort by the writer and his students to understand the behaviour of block copolymers in solution and the extent to which theories developed for homopolymers are applicable to these systems.

The advice of my colleagues during this period is acknowledged and warmly appreciated.

# CONTENTS

1. New methods of preparing block copolymers. Allen, Downer, Hastings, Melville, Molyneux, and Urwin. Nature, 177, 910 (1956).
2. The preparation of block copolymer of styrene and methyl methacrylate. Urwin. J. Polym. Sci. 27, 580 (1958).
3. Turbidimetric titrations. Part 1. The automatic turbidimeter. Stearne and Urwin. Makromolek. Chem. 56, 76 (1962).
4. Turbidimetric titrations. Part 11. The titration of polystyrenes in butanone with isopropanol. Urwin, Stearne, Jordan and Mills. Makromolek. Chem., 72, 53 (1964).
5. Solution properties of block copolymers of styrene and methyl methacrylate. Part 1. The preparation, isolation and purification of the block copolymers. Urwin and Stearne. Makromolek. Chem. 78, 194 (1964).
6. Solution properties of block copolymers of styrene and methyl methacrylate. Part 11. Viscosity, osmotic pressure and light scattering studies. Urwin and Stearne. Makromolek. Chem. 78, 204 (1964).
7. Solution properties of block copolymers of styrene and methyl methacrylate. Part 111. Configurational and thermodynamic parameters. Urwin and Stearne. Europ. Poym. J. 1, 227 (1956)
8. The kinetic characterization of the polymerization of isoprene in benzene initiated by butyl lithium as a first step in the synthesis of block copolymers. Cramond, Lawry and Urwin. Europ. Polym. J. 2, 107 (1966).

9 The synthesis of model block copolymers of poly (cis-1,4-isoprene:styrene), Cramond and Urwin. Aust. J. Chem. 21, 1835 (1968).

10 The analysis of butyl lithium at concentrations used in the initiation of polymerization. Urwin and Reed. J. Organomet. Chem. 15, 1 (1968).

11 Molecular weight distributions of block copolymers of poly(isoprene:styrene) by gel permeation chromatography. Cramond, Hammond and Urwin. Europ. Polym. J. 4, 451 (1968).

12 The effect of heterogeneity in composition on the determination of molecular weight distribution of block copolymers by gel permeation chromatography. Urwin and Cramond. Aust.J.Chem. 22, 543 (1969)

13 Solution properties of block copolymers of poly (isoprene:styrene). Part 1. Molecular dimensions by viscosity and light scattering methods. Cramond and Urwin. Europ. Polym. J. 5, 35 (1969).

14 Solution properties of block copolymers of poly (isoprene:styrene). Part 11. Thermodynamic parameters from osmotic data. Cramond and Urwin. Europ. polym. J. 5, 45 (1969).

15 Interactions in block copolymers in solution: the effects of heterocontacts on the segmental interactions in block copolymers of poly(isoprene:styrene) in solution. Urwin. Aust. J. Chem. 22, 1649 (1969).

16 The specific refractive index increments of polyisoprenes in various solvents. Reed and Urwin. Aust. J. Chem. 23, 1743 (1970).

17 Light scattering parameters of block copolymers by application of computer programming. Urwin and Girolamo. Makromolek. Chem. 142, 161 (1970).

18 Anomalous viscosity behaviour of block copolymers as a function of the temperature for two sequence or AB type poly(isoprene:styrene). Girolamo and Urwin. Europ. Polym. J. 7, 693 (1971).

19 Conformational transitions in block copolymers in solution from light scattering data. Girolamo and Urwin. Aust. J. Chem. 24, 729 (1971).

20 Conformational transitions in solutions of block copolymers in mixed solvents. Urwin and Girolamo. Europ. Polym. J. 7, 785 (1971).

21 Intramolecular phase transitions of block copolymers in solution from viscosity-temperature studies. Urwin and Girolamo. Makromolek. Chem.150, 179 (1971)

22 Multiple glass transitions in block copolymer films cast from cyclohexane at two temperatures. Girolamo and Urwin. Europ. Polym. J. 7, 225 (1971).

23 Thermodynamic parameters from osmotic studies on solutions of block copolymers of polyisoprene and polystyrene. Girolamo and Urwin.
Europ. Polym. J. 8, 299 (1972).

24 The configuration of block copolymers of polyisoprene and polystyrene in dilute solution. Part 1. Unperturbed dimensions. Makromolek. Chem.(in press)

25 The preparation and analysis of high purity organolithium initiators. Reed and Urwin.
J. Organometalliic Chem. (in press).

26 Molecular weight distributions of block copolymers by gel permeation chromatography. Urwin and Cirolamo Aust. J. Chem. (in press).

27 The configuration of block copolymers of polyisoprene and polystyrene. Part 11. Molecular dimensions
Girolamo and Urwin. Europ. J. Chem. (in press).

28 The development of polymer science in Australia.
Urwin. Proc. R.A.C.I. July 1970 p185.

29 The new generation of rubbers.
Urwin. Proc. R.A.C.I. Sept. 1971 p257.

30 Molecular weight distributions by turbidimetric titrations. Chap. 18. in Light scattering from polymer solutions. Physical Chemistry Series.
Academic Press. 1972.

31 Studies on bond type in certain cobalt complexes. Part 111. The polarographic reduction of some cobalt inner-complex compounds. Urwin and West.
J. Chem. Soc. 4, 4727 (1952).

32 The hydrolysis of picolinamide and isonicotinamide in concentrated hydrochloric acid solutions.
Jellinek and Urwin. J. Phys. Chem. 57, 900 (1953).

33 Polarography of picolinic and isonicotinic acids and their amides. Jellinek and Urwin.
J. Phys. Chem. 58, 168 (1954).

34 U.V, Absorption spectra and dissociation constants of picolinic, isonicotinic acids and their amides.
Jellinek and Urwin. J. Phys. Chem. 58, 548 (1954).

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# NEW METHODS OF PREPARING BLOCK COPOLYMERS

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IN recent years increasing attention has been given to the problem of the synthesis of block copolymers; that is, of copolymers in which the long-chain molecule contains long sequences of each type of monomer unit, as opposed to the normal copolymer molecule in which the units are distributed quite randomly. The term 'block' copolymer is not standard. We use it to describe linear molecules, whereas branched structures, arising from the attachment of side-chains of one type of monomer unit on to a backbone of the other type, we call 'graft' copolymers.

During the past few years a number of methods for the preparation of block copolymers have been described[1-9]. In most of these methods the yield of block copolymers is small—sometimes of the order of 10 mgm.—and in many cases separation is complicated by the presence of large quantities of other material of high molecular weight. Another complication in some of these systems arises from the difficulty in distinguishing between block and graft copolymer structures. Of all the processes listed above, only that of Woodward and Smets[5] can safely be said to give high yields of an unequivocable block copolymer which may be separated and obtained in a form uncontaminated by homopolymer or graft and random copolymers.

A number of these methods are purely chemical, involving either the use of a bifunctional initiator such as the phthalyl peroxide used by Woodward and Smets, or the introduction of a labile terminal group on to the growing chain by means of a suitable transfer agent such as bromotrichloromethane[2]. Both these methods lead to a homopolymer of the first monomer *A* containing a labile end-group which may be used to initiate polymerization in a second monomer *B*, or to couple with a suitable terminal group in a polymer of *B*. The great advantage of this method is that the first block may be fractionated before proceeding with the second stage, which greatly simplifies the fractionation of the final product. The method described below in which a dihydroperoxide is used to polymerize styrene is of this type. A polystyrene having a terminal hydroperoxide group is obtained, which is fractionated, and fractions having suitable molecular weight are used to polymerize methyl methacrylate.

Alternatively, the block copolymer may be built up in one stage from a continuously growing radical, the change in character of the chain being effected by transferring the radical end from an environment of monomer $A$ to that of monomer $B$. Methods such as that of Hicks and Melville[3], who devised a method by which polymerizing methyl methacrylate or acrylonitrile may be injected into a large excess of styrene, and that of Dunn and Melville[1] in which the growing radical passes through a phase boundary, from, say, styrene in oil phase to acrylic acid in water, may be included in this group. A method is described here which utilizes the trapped radicals remaining in the polymer particles when an emulsion polymerization is taken to completion.

The methods described so far must all lead to block copolymers of the type $A_n.B_m$, or the sandwich-type molecule $A_lB_mA_n$, depending on the relative proportions of the combination and disproportionation radical termination reactions. The third method does not have this limitation. The essence of the method is to rupture the polymer chain by some mechanical method such as mastication[8], ultrasonic irradiation[5,6], or γ-radiation[9]. Such degradation is not accompanied by the depolymerization reaction characteristic of thermal degradation. If two different polymers are degraded together, as described below, a cross-termination of the radicals results in a block copolymer. Alternatively, a polymer $A$ may be degraded in the presence of monomer $B$ as described by Henglein[4].

## The Dihydroperoxide Method

Monomeric styrene was polymerized in bulk using *m* di-(hydroperoxy-*iso*propyl) benzene at 50° C. The polymer formed was freed from initiator by successive precipitations from benzene to methanol. The presence of hydroperoxy groups in the polymer has been demonstrated by the method of Wagner, Smith and Peters[10]. The polymer was then fractionated by a benzene–methanol solvent–precipitant system.

The second stage was carried out in emulsion. The hydroperoxy-ended styrene was dissolved in methyl methacrylate and the solution emulsified with a 'Manoxol O.T.' soap solution. The polymerization was initiated by ferrous ions according to the redox mechanism :

$$R\text{.OOH} + \text{Fe}^{2+} \rightarrow R\text{O}\text{---} + \text{OH}^{-} + \text{Fe}^{3+}$$

The polymerization was carried out under oxygen-free nitrogen at 0° C. In a typical run the total weight of polymer would increase by about 50 per cent.

A turbidimetric titration of a benzene solution of the polymer against methanol revealed the presence of considerable quantities of polymer intermediate in properties between polystyrene and polymethyl methacrylate. The turbidimetric titration technique is described in more detail below.

A full-scale fractionation was carried out using the benzene–methanol system. Nine fractions were taken, and their polystyrene content determined by examination of the absorption maximum at 2620 A. One fraction of 0·58 gm. was found to be pure polystyrene; three fractions, of total weight 2·28 gm., had a styrene content of 82–89 per cent; two fractions, amounting to 0·22 gm., contained 68 and 69 per cent styrene; and the remainder contained 1·39 gm. of polymer containing 8 per cent styrene. It is suggested that the 82–89 per cent styrene fractions arise from polystyrenes containing one hydroperoxide group, whereas the 68 per cent fraction comes from dihydroperoxy-polystyrenes.

## The Emulsion Method

It has been established[11–13] that the site of the reaction in an emulsion polymerization lies in the polymer particles formed in the initial stages. The reaction is maintained by diffusion of monomer and initiator radicals into the particles from the aqueous medium. A large polymer radical cannot diffuse out of its particle into the aqueous phase, so the only way in which it may be terminated is by the diffusion of another initiator radical into the particle. If the generation of initiator radicals is stopped, the polymer radicals unterminated at that stage will remain trapped in the particles even when the polymerization ceases on the exhaustion of monomer. If an emulsion of a suitable second monomer is now added, the new monomer will diffuse to the polymer particles and, in those particles which contain trapped radicals, polymerization will be resumed, yielding block copolymer molecules.

We have used this process to prepare block copolymers of vinyl acetate and methyl methacrylate. Vinyl acetate emulsions stabilized by 'Manoxol O.T.' were irradiated at 20° C. by γ-radiation from a 100-curie cobalt-60 source. The polymerization was followed dilatometrically, and when the process had reached 70 per cent conversion the source was removed. The polymer latex was mixed with a methyl methacrylate emulsion (a manipulative delay of 30 min. usually occurs) and the second stage of the polymerization was followed dilatometrically at 40° C.

The rate of polymerization of vinyl acetate by γ-radiation has been found to be extremely rapid and $G$ values of $10^5$ for monomer conversion have been found. In a typical run using a 20 per cent by volume vinyl acetate emulsion and a dose-rate of $6 \cdot 5 \times 10^{16}$ eV./c.c./min., a rate of conversion of 0·11 gm. monomer per min. was observed in a volume of 12·5 ml. This is equivalent to a $G$ value of 94,500 monomer molecules/100 eV.

The latex formed under such conditions converted

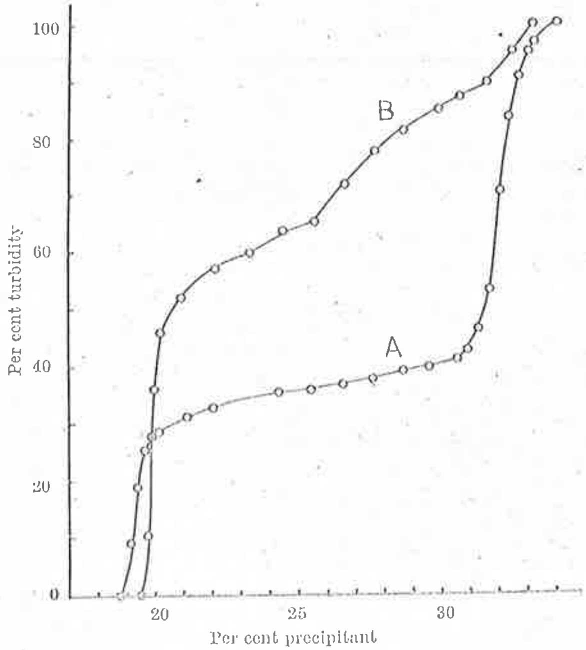

Fig. 1. (*A*) Turbidimetric titration of a solution of polyvinyl acetate and polymethyl methacrylate. (*B*) Turbidimetric titration of a solution containing vinyl acetate-methyl methacrylate block copolymer prepared by the emulsion method

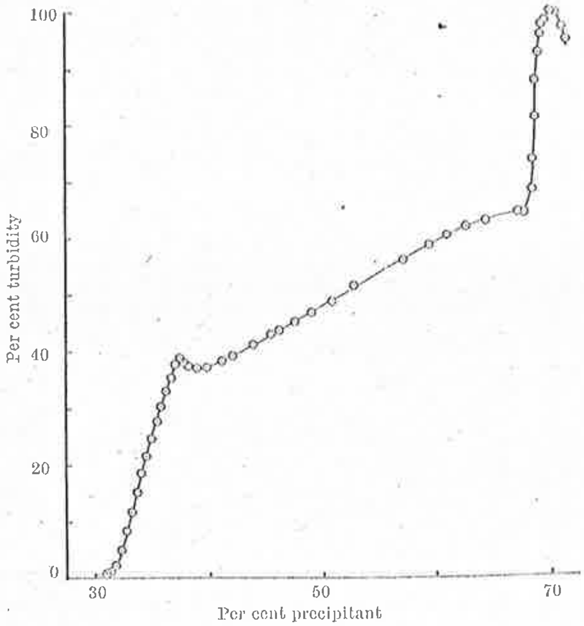

Fig. 2. Turbidimetric titration of a solution of polystyrene and methacrylate after ultrasonic irradiation

a methyl methacrylate emulsion at a rate of about 1 per cent per min.

Turbidimetric titrations were carried out on the polymer produced. This technique has been described elsewhere[14]. It is essentially a titration of a very dilute solution of the polymer (about 5 mgm./100 ml.) against a precipitant, the amount of polymer precipitated at a given point being indicated by the rate of increase in the turbidity of the solution. Curve *A* in Fig. 1 represents a turbidimetric titration of an acetone solution of polyvinyl acetate and polymethyl methacrylate against water. Percentage turbidity, that is, the ratio of optical density to optical density at complete precipitation, is plotted against the percentage of added water. It will be seen that the turbidity increases rapidly between 19 and 22 per cent water and again between 31 and 35 per cent. These steps may be attributed to the precipitation of the polymethyl methacrylate and polyvinyl acetate fractions, respectively.

Curve *B* is a titration of a polymer prepared by the methods described above. A sharp step is again observed between 19·5 and 22 per cent water, so presumably some polymethyl methacrylate is formed, either from hydroxyl radicals trapped in the vinyl acetate latex or from polymerization initiated by heat or a trace of peroxide in the methacrylate emulsion. However, precipitation continues at a steady rate beyond the 22 per cent water point until, in the region of 33 per cent water, the precipitation of large quantities of polyvinyl acetate causes the suspension to coagulate. The titration curve is indicative of a polymer mixture containing large quantities of polyvinyl acetate, a certain amount of polymethyl methacrylate, and a considerable amount of block copolymer varying widely in composition and molecular weight.

## Ultrasonic Method

When a polymer solution is irradiated with ultrasonic waves, degradation occurs under cavitating conditions. It is now established that this occurs with the production of free radicals[15], which are removed presumably by reaction with solvent molecules.

Degradation of polymer in the presence of a second monomer would be expected to result in the formation of a block copolymer, the radicals produced by chain scission initiating polymerization of the monomer. This has been tried successfully for the system polyacrylamide–acrylonitrile[4].

In the method described here, two different polymers are degraded simultaneously in solution, the polymers being chosen so that their radicals combine when they interact. A suitable pair of polymers is polystyrene and polymethyl methacrylate.

Fig. 2 shows the titration of a mixture that had been degraded for 12 hr. This shows a pronounced discontinuity at 37 per cent methanol, and the turbidity increases continuously between this and 68 per cent, at which point polymethyl methacrylate is precipitated. Polystyrene itself is normally precipitated between 31 and 38 per cent methanol. A degraded polystyrene sample is almost completely precipitated at 37 per cent methanol (turbidity, 90 per cent), and polymethyl methacrylate does not begin to precipitate until about 68 per cent methanol. With an undegraded mixture of the two polymers, the curve shows a horizontal portion between the precipitation limits of the two polymers. The central portion of the curve thus represents a third molecular species present in the mixture—in this case a block copolymer formed by cross-termination of the radicals. Its structure would probably be of the 'sandwich' type, since when any copolymer is formed it can undergo further degradation. The copolymer appears to have a wide distribution of molecular weight, but this is expected since ultrasonic degradation is a random process, and radicals produced will have a wide range of sizes. Secondary copolymer degradation will also complicate the picture.

[1] Dunn, A. S., and Melville, H. W., *Nature*, 169, 699 (1952).

[2] Dunn, A. S., Stead, B. D., and Melville, H. W., *Trans. Farad. Soc.*, 50, 279 (1954).

[3] Hicks, J., and Melville, H. W., *Proc. Roy. Soc.*, A, 226, 314 (1954).

[4] Henglein, A., *Makromol. Chem.*, 14, 128 (1954).

[5] Woodward, A. E., and Smets, G., *J. Polymer Sci.*, 17, 51 (1955).

[6] Melville, H. W., *Trans. Plastics Inst.*, 23, 146 (1955).

[7] Bamford, C. H., and Jenkins, A. D., *Nature*, 176, 78 (1955).

[8] Angier, D., and Watson, W. F., *J. Polymer Sci.*, 18, 129 (1955).

[9] Ballantine, D. S., Mesrobian, R. B., and co-workers, *J. Polymer Sci.*, 19, 219 (1956).

[10] Wagner, C. D., Smith, R. H., and Peters, E. D., *Anal. Chem.*, 19, 976 (1947).

[11] Harkins, W. D., *J. Amer. Chem. Soc.*, 69, 1428 (1947).

[12] Smith, W. V., and Ewart, R. H., *J. Chem. Phys.*, 16, 592 (1948).

[13] Smith, W. V., *J. Amer. Chem. Soc.*, 70, 3695 (1948).

[14] Melville, H. W., and Stead, B. D., *J. Polymer Sci.*, 16, 505 (1955).

[15] Henglein, A., *Makromol. Chem.*, 15, 188 (1955).

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$$\begin{array}{rcl}
\mathrm{ClO_2 + SO_3^{2-}} & \rightarrow & \mathrm{ClO_2^- + SO_3^-} \\
\mathrm{ClO_2^- + H^+ \rightarrow HClO_2} & \rightarrow & \mathrm{ClO^+ + OH^-} \\
\mathrm{ClO^+ + SO_3^{2-}} & \rightarrow & \mathrm{ClO + SO_3^-} \\
\mathrm{ClO + SO_3^{2-}} & \rightarrow & \mathrm{ClO^- + SO_3^-} \\
\mathrm{ClO^- + H^+ \rightarrow HClO} & \rightarrow & \mathrm{Cl^+ + OH^-} \\
\mathrm{Cl^+ + SO_3^{2-}} & \rightarrow & \mathrm{Cl + SO_3^-} \\
\mathrm{Cl + SO_3^{2-}} & \rightarrow & \mathrm{Cl^- + SO_3^-} \\
\mathrm{6(SO_3^- + H^+} & \rightarrow & \mathrm{HSO_3)} \\
\hline
\mathrm{ClO_3^- + 6H_2SO_3} & \rightarrow & \mathrm{Cl^- + 3H_2O} + \mathit{6HSO_3}\mathrm{(3H_2S_2O_6)} \quad (\mathrm{I}a)
\end{array}$$

lässt unmittelbar *Herkunft und Natur entstehender Radikale* erkennen: Es sind gewissermassen die "Bruchstücke" von Dithionsäure

$$\mathrm{H_2S_2O_6 \rightarrow 2HSO_3}$$

richtiger ausgedrückt, ihre sie bildenden Komponenten, die in den *HSO₃-Radikalen dem ClO₃⁻-H₂SO₃-System die Fähigkeit verleihen, zu polymerisieren.*

Verläuft bei Ausschluss solchen polymerisierenden $HSO_3$-Verbrauches die anschliessende Oxydation zu Schwefelsäure

$$\mathrm{6HSO_3(3H_2S_2O_6) + ClO_3^- + 3H_2O \rightarrow 6H_2SO_4 + Cl^-} \qquad (\mathrm{I}b)$$

$$^1/_2((\mathrm{I}a) + (\mathrm{I}b)) = (\mathrm{I})$$

wie wohl anzunehmen ist, nach analogem Mechanismus—unter "Ersatz" von $SO_3^{2-}$ durch $SO_3^-$ und von $SO_3^-$ durch $SO_3$, so kommt es nicht zu weiterer Radikalenbildung. Eine detaillierte Diskussion der durch das hier in Rede stehende System eingeleitenten Polymerisation liegt, soweit mir bekannt, noch nicht vor; sollten, wie die Autoren vermuten, auch OH-Radikale im Spiele sein, so wäre dies ein Hinweis auf Mechanismen andersartiger Gestaltung, z.B. mit Schritten, an denen das Lösungsmittel Wasser beteiligt wäre, doch liegt hierfür zur Zeit ein Anhaltspunkt nicht vor.

## Ammerkungen

1. U.S. Patente 2,673,192 (1954); 2,751,371 (1956). W. M. Thomás, E. H. Gleason, und G. Mino, *J. Polymer Sci.*, **24,** 43 (1957).
2. *Kinetics of the Chlorate Sulfite Reaction, J. Phys. Chem.*, **61,** 447 (1957).
3. Die auf Austauschreaktion mittels Sauerstoffisotops sich gründende Ansicht von J. Halperin und H. Taube (*J. Am. Chem. Soc.*, **72,** 3319 (1950)), wonach die bezüglichen Ergebnisse für diesen schrittweisen Reaktionsweg sprechen, halte ich nicht für schlüssig.
4. *J. Am. Chem. Soc.*, **54,** 4606 (1932).
5. Siehe etwa *Monatsh. Chem.*, **79,** 178 (1948); **80,** 122 (1949); *Helv. Chim. Acta*, **33,** 785 (1950).
6. Entsprechend: $\mathrm{HClO_2 \rightleftharpoons ClO_2^- + H^+ \rightleftharpoons ClO^+ + OH^-}$.
7. Siehe etwa Don M. Yost und H. Russell, Jr., *Systematic Inorganic Chemistry*, Prentice-Hall, New York, 1944, p. 358.
8. Die Pfeile → bedeuten lediglich Reaktionsrichtung ohne Rücksichtnahme auf allfällige Gegenreaktionen und Gleichgewichte.

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# *The Preparation of Block Copolymer of Styrene and Methyl Methacrylate*

Hydroperoxide initiators have been used previously in the preparation of block copolymer.[1,2] The dihydroperoxide of di-isopropyl benzene was used in both cases. The author used the meta compound in a bulk polymerization of styrene in which one of the hydroperoxide groups was found to remain undecomposed and therefore available as an initiating center in an emulsion-type polymerization.

In order that the solution properties of block copolymers might be examined, it is highly desirable that a model polymer be prepared containing, say, two single "blocks" thus:

AAAAAAABBBBBBBBB

where the degree of polymerization of each block is known. This was attempted in the preparation described above by taking a narrow fraction of the polystyrene prepared in the first stage. The emulsion step would then yield a polymer in which one part of the chain contains a narrow distribution and to which is added a normal distribution of the second block. Such a polymer is amenable to fractionation, so that it should be possible to isolate several fractions containing various chain lengths of the second block for a given chain length of the first block.

The preparation described previously[1] suffers from the disadvantage that the polystyrene formed contains both monohydroperoxide and dihydroperoxide ended polymer, the latter being present to about 25%. This is due to the normal termination process, which for polystyrene is almost entirely by combination. A method has been devised in which the dihydroperoxide can be almost eliminated and yielding the monohydroperoxide ended polymer.

Styrene was polymerized in bulk, initiated by di-isopropyl benzene monohydroperoxide, with the use of cumenyl mercaptan as transfer agent. It was found that the viscosity molecular weight was reduced from 83,000 to 28,000 when compared with a blank experiment containing no mercaptan. This means, in effect, that $^5/_6$ of the polymer formed was chain terminated by a cumenyl group. This ratio, of course, can be increased by the use of larger amounts of mercaptan, and further, this step may be carried out as an emulsion polymerization, thereby eliminating initiation by the hydroxyl radical.

In these experiments 1.5 g. mercaptan and 0.5 g. peroxide were dissolved in 25 ml. styrene and the solution polymerized at 60°C. for 24 hours. The polymer solution was mixed with benzene and sprayed into methanol by the Sprühdüse technique.[3] The precipitation was repeated twice.

Metz and Mesrobian,[4] in branching experiments, have shown that isopropylated polystyrene forms good yields of hydroperoxide by oxidation of the isopropyl group with molecular oxygen in cumene solution, whereas polystyrene remains unchanged. This method was adopted to oxidize the cumenyl groups terminating the polystyrene formed above. A 1% solution of the cumenyl ended polymer was heated to 80° in cumene, and oxygen was bubbled through the solution for 8 hours. The polymer was again precipitated into methanol and the precipitation repeated three times to eliminate any hydroperoxide of the cumene which might have been adsorbed. A large excess of methanol was used each time.

The peroxidic polymer was employed as initiator in an emulsion type polymerization of methyl methacrylate using $\text{Fe}^{\text{II}}$ pyrophosphate complex and Teepol as emulsifier at room temperature. A threefold increase in weight was obtained. The final polymer was again subjected to several precipitations and dried on the high vacuum line. The styrene content was determined by measuring the molecular extinction at 2620 A.U. as described by Dunn, Stead, and Melville.[5] The polymer contained 28% polystyrene.

It could be expected that the final product would contain some residual polystyrene and probably polymethyl methacrylate along with "block" copolymer of the simple model type "A.B." In this preliminary investigation the fractionation step was eliminated but in subsequent preparations a narrow fraction will be used.

The examination of reaction mixtures for evidence of block copolymer formation by turbidimetric titration has been described.[6] The polymer formed in these experiments was examined by this method. The instrument used was a Zeiss Turbidimeter in which light scattered at 45° from the turbid solution is compared with that from a standard opalescent plate. Mixtures of polystyrene and polymethyl methacrylate were examined in this instrument and found to behave in a manner which indicated that the turbidity followed the same course as the equivalent solutions of the separate polymers. On the other hand, an entirely different behavior was observed with the mixture of homopolymer and block copolymer, indicating the presence of an entirely new species.

### References

1. P. E. M. Allen, J. M. Downer, G. W. Hastings, H. W. Melville, P. Molyneux, and J. R. Urwin, *Nature,* **177,** 910 (1956).
2. R. J. Orr and H. L. Williams, *Am. Chem. Soc.*, **79,** 3139 (1957).
3. R. Schulz and A. Sabel, *Macromol. Chem.*, **14,** 115 (1954).
4. D. J. Metz and R. B. Mesrobian, *J. Polymer Sci.*, **16,** 346 (1955).
5. A. S. Dunn, B. D. Stead, and H. W. Melville, *Trans. Faraday Soc.*, **50,** 279 (1954.)
6. H. W. Melville and B. D. Stead, *J. Polymer Sci.*, **16,** 505 (1955).

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## *Sur la détermination de la fonction de distribution en masse d'un échantillon de dextrane par sédimentation et diffusion de translation*

L'une des méthodes classiques pour obtenir la distribution des masses moléculaires d'un polymère en solution, consiste à représenter la courbe de distribution en poids

$$F(M) = dc/dM$$

par une fonction à deux ou trois paramètres qu'on peut ensuite déterminer à partir des différentes moyennes obtenues sur la masse moléculaire ou sur toute grandeur physique reliée à la masse d'une façon biunivoque.

Nous avons montré[1,2] que l'emploi de la méthode de Scheibling dans l'étude de la diffusion de translation conduit à trois valeurs moyennes $D_1$, $D_2$, $D_3$ de la constante de diffusion.

A partir des rapports $D_1/D_2$, $D_2/D_3$ et de la valeur de $\alpha$ intervenant dans la relation $D = KM^{-\alpha}$, on peut choisir parmi les fonctions de distribution à deux paramètres celle qui convient le mieux et en déterminer la largeur.

Sur la figure 1 nous avons porté les valeurs de ces deux rapports, calculés pour $\alpha = {}^1/_2$, en fonction de $M_w/M_n$ et dans les deux cas classiques: distribution de Lansing et Kraemer (LK) et distribution de Zimm (Z).

Par conséquent une mesure de diffusion brownienne et une mesure de $M_n$ ou $M_w$ permettent de choisir et de déterminer $F(M)$.

Dans notre travail nous avons appliqué cette méthode à un échantillon de dextrane et nous l'avons confrontée avec des mesures de sédimentation.

L'échantillon de dextrane (produit par Leuconostoc Mesentéroïdes NRRL B 512) aimablement mis à notre disposition par le Senti de la Northern Utilization Research Branch, a été étudié en solution aqueuse à 20°C.

Nous avons trouvé:

$$D_1 = 3{,}64.10^{-7}; \qquad D_2 = 3{,}44.10^{-7}; \qquad D_3 = 3{,}41.10^{-7}$$

c'est-à-dire les rapports $D_1/D_2 = 1{,}06$ et $D_2/D_3 = 1{,}07$.

Ceci conduit pratiquement, quel que soit le type de distribution et pour des valeurs de $\alpha$ voisines de 0,5, à $M_w/M_n = 1{,}3$. Un tel résultat est en désaccord avec la valeur de 1,77 obtenue à partir des mesures de $M_w$ par diffusion de la lumière ($M_w = 80\,000$) et de $M_n$ par pression osmotique et dosage de bouts de chaîne ($M_n = 45\,000$).

L'écart ne pouvant s'expliquer ni par les erreurs de mesure ni par l'incertitude sur la valeur de $\alpha$, nous avons complété nos résultats par des mesures de vitesse de sédimentation.

A partir de la constante de sédimentation l'on peut définir deux masses moyennes $M_1$ et $M_2$ par les relations classiques

$$M_1 = RTs/D_1(1 - \bar{V}\rho); \qquad M_2 = RTs/D_2(1 - \bar{V}\rho)$$

$\bar{V}$ étant le volume spécifique du soluté et $\rho$ la densité du solvant.

En supposant que la constante s corresponde à la valeur la plus probable il est possible de calculer $M_1$ et $M_2$, toujours dans le cas d'une distribution à deux paramètres (LK et Z) et nous avons représenté sur la figure 2 les variations des rapports $M_1/M_w$ et $M_2/M_w$ en fonction de $M_w/M_n$.

A partir des valeurs expérimentales $s_{20}{}^\circ = 3{,}33.10^{-13}$ $\bar{V} = 0{,}60$ on obtient $M_1 = 55\,000$, $M_2 = 58\,000$ et par suite $M_1/M_w = 0{,}67$ et $M_2/M_w = 0{,}71$.

Ceci conduit à admettre pour $F(M)$ une distribution de Lansing-Kraemer correspondant à $M_w/M_n = 1{,}75$ en excellent accord cette fois avec la valeur expérimentale. La

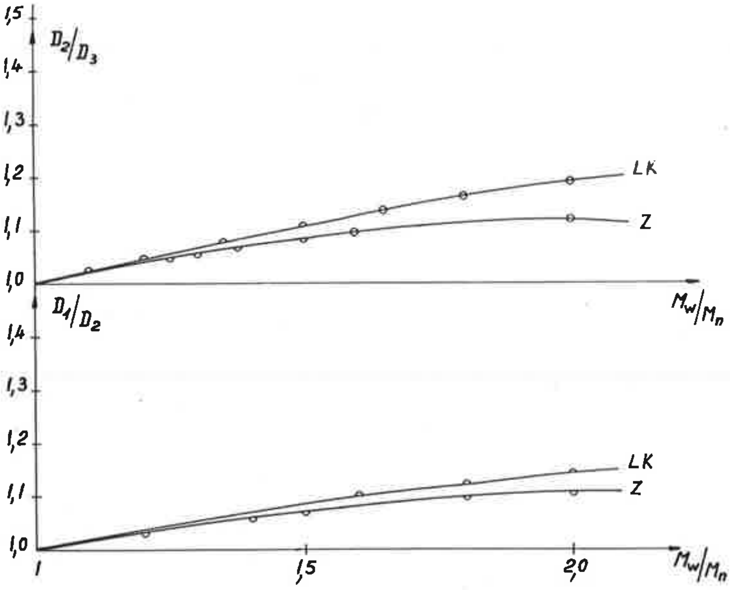

Fig. 1. Variation des rapports $D_1/D_2$ et $D_2/D_3$ en fonction de $M_w/M_n$ pour la distribution de Zimm (Z) et celle de Lansing-Kraemer (LK) ($\alpha = 0{,}5$).

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# Turbidimetric Titrations

## Part I. The Automatic Turbidimeter

by

JOHN MCKENZIE STEARNE and JACK ROBSON URWIN

HÜTHIG & WEPF VERLAG · BASEL

SUMMARY:

A turbidimetric titration apparatus is described for the automatic recording of transmitted and scattered light. The construction of the instrument is based upon the usual principles of light-scattering apparatus but includes a number of new features. The instrument employs A.C. amplifiers and measures automatically and continuously the transmission and the scattering at angles of 45, 90 and 135° to the incident beam. Provision has also been made for checking the linear operating characteristics of the instrument.

ZUSAMMENFASSUNG:

Ein Trübungstitrierapparat für die automatische Messung des durchgehenden und gestreuten Lichtes wird beschrieben. Der Plan des Gerätes beruht auf den üblichen Prinzipien der Streulichtphotometer, aber er enthält mehrere neuartige Verbesserungen. Das Instrument verwendet Wechselstromverstärker und mißt automatisch und kontinuierlich die Streuung bei Winkeln von 45, 90 und 135° relativ zum einfallenden Strahl. Es besteht die Möglichkeit, die Linearität der Charakteristik des Apparates zu prüfen.

## *Introduction*

Turbidimetric titrations have been used previously to determine the molecular weight distribution of high polymers[1-4)] and for the characterization of block and graft copolymers[5-7)]. For the latter purpose the measurement of the intensity of the transmitted light is usually employed and instruments designed specifically for this determination do not give the scattering pattern. For the determination of molecular weight distribution, however, it is necessary to measure the intensity of both the transmitted light and of the scattered light at fixed angles[9,3)]. Such instruments have the wider application to polymer systems and are thus to be preferred. The instrument described below has therefore been modelled on the usual principles of light-scattering apparatus for the determination of molecular weight and molecular weight distribution and employs a photomultiplier coupled with a suitable mirror optical system for the measurement of the scattered-light at three fixed angles.

It has recently been pointed out [10)] that it is essential, when determining the intensities of scattered light, that experimentally reproducible results be obtained and that resort is not made to a normalising procedure which may reduce the apparent error. To achieve reproducibility one must be able to correct for optical effects, dilution, and changes in the scattering pattern. Furthermore, it is necessary to control accurately, the rate of addition of the non-solvent, the temperature and the rate of stirring, and to be able to observe the scattering pattern during titration.

The instrument to be described has been designed to work with quite dilute solutions so as to avoid the effects of multiple scattering and aggregation. The cell design has been based upon the need to maintain temperature equilibrium and to eliminate internal reflections. The amplifiers are relatively simple and the mirror optical system avoids the use of three separate photomultipliers in the measurement of the intensity of the scattered light.

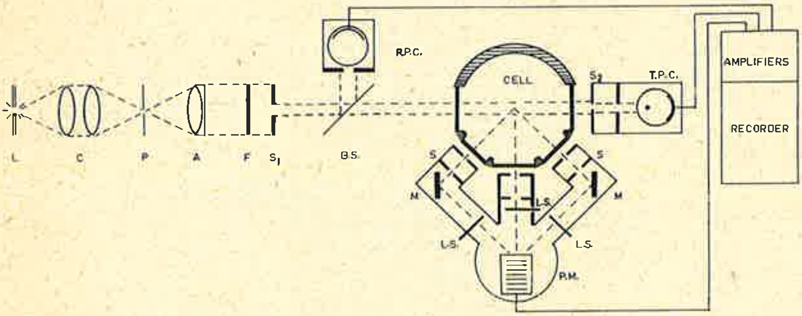

Fig. 1. Diagrammatic layout of the instrument. L, light source; C, condenser lens; P, pinhole; A, achromat lens; F, Zeiss monochromatic filter; S, $S_1$, $S_2$, slits; B.S., beamsplitter; R.P.C., reference photocell; T.P.C., transmission photocell; M, mirrors for deflecting the scattered light at 45 and 135° to photomultiplier; P.M., photomultiplier (11 stage E.M.I. 6097B); L.S., electrically operated light stops

## *Description of the Instrument*

The layout of the instrument is shown in Fig. 1. The light source is a 250 watt ME/D box-type mercury arc lamp (British Thomson Houston) operating on 250 volts A.C. mains supply. These lamps show considerable variation in intensity and the arc is subject to "hot-spotting". To overcome this problem a beam-splitter is employed in which a portion of the incident beam is deflected and allowed to fall onto a reference photocell, which in turn controls the slide-wire voltage of the recorder. The efficiency of this system was checked by rapidly varying the voltage applied to the lamp and observing the output voltage from the transmission photocell. It was found that there was no observable change with fluctuations in voltage up to 10 %.

Collimation is achieved by adjusting the condenser lens C, so that the image of the arc is in the plane of the pin-hole P. A mirror is placed in front of the achromat lens A and the lens adjusted to bring the reflected image into the plane of the pin-hole. It was found that a good parallel beam resulted. The beam is then cut to 2.5 mm. · 12 mm. by the slit $S_1$. The dimensions of the accepted transmission beam are 2.0 mm. · 10 mm. and the accepted scattered beam is 1.5 mm · 10 mm. The filters F are Zeiss monochromat glass filters for use with mercury and helium light. They are made from several optically constant glasses cemented together

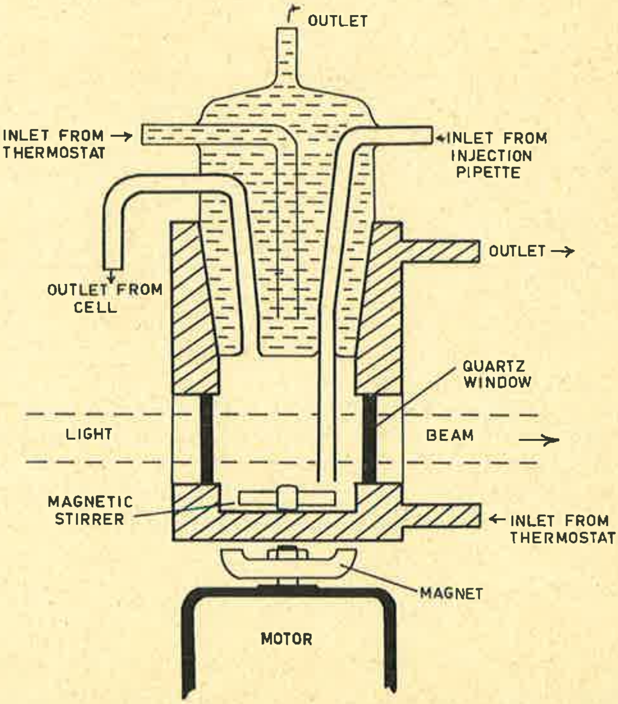

Fig. 2. The constant volume cell fitted with thermostated glass-head

with Canada balsam. They transmit a particular wavelength with negligible amounts of unwanted radiation. Gelatine filters were found to be unsatisfactory.

The open type of cell has several disadvantages, notably its large capacity, and the difficulty of maintaining proper temperature equilibrium. The totally enclosed constant volume cell described by OTH and DESREUX[3)] was therefore adopted.

The cell has been fabricated from brass with optically flat quartz windows set in WOODS metal. The inner surface is finished in matt black nickel to avoid stray reflected radiation. A water jacket is included in the walls and the base of the cell and also in the glass-head as shown in Fig. 2. The metal cell ensures rapid temperature adjustment and the thermostat maintains the temperature of the cell to within ± 0.02 °C. during a titration. The volume of the cell was taken as the volume with the magnetic stirrer in position, the capillary of the delivery tube sealed off and liquid up to the outlet opening in the glass head. The actual volume (55.90 ml.) was determined by direct weighing.

The intensity of the transmitted beam is measured by the photocell, T.P.C. (Fig. 1). The scattered intensities at the fixed angles 45, 90 and 135° are measured by the photomultiplier, P.M. (Fig. 1). The scattered intensities are reflected by mirrors to the cathode of the photomultiplier. Rotation of the cathode about the vertical axis produced no change in the output voltage.

A Cambridge multipoint model D.E. recorder which had been modified to suit the amplifiers was used to record the data. Chart speeds from $^1/_2''$

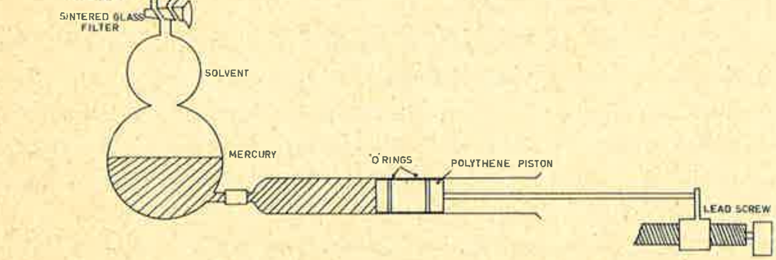

Fig. 3. The injection pipette

to 12″ per hr. can be used. The A.C. amplifiers were designed and built by the Electronics Instrument and Lighting Co., Adelaide, South Australia.

The injection pipette (Fig. 3) was constructed from 1″ diameter precision bore glass tubing. The plunger is polythene and is operated by a motor-driven lead screw. The plunger forces mercury into the vessel containing non-solvent and since it is important that there should be no back-leakage the plunger is fitted with two rubber "0" rings. In two years of operation no loss of mercury has been observed.

A variable speed motor allows a choice of the rate of addition of non-solvent to be made. Speeds corresponding to a rate of addition between 0.010 and 0.225 ml./min. have been employed. A pin on the lead screw operates a limit switch to the relay mounted on the recorder. The relay in turn lifts a pen running on the side of the recorder chart. This allows the volume of non-solvent added to be accurately recorded. One turn of the lead screw is equivalent to 0.651 ml. The volume delivered at various numbers of turns compared with the calculated volume showed a maximum error of 0.25 %.

### *The Principle of Operation and Calibration*

Calibration of the transmitted light is carried out by setting the recorder at 100 % transmission with solvent in the cell and at 0 % with the light beam extinguished. The transmitted light falls onto the photocell, the output of which is amplified and the signal fed to the recorder. The beam splitter, BS (Fig. 1), deflects a portion of the beam onto the reference photocell and the output of this is used to develop the slidewire reference voltage in the recorder. Any change in intensity of the incident light thus affects both signal and reference voltage by the same ratio and therefore is not recorded, provided that (a) the change in light intensity does not exceed the working range of the system and (b) the optical system is properly adjusted.

The scattered light is similarly recorded except that, in this case, a photomultiplier coupled with suitable mirror optics is used. Primary calibration is effected by using a reference scattering medium such as a perspex block or diluted colloidal silica solution of known turbidity. It is always necessary to use turbidities of the same order as the solutions to be measured. Controlled relays (L.S. Fig. 1) energized by a switch mounted on the pen mechanism of the recorder allow the instrument to plot successively the scattered light at 45, 90 and 135° to the incident beam. The switch sequence has been arranged to record the following data successively: transmission, 45°, transmission, 90°, transmission, 135°. This tequence was adopted to allow the maximum time between successive scattered light readings in order to permit the associated amplifier system so reach a steady state value before recording the response.

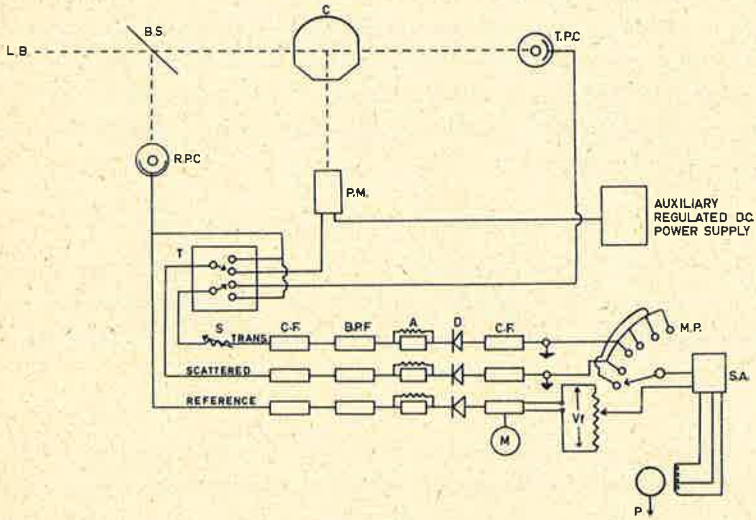

Fig. 4. Diagrammatic sketch of the amplifier and recording system. L.B., light beam; B.S., beam splitter; C, light-scattering cell; T.P.C., transmitted photocell; R.P.C., reference photocell; P.M., the photomultiplier; T, the test mechanism; S, the gain switch for the transmitted channel; C.F., cathode follower; B.P.F., band pass filter; A, small amplifier circuit; M, metering system showing linear operating range of the equipment; $V_f$, voltage from reference photocell fed to slide-wire of recorder; M.P., multipoint switch in recorder; S.A., servo-amplifier; P, multipoint recording pen

To avoid the effects of drift in the amplifier system, the 100 cycle per second (c/s) alternating component of the light beam has been used. The output from the incident light photocell (R.P.C. Fig. 4) feeds a parallel-T band pass filter centred on 100 c/s *via* a cathode follower. The output from the filter is further amplified and fed to a detector from which is derived a D.C. voltage proportional to the intensity of the incident light. This D.C. output from the detector is coupled to the recorder by a cathode follower stage and incorporates controls which set up the operating conditions for the instrument and provide the slide-wire reference voltage. A metering system shows the linear operating range of the equipment enabling the operator to ensure that the equipment is in adjustment and that sufficient light is present in the system. A further check on the performance of the system can be made by connecting either the scatter or the transmission channel in parallel with the reference channel, whence a fixed ratio of the two should be obtained on the recorder.

The transmitted and scattered component amplifier and detector chains are identical with the reference channel so that as far as is possible, amplifier characteristics are eliminated from the measurements. The amplifier equipment incorporates regulated power supplies, and sufficient negative feed-back has been included to achieve acceptable linearity. The general arrangement of the complete system is shown in Fig. 4. A detailed account of the electronics has not been included here but will be published elsewhere.

### *The Constant Volume Cell and Dilution Correction*

Whatever the type of cell used, the measured turbidity must be corrected for dilution. It is usual to express the composition of the suspending medium in terms of the function $\gamma$, defined by the relation,

$$\gamma = \frac{V}{V_0 + V} \tag{1}$$

where V is the volume of non-solvent added in the mixture and $V_0$ is the original volume of solution. In the constant volume cell, $\gamma$ does not change according to equation (1) since the same volume increment of solution is ejected as is added. The correct relationship has been established by **Bischoff** and **Desreux**[9)] as follows. If the system has the composition $\gamma$ and a volume of non-solvent dV is added to the constant volume cell of volume $V_0$, then a volume increment $\gamma dV$ is ejected from the cell and the actual increase in volume of non-solvent is given by,

$$\begin{aligned} dV_P &= dV - \gamma dV \\ &= dV(1-\gamma) \end{aligned}$$

The change in $\gamma$ is

$$d\gamma = \frac{dV_P}{V_0} \qquad = dV\left(\frac{1-\gamma}{V_0}\right)$$

On integration

$$V = -V_0 \ln(1-\gamma)$$

or

$$\frac{V}{V_0} = -\ln(1-\gamma) \tag{2}$$

Because of the addition of non-solvent, the solution in the constant volume cell is diluted. If $C_0$ is the original concentration, then the concentration C at a particular value of $\gamma$ is given by,

$$C = C_0(1-\gamma) \tag{3}$$

If the Beer-Lambert law holds then $\tau$ (turbidity) is proportional to C (concentration) and equations (2) and (3) may be combined so that,

$$\frac{V}{V_0} = -2.3 \log \frac{\tau}{\tau_0} \tag{4}$$

The turbidity and the volume of addition of solvent or non-solvent can be measured directly from our instrument. Thus a plot of $V/V_0$ *vs.* $-\log \tau/\tau_0$ should give a straight line of slope 2.3. We have verified equation (4) experimentally by diluting a solution of $4 \cdot 10^{-4}$ % fluorescein and also an approximately 0.5 % solution of colloidal silica. The results are shown in Fig. 5. Good agreement over a considerable range of $\gamma$ was obtained.

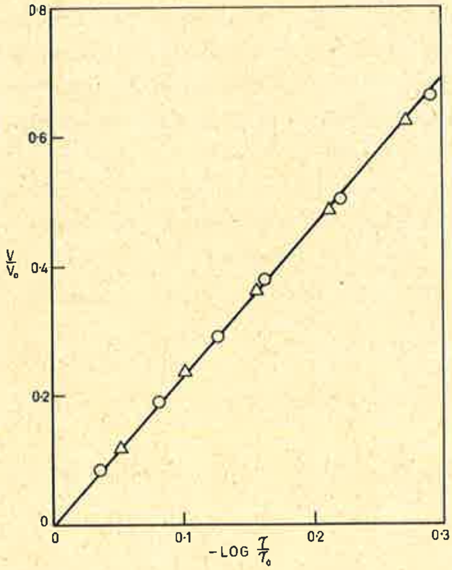

Fig. 5. Plot of $V/V_0$ *vs.* $-\log \tau/\tau_0$. The solid line is the theoretical slope 2.3, (△) fluorescein, (○) colloidal silica

We have also checked the effect of the rate of addition of non-solvent on equations (2) and (3) and find that there is no observable difference over the range of addition rates employed.

### *The Measurement of Turbidity*

Oth and Desreux[3)] have shown that it is necessary to take into account the intensities of both the scattered and transmitted light, since during a titration the light incident to the scattering volume decreases as the solution becomes more turbid. However, if the scattering volume is at the centre of the cell and the light path in the 90° direction is equal to one half the length of the cell, then

$$i^*_{90}/I^*_0 = (i_{90}/I_t)_{\text{measured}}$$

where $i^*_{90}$ is the intensity of the scattered light at 90° and $I^*_0$ is the intensity of the light incident upon the scattering volume. $i_{90}$ and $I_t$ are the measured intensities of the scattered and transmitted light.

Calibration of the transmission was achieved by measurement of turbidities defined by,

$$I = I_0 e^{-\tau L}$$

for solutions of colloidal silica at various concentrations and at several wavelengths. These values were compared with those obtained using a Unicam photo-electric absorptiometer, and the agreement was found to be very good. The colloidal silica was firstly diluted to approximately 3 % with water, centrifuged at 13,000 R.P.M. for 2 hrs. to remove dust and large aggregates, and then diluted to required values of turbidity. The results obtained from our instrument are shown in Fig. 6. The absolute concentrations were not determined, but have been expressed on a relative scale, in which the stock solution is put as being unit concen-

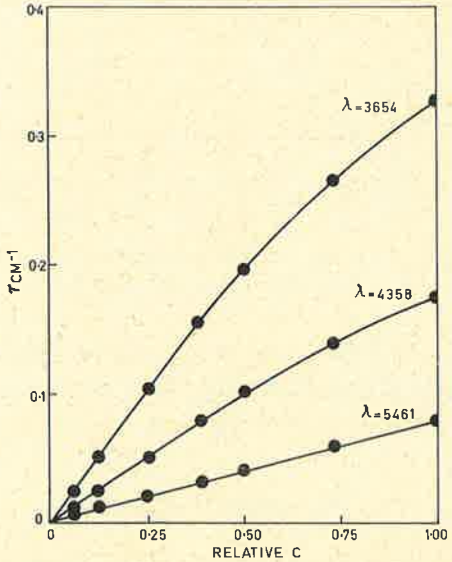

Fig. 6. Turbidity ($\tau$ cm$^{-1}$) *vs.* relative concentration for colloidal silica. Turbidities have been measured on the turbidimeter at 3654, 4358 and 5461 Å

tration. At levels of high turbidity the **Beer-Lambert** law is not obeyed, however within the limits of turbidity normally encountered ($\tau\,\mathrm{cm}^{-1} < 0.1$) there is a linear relationship.

Colloidal silica was also used to calibrate the scattered light, since it has been shown to exhibit no selective absorption and negligible dissymmetry and depolarization[11].

The calibration constant is defined by the expressions

$$\tau = C \cdot S_{90} = 2.303\ D/L$$

where C is the calibration constant, $S_{90}$ is the reading at 90° recorded on the chart, D is the optical density of the solution obtained from transmission measurenents and L is the length of the cell in cm. Before calibration could be effected, however, corrections had to be made to the measurement of the intensity of the scattered light at 45, 90 and 135°. These corrections had to be applied to ensure that the three mirror systems which reflect the scattered light to the photomultiplier were each equivalent. The light scattering cell was filled with dilute colloidal silica and the photomultiplier assembly rotated to bring the 45° lightpath into the 90° position. The process was repeated for the 135° position. The ratio of the 45 and 135° readings to that at 90° was then applied as a correction. It was found that the correction factor at 45° was 1.43, and that at 135°, 1.56. To test the validity of these corrections several solutions of colloidal silica of differing turbidity were placed into the light scattering cell. The intensities of the scattered light were recorded and corrected for volume and polarization effects. The results of a typical experiment are shown in Table 1.

Table 1. $i \cdot \frac{\sin\Theta}{1+\cos^2\Theta}$ calculated for the three angles 45, 90 and 135° from measurements on colloidal silica at $\lambda = 4358$ Å · i is the percentage intensity of the scattered light as read from the recorder chart

| Angle ($\Theta$) | 45° | 135° | 90° |
|---|---|---|---|
| Measured Intensity (i) ..... | 24.50 | 22.50 | 16.50 |
| Corrected (i) .............. | 35.04 | 35.10 | 16.50 |
| $i \cdot \frac{\sin\Theta}{1+\cos^2\Theta}$ .............. | 16.50 | 16.53 | 16.50 |

The results also indicate that the cell design and the geometry of the optical system are satisfactory.

The turbidity measured by transmission should be related to the ratio of the intensity of the scattered light at 90° and the intensity of the transmitted light for a symmetrical scattering medium such as colloidal silica. The relationship between $(i_{90}/I_t)_{\text{measured}}$ and turbidity has been checked and a linear relationship does exist at low turbidity values as shown in Fig. 7.

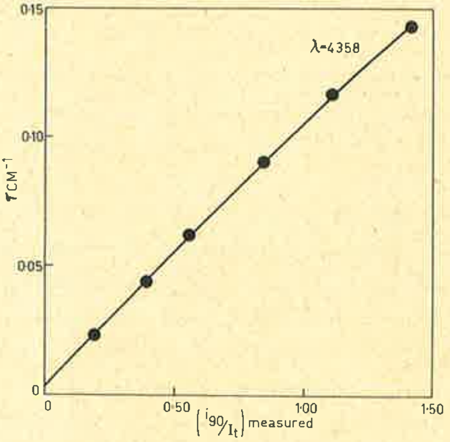

Fig. 7. $(i_{90}/I_t)_{\text{measured}}$ plotted against the turbidity ($\tau$) for colloidal silica at $\lambda = 4358$ Å

In checking this relationship it was found necessary to correct the measured values for differences in the spectral response of the photomultiplier and the photocell. It was also necessary to take into account the voltage dependence of the photomultiplier channel and to calibrate the recorder scale setting accordingly.

## *Acknowledgements*

The authors would like to thank Professor D. O. Jordan for helpful discussion, Dr. W. G. P. Robertson, Weapons Research Establishment, Salisbury, South Australia, for the construction of the light-scattering cells used and Messrs. A Wood and I. Wall for their advice during the construction of the electronic equipment. One of us (J. McK. S.) wishes to record his thanks for the award of a Commonwealth Post-Graduate Research Scholarship.

1) D. R. Morey and J. W. Tamblyn, J. appl. Physics **16** (1945) 419.

2) A. Oth, Bull. Soc. chim. belges **58** (1949) 285.

3) A. Oth and V. Desreux, Bull. Soc. chim. belges **63** (1954) 261.

4) I. Harris and R. G. J. Miller, J. Polymer Sci. **7** (1951) 377.

5) A. S. Dunn, B. D. Stead, and H. W. Melville, Trans. Faraday Soc. **50** (1954) 279.

6) H. W. Melville and B. D. Stead, J. Polymer Sci. **26** (1955) 505.

7) P. E. M. Allen, J. M. Downer, G. W. Hastings, H. W. Melville, P. Molyneux, and J. R. Urwin, Nature [London] **177** (1956) 910.

8) R. W. Hall, Techniques of Polymer Characterization, ed. P. W. Allen, Butterworths, London 1959, p. 53.

9) J. Bischoff and V. Desreux, Bull. Soc. chim. belges **60** (1951) 137.

10) P. E. M. Allen, R. Hardy, J. R. Meyer, and P. Molyneux, Makromolekulare Chem. **39** (1960) 52.

11) K. A. Stacey, Light-Scattering in Physical Chemistry, Butterworths, London 1956, p. 87.

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# Turbidimetric Titrations

## Part II. The Titration of Polystyrenes in Butanone with Isopropanol

by

Jack Robson Urwin, John McKenzie Stearne, Denis Oswald Jordan,
and Richard Andrew Mills

HÜTHIG & WEPF VERLAG · BASEL

From the Department of Physical and Inorganic Chemistry of the University of Adelaide,
South Australia

# Turbidimetric Titrations

## Part II. The Titration of Polystyrenes in Butanone with Isopropanol

By JACK ROBSON URWIN, JOHN MCKENZIE STEARNE*, DENIS OSWALD JORDAN,
and RICHARD ANDREW MILLS

(Eingegangen am 6. August 1963)

SUMMARY:

The turbidimetric titrations of samples of polystyrene prepared anionically have been examined critically. The solubility relationships have been determined experimentally and a method for evaluating the number mean and weight mean molecular weights has been proposed.

ZUSAMMENFASSUNG:

Die Trübungstitration von anionisch hergestellten Polystyrolen wurde kritisch untersucht.

Die Löslichkeitsverhältnisse wurden experimentell bestimmt; es wird eine Methode zur Errechnung des Zahlenmittels und des Gewichtsmittels des Molekulargewichts vorgeschlagen.

### *Introduction*

Turbidimetric titrations have been used by many workers, as a rapid analytical method for investigating the composition of the product of polymerization[1–14]. In principle it should be possible to determine the composition of a polymer solution both qualitatively and quantitatively; in practice, however, this is not easily achieved[15]. The poor reproducibility which has characterized much of the early work is probably due in part to the wrong choice of the solvent/precipitant system and to the use of instruments which do not allow observation of changes in scattering pattern during titration. An instrument designed to record simultaneously transmission, scattering at 90° and dissymmetry has been described by us recently[16].

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To obtain reproducible results, care must be observed when determining the experimental conditions. The temperature stability, particularly of the titration cell, the rate of stirring, and the rate of addition of the non-solvent must all be accurately controlled. The proper choice of solvent/ precipitant system must be made; this system must be sufficiently selective, particularly near the end point, so as to effect a good separation of the polymer species and to avoid coagulation. It is necessary to make the proper corrections for dilution and optical effects where these are applicable. Unsatisfactory results can often be put down to neglect to take account of some or all of these factors.

The main purpose of these studies was to raise the level of accuracy and thereby extend the usefulness of the technique. More specifically we wished to put the analysis of polymer solutions, particularly those containing mixtures of block copolymers and their homopolymers on a sounder basis than had been the case in the past4). With this in mind, a series of polystyrenes was prepared, initiated anionically by the method first reported by SZWARC17) and later modified by WENGER18).

It is the general procedure in light scattering studies to equate the intensity of scattered light to some multiple of the total amount of polymer present in suspension. However, since the scattering power of the precipitate is also a function of the refractive index difference between the particle and the suspending medium it is desirable to avoid corrections due to differences between the solvent and non-solvent. In this work we chose the systen butanone (r.i. = 1.3740) and isopropanol (r.i. = 1.3736) where there is a negligible refractive index difference. The wavelength used was the 5460 A.U. line of the mercury arc. Only dilute solutions were employed (0.4–2.0 mg./100 ml.). The rate of addition of non-solvent was limited to 0.01–0.02 ml./min. The instrument described in Part I was used for this work except that the Mazda-box type mercury arc lamp was replaced by a Philips S.P. 500 water cooled mercury arc which considerably improved the stability of the light source.

### *The size and shape of the suspended particles*

An expression for large particles where the scattering intensity is no longer symmetrical about $\Theta = 90°$ is given by

$$i_{\Theta} = K I_0 (1 + \cos^2 \Theta) P(\Theta) \tag{1}$$

for unpolarized light where

$$K = \frac{8\pi^4\alpha^2}{r^2\lambda^4} \qquad (2)$$

$I_0$ = intensity of the incident beam,
$P(\Theta)$ = the particle scattering factor,
$\alpha$ = the polarizability of the particle,
$r$ = the distance from the scattering volume to the receiver.

and

$$P(\Theta) = [3/X^3 (\sin X - X \cos X)]^2 \qquad (3)$$

where

$$X = \frac{2\pi D}{\lambda'} \sin \Theta/_2 \qquad (4)$$

$\lambda'$ = the wavelength of light in the medium,
$D$ = the diameter of the particle.

The Rayleigh-Gans-Debye (R-G-D) theory holds for particles approaching the wavelength of light when the relative refractive index m is near unity, ($m = \mu/\mu_0$) where $\mu$ = refractive index of the particle, $\mu_0$ = refractive index of the suspending medium.

In the system polystyrene-butanone-isopropanol, ($m \simeq 1.15$) the R-G-D theory cannot yield satisfactory quantitative values for particle size[19]. Nevertheless, application of the (R-G-D) theory to dissymmetry measurements should give a qualitative estimate of the size and shape of the precipitate, particularly when the diameter of the particle remains less than one wavelength. For large spherical particles the dissymmetry function

$$z = \frac{i(\Theta)}{i(90-\Theta)} \qquad (5)$$

may be calculated from tables of $P(\Theta)$[20] for various values of $D/\lambda'$.

The angular distribution of the scattered light has been measured for a sample of polystyrene ($\overline{M}_W = 77{,}000$) at an initial concentration of 1.2 mg./100 ml. over the range of angles from 40 to 140° at intervals of 10°. The measured dissymmetry has been recorded (Fig. 1) for a sample taken after 4% precipitation and again after complete precipitation. The latter solution was re-examined after a lapse of 48 hrs. and the negligible change demonstrates the absence of aggregation in this system.

These results indicate a growth of particle size during titration; the full lines have been calculated for $D/\lambda' = 0.4$, $D/\lambda' = 0.5$ but it is likely that the size of particle calculated may be in considerable error. However, the fact that except for very low angles the experimental points follow the theoretical curves indicates that the particles are essentially spherical in shape.

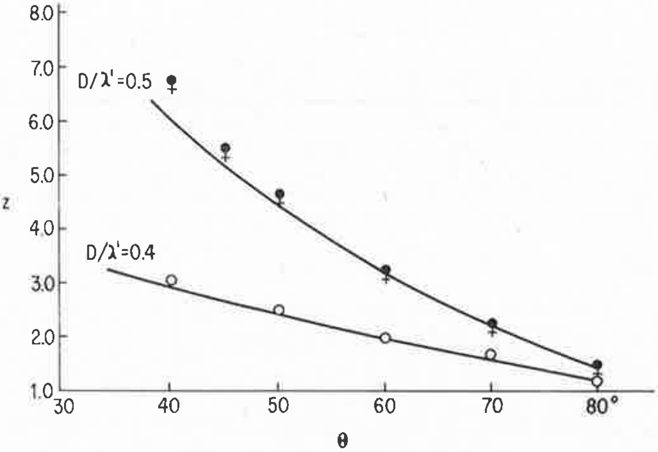

Fig. 1. The dissymmetry z as a function of the angle Θ for the polystyrene ($\overline{M}_\eta = 77{,}000$) precipitated from butanone by continous addition of isopropanol. The lines have been calculated assuming the values of D/λ′ shown. Experimental points are shown thus: ○ after 4% precipitation; + after complete precipitation; ● 48 hrs. after complete precipitation

These results differ from the system benzene-methanol reported by HASTINGS and PEAKER[15)], and confirmed by SLOAN[20)], who found that there was considerable aggregation of particles. Whether the aggregation in this system is due to the system itself or the method of titration cannot be concluded on this evidence alone.

### *The corrected turbidities as a function of concentration*

As was pointed out in part I the function to be measured is $(i_{90}/I_t)$ which is directly related to the ratio $i^*_{90}/I^*_0$. This function was demonstrated to be equivalent to the turbidity ($\tau$) measured by transmission and defined by

$$I = I_0 e^{-\tau l} \tag{6}$$

We have also shown that a linear relationship exists between $(i_{90}/I_t)_{\text{meas.}}$ and concentration for colloidal silica. For polymer solutions, however, a correction must be applied for dissymmetry and **Fresnel** reflections. The first correction is applied by measuring the dissymmetry at each stage of the precipitation and reading off from a correction curve of

$$f(z) = \frac{1}{P(90)} \quad \textit{versus} \quad z = i_{45^\circ}/i_{135^\circ} \tag{7}$$

which was constructed from the tables of these functions for spherical particles[21, 22]. The observed intensity multiplied by the reciprocal of $P(\Theta)$ gives the value that would have been observed had there been no interference.

The **Fresnel** correction is applied, taking both glass/air and liquid/glass interfaces into consideration, by the relation[23]

$$z = \frac{z_{obs.} - (1-r)^2R + r}{1 - [(1-r)^2R + r]z_{obs.}} \tag{8}$$

Taking the value for n ($\lambda = 4358$ A.U.) as 1.467 and $n_0 = 1.380$ for the butanone-isopropanol system this reduces to

$$z = \frac{z_{obs.} - 0.037}{1 - 0.037\, z_{obs.}} \tag{9}$$

The corrected values of z were used in determining the correction for dissymmetry.

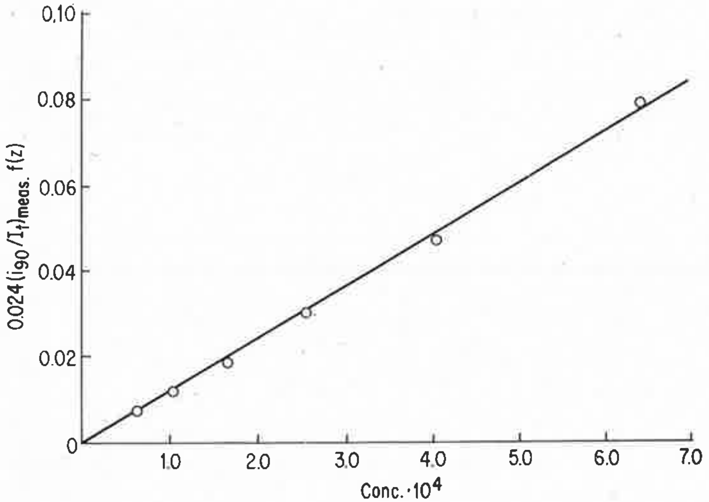

Fig. 2. The turbidity corrected for dissymmetry $[K(i_{90}/I_t)_{meas.}f(z)]$ as a function of the concentration for the polystyrene $\overline{M}_\eta = 77{,}000$ found by dilution of the polymer after complete precipitation

In this study we have assumed with SCHULZ[24)] that the swelling volume is independent of molecular weight and further that the swelling volume remains unchanged during the titration. If then the intensity at $\Theta = 90°$ is corrected for change in particle size the intensity of scattered light will be directly related to the amount of polymer precipitated. To test this conclusion we titrated one sample of polystyrene to complete precipitation and then diluted with a mixture of solvent/non-solvent equivalent to the composition at the end point. The value of the intensity of scattering for the solution was subtracted from the value of the suspension. Values of $(i_{90}/I_t)_{\text{meas.}}$ corrected for particle size, *etc.* have been plotted against concentration in Fig. 2. It can be seen that over a tenfold range of concentration, scattering ratio $(i_{90}/I_t)_{\text{meas.}}$ is directly proportional to the concentration of precipitated polymer.

### *Solubility of the polymer as a function of the concentration and molecular weight*

In turbidimetric titrations the solubility is characterized by the composition of the solvent/non-solvent mixture at the point of saturation represented by the point of precipitation. This composition is given by the ratio

$$\gamma = \frac{V}{V_0 + V} \qquad (10)$$

representing the volume fraction of non-solvent added to the mixture. In the constant volume cell $\gamma$ is related to the volume of non-solvent added by

$$V/V_0 = \ln (1-\gamma) \qquad (11)$$

as shown in Part I.

A problem arises as to which point is to be chosen to represent the value of $\gamma$ corresponding to the saturation point for a given molecular weight, since even monodisperse material will precipitate over a small $\gamma$ range. The choice of the initial onset of turbidity will weight this value of $\gamma$ too far towards the high molecular weight region. The point at which 50 % of the polymer has been precipitated is a reasonable choice although here some error is involved since it will not in general correspond to any of the usually measured averages. In this study the mid-point of the curve has been arbitrarily taken as the precipitation point and the corresponding value of $\gamma$ designated $\gamma_p$. This point would refer to the precipitation of polymer of molecular weight equal to the weight average molecular weight if the polymer were monodisperse. It is assumed that the molecular weight (M) precipitating at any instant depends only on the saturation composition of the solution appropriate to that particular molecular weight. This saturation value will depend upon (i) the initial concentration of the solution $C_0$ and (ii) the stage of the titration $\gamma$, *i.e.* we may write

$$M = M(C_0, \gamma) \tag{12}$$

Since evaluation of the saturation concentration at each point in the precipitation is difficult to obtain with any accuracy, the choice of the initial concentration is more convenient.

A series of polystyrenes initiated anionically was prepared and assumed to be of narrow distribution[25–29]. Five polymers were chosen for this study and their molecular weights determined by viscosity using the values of GREEN[30] for the MARK-HOUWINK equation. The molecular weights ranged from 77,000 to 920,000.

The concentration (C) at any $\gamma$ can be calculated from the initial concentration $C_0$ by the relation

$$C = C_0\,(1-\gamma) \tag{13}$$

provided that there is no loss of precipitate. The precipitant was generally added up to a point close to precipitation but not so close as to affect the titration. The actual value of $\gamma$ at any point is given by the relation[11].

$$(1-\gamma)_{\text{actual}} = (1-\gamma)_{\text{initial}}\,(1-\gamma)_{\text{apparent}} \tag{14}$$

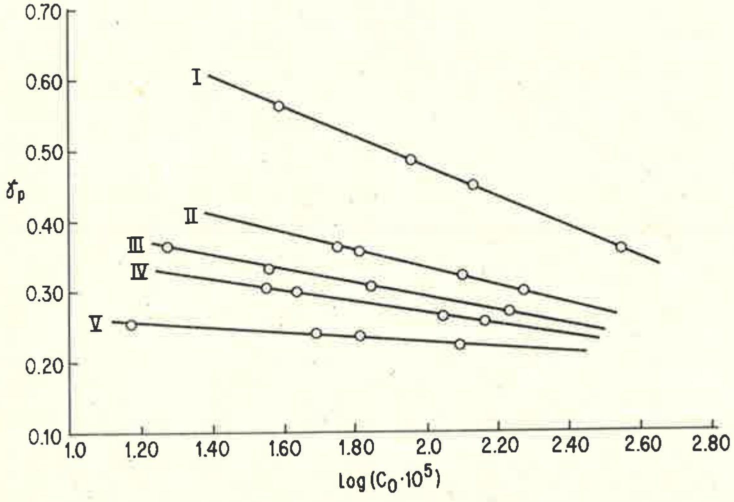

Fig. 3. $\gamma_p$ as a function of log $C_0$ for the polystyrenes of various molecular weights: I. $7.7 \cdot 10^4$; II. $19.8 \cdot 10^4$; III. $30.0 \cdot 10^4$; IV. $40.4 \cdot 10^4$; V. $92.0 \cdot 10^4$

where $\gamma_{\text{initial}}$ is the value after the initial addition of non-solvent before titration begins, $\gamma_{\text{apparent}}$ is determined by the volume added at any stage in the titration using equation (11). In these titrations, the concentration of polymer was known at $\gamma_{\text{initial}}$. Hence, $C_0$ could be found by (13).

In Fig. 3 values of $\gamma_p$ are plotted against the corresponding values of C for the five polystyrenes. Extrapolation of the straight lines through these points suggests that there is some critical value of $C_0$ at which all molecular weights will precipitate on reaching a critical value of $\gamma_p$. This result implies that the most efficient separation of molecular weights will occur at very low concentrations. A linear relationship of the form

$$\log C_0 = a - b\,\gamma_p \tag{15}$$

where a and b are constants, has been found to apply for this particular system. These results show that a relationship having the same form as that found using saturation concentrations[31)] holds for the initial concentrations.

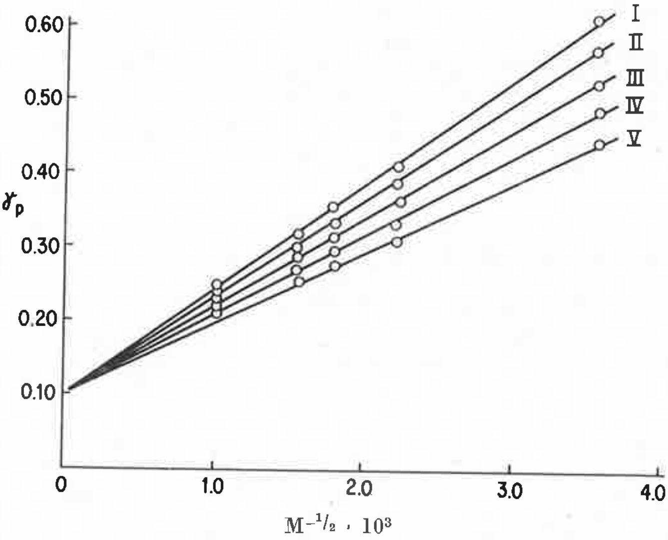

Fig. 4. $\gamma_p$ as a function of $M^{-1/2}$ for various values of log $(C_0 \cdot 10^5)$ = I. 1.4; II. 1.6; III. 1.8; IV. 2.0; V. 2.2

The variation of $\gamma_p$ with molecular weight is shown in Fig. 4. The data were extracted from Fig. 3 and indicate that at infinite molecular weight there is a critical value of $\gamma_p$, corresponding to a particular temperature.

This is equivalent to a $\Theta$ point for the temperature of operation. A linear relation of the type

$$\gamma_p = X + YM^{-1/2} \tag{16}$$

where X is the intercept (0.108) and Y may be determined by plotting the slopes of the various $C_0$ lines against log $C_0$.

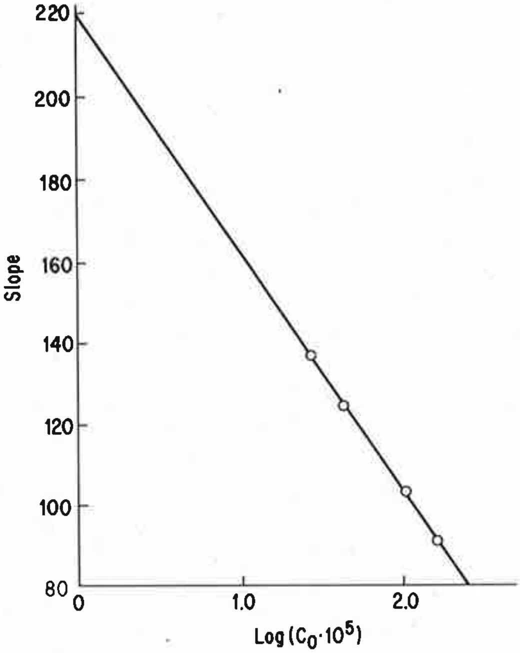

Fig. 5. Slope of the lines $\gamma_p = 0.108 + \dfrac{\log (C_0 \cdot 10^5)}{M^{1/2}}$ *versus* log ($C_0 \cdot 10^5$)

Y has the form

$$Y = 218.13 - 57.85 \log (C_0 \cdot 10^5) \tag{17}$$

The complete relationship then becomes

$$\gamma_p = 0.108 + \frac{(218.13 - 57.85 \log [C_0 \cdot 10^5])}{M^{1/2}} \tag{18}$$

This is in agreement with the original assumption that a knowledge of the stage of the precipitation ($\gamma$) and the initial concentration ($C_0$) allows us to determine the molecular weight precipitating.

### *Correction for loss of precipitate during titration*

One disadvantage of the constant volume cell is the continuous loss of polymer as the titration progresses. The weight of precipitate observed at any instant is not the accumulative weight required for the interpretation of the molecular weight distribution and therefore must be corrected for the loss during titration in order to obtain that quantity. A solution of this problem is as follows.

Let the increment of precipitate lost be given by

$$d(W_p)_L = W'_p d\gamma \tag{19}$$

where $W'_p$ is the weight of precipitate remaining in the cell at a particular value of $\gamma$. Then the total amount of precipitate lost up to any stage $\gamma_i$ is given by

$$(W_p)_L = \int_0^{\gamma_i} W'_p d\gamma \tag{20}$$

The total weight precipitated up to the stage $\gamma_i$ is then

$$(W_p)_i = (W_p)_i' + \int_0^{\gamma_i} W_p' d\gamma \tag{21}$$

where $(W_p)_i'$ is the amount of polymer remaining in the cell up to $\gamma_i$. Since the accuracy with which the integral may be determined decreases as the correction becomes larger, it is more satisfactory to use AITKEN's process[32)] to find a limiting value for the sequence of $(W_p)_i$ obtained for the values $\gamma_1, \gamma_2, \gamma_3 \ldots$ where the correction is not large. Denoting the last three values by $n-2$, $n-1$, $n$, then the limit $(W_p)_\infty$ is given by

$$(W_p)_\infty = \lim_{i \to \infty} (W_p)_i = (W_p)_n - \frac{[(W_p)_n - (W_p)_{n-1}]^2}{[(W_p)_n - 2(W_p)_{n-1} + (W_p)_{n-2}]} \tag{22}$$

The accuracy of this expression is greatest when the deviations $(W_p)_\infty - (W_p)_i$ form a geometric progression. To evaluate the integral of equation (20) the range of $\gamma$ over which the titration was carried out was divided into equal intervals $\Delta\gamma$ giving

$$(W_p)_L \simeq \Delta\gamma \sum_{n=0}^{n=i} (W_p)_n \tag{23}$$

This expression was employed to correct for the loss of polymer on all samples measured.

### *The location of the point of precipitation in relation to the weight average molecular weight*

If we assume a molecular weight distribution of the type shown in Fig. 6, three characteristics are related to its shape; (i) the weight modal molecular weight corresponding to the maximum (point x on the curve), (ii) the weight median molecular weight (point y on the curve), (iii) the weight mean molecular weight. The first point refers to the greatest weight of material having a molecular weight x. The second point (located by inspection since the area under A is equal to the area under B) shows that one half the weight of polymer has a molecular weight in excess of the value at y. The weight mean value cannot be located by inspection at all.

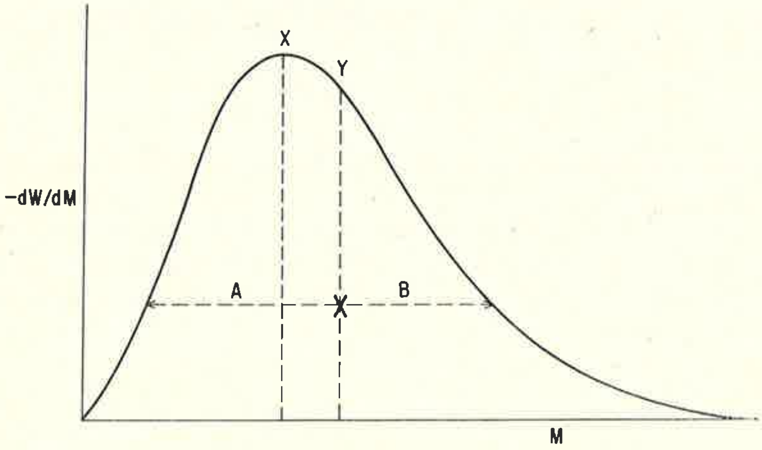

Fig. 6. Idealized molecular weight distribution curve

The weight mean molecular weight is defined by

$$\overline{M}_w = \int_0^\infty WMdM \tag{24}$$

for a continuous distribution, where W = W(M) is the differential weight molecular weight distribution function, such that the weight fraction ($w_{12}$) of polymer having a molecular weight between $M_1$ and $M_2$ (for all $M_1$ and $M_2$) is given by

$$w_{12} = \int_{M_1}^{M_2} W(M)dM \tag{25}$$

However, in this work W was measured in arbitrary units and therefore the area under the distribution curve is no longer unity. Introducing the scale factor $\int_0^\infty \mathrm{W dM}$ we have

$$\overline{\mathrm{M}}_{\mathrm{w}} = \frac{\int_0^\infty \mathrm{WMdM}}{\int_0^\infty \mathrm{WdM}} \tag{26}$$

If the distribution curve were symmetrical then the modal, median and mean molecular weights would coincide. It can be seen that the assumption that the point of precipitation which corresponds to the mid-point of the titration curve is equal to the weight average molecular weight as determined by viscosity measurements is likely to be in error, since this point is the weight median molecular weight for skewed distribution curves. In this work we have assumed that for distribution curves which are moderately skewed, the relation

$$(\text{mean} - \text{mode}) = 3\,(\text{mean} - \text{median}) \tag{27}$$

holds, and therefore the weight mean molecular weight may be estimated using this equation.

The analyses of two of the polystyrenes were made in this manner and one of them will be described in detail here. The titration curve corrected for loss of polymer in the constant volume cell is shown in Fig. 7.

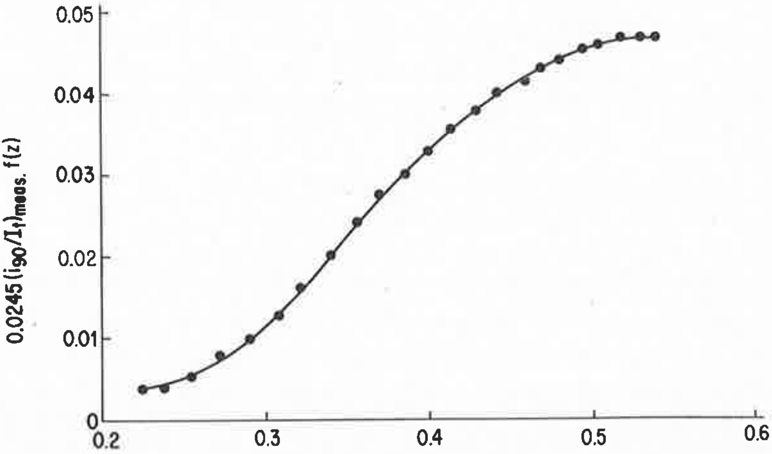

Fig. 7. Titration curve corrected for loss of polymer during the titration for the polystyrene P. 1. ($\overline{\mathrm{M}}_\eta = 1.98 \cdot 10^5$)

From the weight values and molecular weights determined from equation (18) at equal intervals of $\gamma$ the integral molecular weight distribution curve (Fig. 8) was constructed. The differential molecular weight distribution was obtained from the integral curve by graphical differentiation.

The calculation of the weight mean molecular weight was made by first constructing a curve of the product (WM) against M. The area of the (WM) *versus* M curve was then divided by the area of the W *versus* M curve to give the weight mean molecular weight. The areas were obtained by using a planimeter and the weight mean molecular weight was found to be $2.10 \cdot 10^5$. Using the approximation of eq. (27) the weight mean molecular weight is $2.20 \cdot 10^5$. This value is 10% higher than the value obtained from viscosity measurements ($1.98 \cdot 10^5$); this difference being

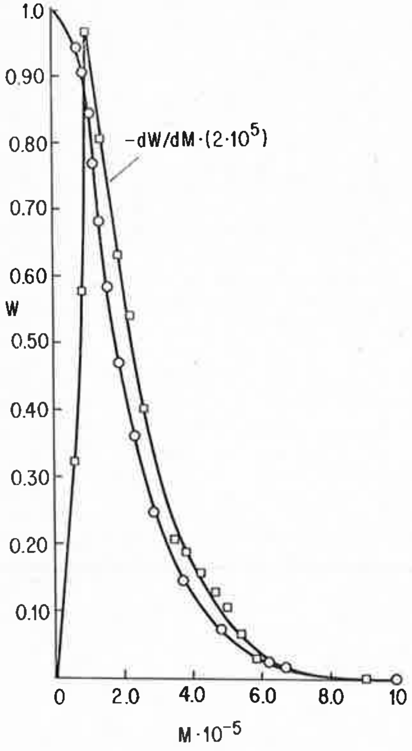

Fig. 8

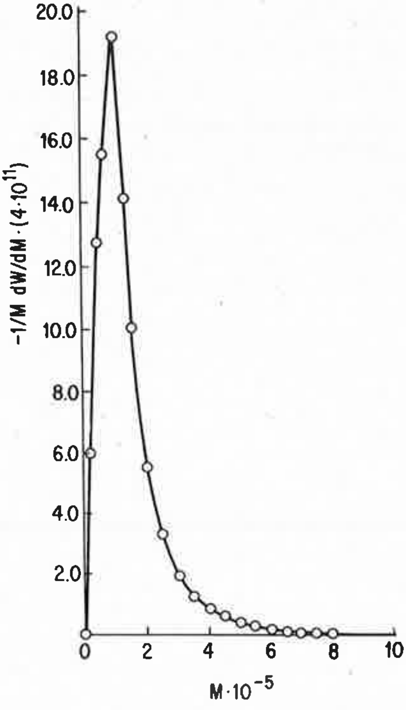

Fig. 9

Fig. 8. The integral and differential weight average molecular weight distribution curves for the polystyrene P. 1 used to determine the weight mean molecular weight

Fig. 9. The differential number average molecular weight distribution curve

attributed to the assumption of moderate skewness being inapplicable to this distribution curve. The value found by the areas method is nearer to that given by viscosity measurements.

A curve of the distribution in terms of moles was obtained by dividing the weight function W(M) by molecular weight as shown in Fig. 9. The number mean molecular weight $\overline{M}_n$ was then evaluated from the relation

$$\overline{M}_n = \frac{\int_0^\infty NMdM}{\int_0^\infty NdM}$$

where $N = N(M) = W(M)/M$ and found to be $1.42 \cdot 10^5$. The ratio $\overline{M}_w/\overline{M}_n = 1.48$ indicates that the samples of polystyrene produced have a much broader distribution of molecular weights than was expected. The second polystyrene was examined using equation (27) and $\overline{M}_w = 4.40 \cdot 10^5$ found. Comparing this value with the value found by viscosity $\overline{M}_\eta = 4.04 \cdot 10^5$, which is within 10%, the agreement seems satisfactory, considering the approximate nature of equation (27). However, it is clear that calibration using polystyrene preparations having a narrower distribution should produce better agreement between average molecular weights determined by turbidimetry and by viscosity, osmometry or light scattering.

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1) H. W. Melville and B. D. Stead, J. Polymer Sci. **8** (1952) 529.

2) A. S. Dunn, B. D. Stead, and H. W. Melville, Trans. Faraday Soc. **50** (1954) 279.

3) P. E. M. Allen, J. M. Downer, G. W. Hastings, H. W. Melville, P. Molyneux, and J. R. Urwin, Nature [London] **177** (1956) 910.

4) J. R. Urwin, J. Polymer Sci. **27** (1958) 580.

5) P. Molyneux, Makromolekulare Chem. **43** (1961) 31.

6) P. R. Morey and J. W. Tamblyn, J. appl. Physics **16** (1945) 419.

7) A. Oth, Bull. Soc. chim. Belges **58** (1949) 285.

8) I. Harris and R. G. J. Miller, J. Polymer Sci. **7** (1951) 377.

9) J. Bischoff and V. Desreux, Bull. Soc. chim. Belges **60** (1951) 137.

10) G. Smets and M. Claesson, J. Polymer Sci. **8** (1952) 289.

11) A. Oth and V. Desreux, Bull. Soc. chim. Belges **63** (1954) 261.

12) M. Claesson, J. Polymer Sci. **16** (1955) 193.

13) W. Scholtan, Makromolekulare Chem. **24** (1957) 104.

14) G. Gooberman, J. Polymer Sci. **40** (1959) 469.

15) G. W. Hastings and F. W. Peaker, J. Polymer Sci. **36** (1959) 351.

16) J. McK. Stearne and J. R. Urwin, Makromolekulare Chem. **56** (1962) 76.

17) M. Szwarc, M. Levy, and R. Milkovitch, J. Amer. chem. Soc. **78** (1956) 2656; R. Waack, A. Rembaum, J. D. Coombes, and M. Szwarc, J. Amer. chem. Soc. **79** (1957) 2026.

18) F. Wenger, Makromolekulare Chem. **36** (1960) 200; Preprints Polymer Division **2** (2) (1961) 262.

19) W. Heller, J. chem. Physics **26** (1957) 1258 and subsequent papers.

20) C. K. Sloan, J. physic. Chem. **59** (1955) 834.

21) P. Doty and R. F. Steiner, J. chem. Physics **18** (1950) 1211.

22) K. A. Stacey, Light Scattering in Physical Chemistry, Butterworth, London 1956, p. 63.

23) K. A. Stacey, Light Scattering in Physical Chemistry, Butterworth, London 1956, p. 85.

24) G. V. Schulz, Z. physik. Chem. A **179** (1937) 321.

25) Ref. 17).

26) H. W. McCormick, J. Polymer Sci. **36** (1959) 341.

27) J. M. G. Cowie, D. J. Worsfold, and S. Bywater, Trans. Faraday Soc. **57** (1961) 705.

28) F. Wenger, Technical Report No. 2 O.N.R. N.R. 356–407, Sept. 1959.

29) F. Wenger, Preprints Polymer Division, 238th Meeting of the American Chem. Soc., New York, Sept. 1960.

30) J. H. Green, J. Polymer Sci. **34** (1959) 514.

31) G. V. Schulz and B. Jirgensons, Z. physik. Chem. B **46** (1940) 105.

32) A. C. Aitken, Proc. Roy. Soc. Edinburgh **46** (1926) 289.

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# Solution Properties of Block Copolymers of Styrene and Methyl Methacrylate

## Part I. The Preparation, Isolation, and Purification of the Block Copolymers

by

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# Solution Properties of Block Copolymers of Styrene and Methyl Methacrylate

## Part I. The Preparation, Isolation, and Purification of the Block Copolymers

By J. R. Urwin and J. M. Stearne

(Eingegangen am 18. Februar 1964)

SUMMARY:

Block copolymers of styrene and methyl methacrylate have been prepared anionically. The preparation, isolation, and purification are described. The homogeneity with respect to molecular weight distribution and composition has been determined and is discussed.

ZUSAMMENFASSUNG:

Isolierung und Reinigung von anionisch hergestellten Blockcopolymeren aus Styrol und Methylmethacrylat werden beschrieben. Die Homogenität in bezug auf Molekulargewichtsverteilung und chemische Zusammensetzung wurde bestimmt und wird diskutiert.

Until quite recently, much of the effort devoted to the study of block copolymers was concerned with the synthesis and the isolation of these polymers from the reaction product. The methods which have been used to prepare block copolymers are legion, however, these have recently been collected and published in a comprehensive monograph by CERESA 1). Probably the main reason for the dearth of information on solution properties is that in the past most workers have experienced difficulty in preparing polymers with narrow distributions in molecular weight and composition; which of course is essential if any serious attempt is to be made to elucidate the effect of molecular weight and composition on these properties. Several theoretical treatments 2–4) have been proposed which predict the dilute solution behaviour of block copolymers, but detailed experimental studies are required in order to test these theories. The choice of the preparatory method to be used is limited to either batch polymerization in which monomer and initiator are mixed in a single operation or continuous monomer addition in which monomer is added continuously and gradually over a considerable period. The former method is only applicable when the reaction rate is relatively slow; the latter method is employed when fast polymerization is to be expected. The polymerization of styrene in tetrahydrofuran using sodium biphenyl is rapid and therefore continuous monomer feed is the only practical method of synthesizing the polymer[5,6)].

Block copolymers of styrene and methyl methacrylate were chosen for this study because (i) the solution behaviour of the two homopolymers has been well characterized in a number of solvents, (ii) mixtures of both homopolymers have been studied, and (iii) random copolymers of styrene and methyl methacrylate have been investigated.

Difunctional initiators like sodium biphenyl react with styrene forming radical ions which combine to yield dianions capable of propagation from both ends. In the absence of impurities and under uniform polymerization conditions conversion of monomer to polymer is quantitative and yields monodisperse product. If there is no termination and no depropagation during polymerization, unterminated polymer capable of adding monomer from each end of the chain results. Block copolymer may therefore be synthesized by addition of a different monomer. The final polymer will contain three linear sequences which may be represented by A......AB......BA......A where A represents methyl methacrylate segments and B represents styrene segments in the chain. The polymer must always be of this form since the methyl methacrylate ion, which is a weaker base than styrene, does not initiate polymerisation of styrene.

The preparation of monomer free from de-activating impurities is a difficult problem, yet this must be achieved in order to synthesize a polymer containing a single species. Impurities in the monomer, if not removed, will deactivate one or both ends of the polymer finally yielding a block with two linear sequences thus: A......AB.....B along with the polystyrene. Turbidimetric titration provides a rapid check on the presence of the second species since each will precipitate at a different point in the titration corresponding to their different molecular weights. A sample of the polystyrene formed in the first stage of the preparation was isolated and subjected to turbidimetric titration for each block prepared. In some of the earlier preparations, in which the purging technique was not used, three polymers were found in the mixture. Two polymers were narrow distribution polystyrenes differing in molecular weight by a factor of two similar to that observed by McCormick[7)], and a broad distribution polystyrene of lower molecular weight than either of the others. In subsequent preparations the lower molecular weight material did not appear;

instead a single curve was obtained, corresponding to the difunctional species only.

## *The preparation of the block copolymers*

Tetrahydrofuran (T.H.F.) was purified by firstly removing the peroxides present as impurities and then refluxing over sodium wire for several hrs. The solvent was then distilled onto calcium hydride and after 24 hrs. distilled onto sodium wire and biphenyl and refluxed until the blue colour characteristic of sodium biphenyl appeared. The T.H.F. was finally distilled under dry nitrogen into 500 ml. storage bulbs and transferred to the vacuum line where the solvent was degassed. The storage bulbs had been baked out on the vacuum line prior to the distillation. A further quantity of biphenyl was recrystallized from pure diethyl ether and dried in a vacuum desiccator over $P_2O_5$ before use. Freshly cut sodium and the biphenyl were introduced into a storage bulb and the T.H.F. distilled onto

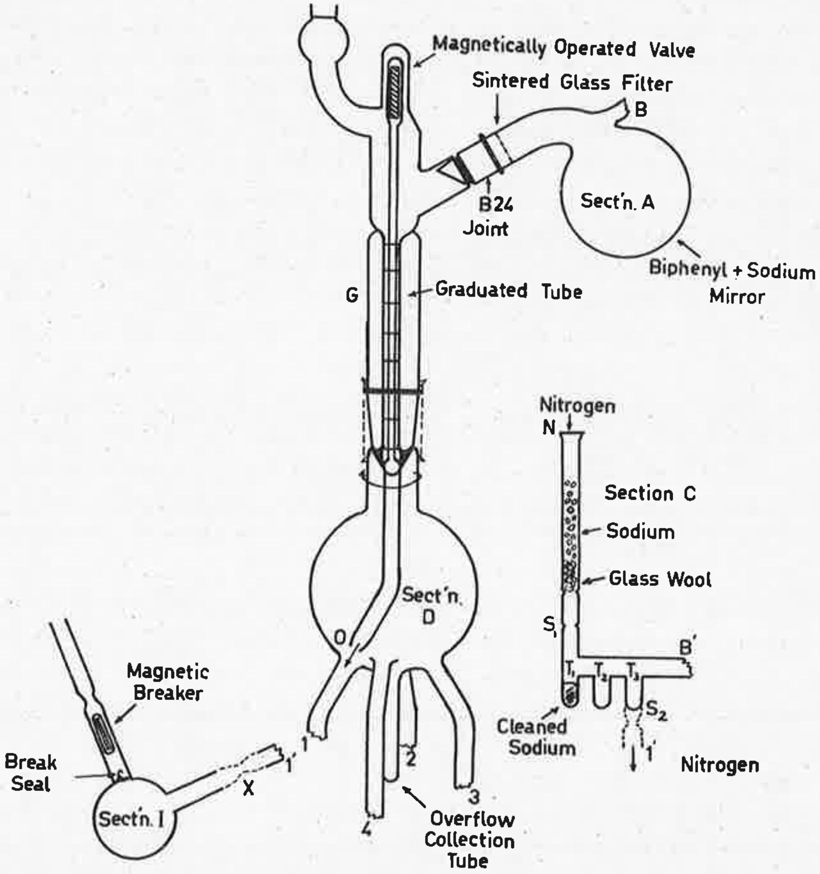

Fig. 1. Apparatus for preparing initiator samples

the solid. The characteristic blue colour of the complex appeared almost immediately. The T.H.F. was kept in this condition on the vacuum line until required.

The monomer styrene was obtained from Colonial Sugar Refining Co. Ltd. and the methyl methacrylate from I.C.I. (Australia). Both monomers were freed from inhibitor in the usual way by washing with caustic soda solution and then water and finally dried over anhydrous sodium sulphate for 24 hrs. The styrene was fractionated under dry nitrogen at atmospheric pressure and the fraction boiling in the range 145.9–146.1 °C. was separated and then transferred to the vacuum line, degassed and finally distilled into a storage bulb containing calcium hydride. The bulb was removed from the vacuum line and stored in the dark at –20 °C. Before use, the monomer was distilled onto activated Linde molecular sieves and then onto calcium hydride again prior to being distilled into the reaction vessel. Methyl methacrylate distilling over in the range 99.8–100.1 °C. was collected and treated in the same way as was the styrene.

The initiator was prepared by adding a solution of biphenyl in ether to the reaction vessel and removing the solvent, leaving the solid biphenyl in section A (Fig. 1). Sodium was introduced into section S, under purified nitrogen and then heated under vacuum to form a mirror in section A. The biphenyl was kept cooled to avoid sublimation. T.H.F. from the storage vessels was then distilled into section A and the characteristic blue colour appeared immediately. The initiator solution was filtered through the sintered glass filter into the graduated tube and run off into the initiator storage vessels by raising the magnetic seal. These were sealed off from section D whilst the initiator was frozen down under vacuum. The advantage of this method is that exact amounts of initiator can be measured out and the molecular weight varied by adding different amounts of monomer.

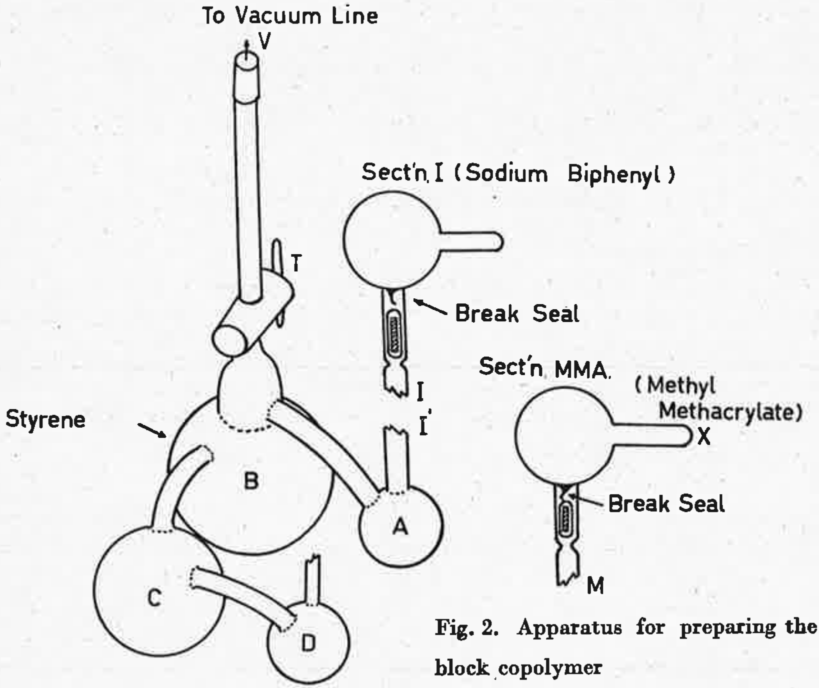

Fig. 2. Apparatus for preparing the block copolymer

The apparatus for preparing the block copolymers is shown in Fig. 2. Storage vessels containing initiator in T.H.F. and methyl methacrylate in T.H.F. were sealed on to the bulbs A and D as shown. Styrene and T.H.F. were distilled into bulb B, from the vacuum line; the tap was closed and the whole system removed from the vacuum line. By this technique, the whole apparatus could be baked out by flaming before carrying out the reaction. The bulbs A and B were cooled to 0 °C., the break seal on the initiator storage bulb broken and initiator run into bulb A. The styrene was purged by running in small amounts of initiator very carefully until the red colour due to styryl ions was observed to just disappear very slowly. It is assumed at this stage that the level of impurity had been reduced to a minimum. After allowing time for all impurities to be consumed a small amount of the freshly purged styrene was distilled into bulb A. The colour of the initiator immediately changed to red, indicating the production of styryl ions. The bulb A was left at 0 °C. for 15 mins. and then cooled to –78 °C. in an alcohol/dry ice bath and the styrene monomer added slowly to bulb A. Continuous swirling of the mixture ensured proper mixing of the solutions. A period of about 1 hr. was allowed for the addition.

The "living" polystyrene was then divided into approximately equal parts by running half of the living polymer into bulb C. All bulbs were then cooled to –78 °C., the break seal on the methyl methacrylate storage bulb broken, and the contents run into bulb D. The contents of bulb D were added to the "living" polymer in bulb C with constant swirling. The red colour disappeared immediately on adding the methyl methacrylate. The reaction mixture was left at –78 °C. for 30 mins. and then allowed to reach room temperature and finally left for a further 30 mins. During this time the unterminated polystyrene in bulb A remained red in colour without change. Air was allowed to enter the system to terminate the polymers and the sample of block copolymer and its parent polystyrene removed and added separately to a large excess of methanol. Yields of block copolymer were between 93–94%.

All samples of block copolymer and the parent polystyrene were dissolved in A.R. benzene, filtered through a No. 3 sintered glass filter and finally recovered by freeze drying. All samples were then dried again in the vacuum oven for 5 hrs. at 60 °C.

## *Isolation of the block copolymers*

### (a) *Selective extraction*

This technique requires the use of two solvents such that each solvent dissolves only one of the polymeric species (and yet be a non-solvent for the other). Both solvents must be non-solvents for the block copolymer.

Cyclohexane is a solvent for polystyrene and acetonitrile a solvent for polymethyl methacrylate only. Neither solvent dissolves the block copolymer. This system was employed in this work as follows.

The finely divided polymer obtained by freeze drying from benzene, was extracted with cyclohexane using a soxhlet extraction apparatus. The extraction was continued for about 100 hrs. fresh solvent being used after 50 hrs. The polymer in the thimble was then extracted with benzene and again recovered by freeze drying. The process was then repeated using acetonitrile to remove free polymethyl methacrylate. Again the polymer was extracted with benzene, and recovered by freeze drying.

The efficiency of this technique was tested using the turbidimetric titration apparatus described elsewhere[8,9]. The titration of one of the samples tested is shown in Fig. 3. It can be seen from the titration curve that a small amount (about 5% of the total polymer) of polystyrene remains. Obviously the extraction technique using these solvents is inefficient as a means of separation. It has been suggested[10] that dimethyl sulphoxide and carbon disulphide are better extraction solvents for removing polymethyl methacrylate and polystyrene respectively. However, dimethyl sulphoxide can only be used in the cold since it decomposes on heating.

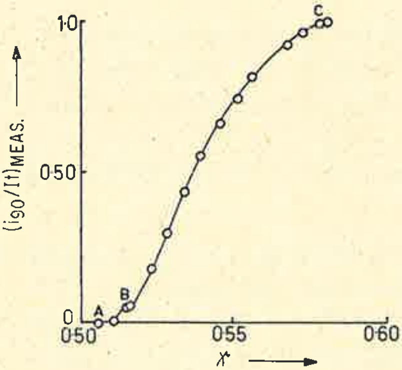

Fig. 3. Turbidimetric titration curve for block copolymer B 4 in the butanone-isopropanol system. The curve AB shows the presence of a small amount of the homopolymer P.S. 4

(b) *Selective precipitation*

This technique has been described in detail by CERESA[24, 25] and in this work the block copolymer samples were dissolved in benzene to form a 2% solution and then diluted with an equal volume of acetone. Petroleum ether was then added slowly to the solution with continuous stirring. As the ratio of volume of precipitant to volume of solution approached the value 0.8 the rate of addition was carefully controlled in such a way that after the next 2 mls. addition the contents of the titration flask were centrifuged for 15 mins. at 5,000 g. in a Servall SS1 angle head centrifuge using stainless steel tubes. The supernatant liquid was removed from the centrifuge tubes and the titration continued using 1 ml. additions until a point was reached at which further addition of petroleum ether produced no further precipitation. At this stage free polymethyl methacrylate should have been removed completely, leaving only free polystyrene and block copolymer in solution. This point corresponded to a ratio of precipitant to solvent of 0.98.

The precipitated polymer was removed from the centrifuge tubes and recovered by freeze drying as previously described. After drying in the vacuum oven at 60 °C. for 3 hrs., the polymer was examined for purity using the ultra-violet spectrographic method to be described later. The amount of polymer recovered was only 2% of the total showing that the block copolymer was reasonably free of polymethyl methacrylate homopolymer.

The remaining polystyrene-block copolymer mixture was recovered by freeze drying, dried and redissolved in benzene to give a 2% solution. The solution was then diluted with an equal volume of chlorobenzene, and dried methanol slowly added with stirring. As previously, the rate of addition was slowed down and centrifuging at 2 and finally 1 ml. intervals carried out until no further precipitate resulted. Examination of the recovered polystyrene indicated a purity of 97%. The maximum amount of polystyrene separated was 5% in the case of B4. Only sufficient polystyrene was recovered for a single examination in each case.

The block copolymers were precipitated from the benzene-chlorobenzene-methanol mixture using a large excess of methanol-water mixture. The samples were then dried at 60 °C. and again dissolved in benzene and recovered by freeze drying and finally drying in vacuo.

The samples of isolated block copolymers were examined by turbidimetric titration and found to be completely free from polystyrene and polymethyl methacrylate formed in the reaction.

## *Characterization of the block copolymers*

### 1. *Composition*

The analysis of each block copolymer to determine composition was carried out using ultraviolet absorptiometry. This method appears to be the most reliable technique. Direct oxygen determination and the ratio of number average molecular weights of the polystyrene parent and the block copolymer, determined by osmometry, were also used in the characterization.

The specific extinction coefficient K of a mixture of polymers is given by the expression

$$K = xK_S + (1-x)K_M$$

where $K_S$ is the specific extinction coefficient of polystyrene,
$K_M$ is the specific extinction coefficient of polymethyl methacrylate,
and x is the weight fraction of polystyrene.

Chloroform (A.R. grade) was employed as a solvent and all measurements were made on a Unicam S.P. 500 spectrophotometer.

For a mixture of polystyrene and polymethyl methacrylate

$$K = \frac{\text{Optical density at } 262\,\mu}{\text{Cell length (cm.)} \cdot \text{concentration (g./l.)}}$$

The direct oxygen determination, used as a check on the first method, is based on the percentage oxygen existing in the polymethyl methacrylate. If x is the weight fraction of polystyrene the percentage of oxygen present in the polymer is given by

$$\%\,(O_2) = 32\,(1-x)$$

The oxygen determinations were done at the University of Melbourne by Dr. K. W. ZIMMERMANN in the Department of Chemistry. The number average molecular weights were determined using PINNER-STABIN osmometers.

The compositions of the block copolymers used in this work are shown in Table 1. The three methods can be compared, and it is seen that, within experimental error, the results of individual methods compare favourably with each other.

Table 1. Analysis of block copolymers of polystyrene and polymethyl methacrylate.

Composition is expressed as a percentage of polystyrene present

| Sample | U.V. | $O_2$ detn. | O.P. |
|---|---|---|---|
| B 1 | 15.1 | 16.7 | 13.0 |
| B 2 | 30.2 | 32.8 | 29.8 |
| B 3 | 38.1 | 39.4 | 37.8 |
| B 4 | 52.1 | 54.1 | 51.9 |

## 2. *Molecular weight*

Some indication of the homogeneity of the block copolymers can be obtained from the degree of heterogeneity ($\overline{M}_w/\overline{M}_n$) of both the block copolymer itself and the parent polystyrene. For the polystyrenes the ratio $\overline{M}_v/\overline{M}_n$ was obtained from viscosity data based on GREEN's values[11] and number average molecular weights from osmometry. This ratio should be equivalent to the heterogeneity ratio since GREEN's values of K and $\alpha$ in the KUHN-HOUWINK equation were determined from light scattering data. Values for $\overline{M}_v$, $\overline{M}_n$ and the ratio $\overline{M}_v/\overline{M}_n$ are shown in Table 2. Although these results show that a narrow molecular weight distribution exists for each polystyrene these values are higher than those previously reported by other authors[12, 13] who employed the same preparative techniques.

Table 2. Molecular weights and heterogeneity ratio of the polystyrenes

| Sample | $\overline{M}_v \cdot 10^{-5}$ | $\overline{M}_n \cdot 10^{-5}$ | $\overline{M}_v/\overline{M}_n$ |
|---|---|---|---|
| P.S. 1 | 3.83 | 3.42 | 1.12 |
| P.S. 2 | 2.40 | 2.12 | 1.13 |
| P.S. 3 | 1.62 | 1.40 | 1.16 |
| P.S. 4 | 1.03 | 0.90 | 1.14 |

The weight average molecular weights of the block copolymers were measured by light scattering and the number averages by osmometry. The data are given in Table 3. Experimental details of these techniques will be discussed later. The heterogeneity ratio for the blocks are all higher than the corresponding parent polystyrenes, however even these values are better than one usually obtains by fractionation techniques. The results show that the four block copolymers prepared are reasonably homogeneous with respect to both molecular weight distribution and composition.

Table 3. Weight average and number average molecular weights of block copolymers of polystyrene and polymethyl methacrylate

| Sample | $\overline{M}_w \cdot 10^{-5}$ | $\overline{M}_n \cdot 10^{-5}$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|
| B 1 | 4.70 | 3.90 | 1.21 |
| B 2 | 3.70 | 3.02 | 1.23 |
| B 3 | 2.66 | 2.25 | 1.27 |
| B 4 | 2.30 | 1.87 | 1.22 |

## *Discussion*

Four block copolymers of polystyrene and polymethyl methacrylate have been prepared and isolated from the polystyrene formed by deactivation and polymethyl methacrylate initiated by centres other than unterminated polystyrene ions. Dimensions of the polystyrene sequence in the block copolymer have been deduced from analysis of the samples of polystyrene separated from the material used to form the block. The results indicate a fairly narrow molecular weight distribution in this portion of the copolymer. The overall molecular weight of the block, however, shows a broader distribution, although it must be borne in mind that the results of Bushuk and Benoit12) show the light scattering value for $\overline{M}_w$ to be dependent upon the solvent and the refractive index increment. The larger the refractive index increment, the closer are the true and apparent or measured values. We calculate that $\overline{M}_w$ determined could be high by as much as a factor of 1.1. However, some broadening in the overall distribution must be expected due to possible contamination introduced during handling.

[1] R. J. CERESA, Block and Graft Copolymers, Butterworths, London 1962.

[2] R. W. KILB and A. M. BUECHE, J. Polymer Sci. **28** (1958) 285.

[3] M. LAUTOUT and M. MAGAT, Z. physik. Chem. [Frankfurt/M.] **16** (1958) 292.

[4] M. LAUTOUT and M. MAGAT, J. Polymer Sci. **57** (1962) 421.

[5] T. A. OROFINO and F. WENGER, J. chem. Physics **35** (1961) 532.

[6] F. WENGER, J. Polymer Sci. **60** (1962) 99.

[7] H. W. McCORMICK, J. Polymer Sci. **41** (1959) 327.

[8] J. M. STEARNE and J. R. URWIN, Makromolekulare Chem. **56** (1962) 76.

[9] J. R. URWIN, J. M. STEARNE, D. O. JORDAN, and R. A. MILLS, Makromolekulare Chem. 72 (1964) 53.

[10] G. CHAMPETIER, M. FONTANILLE, and P. SIGWALT, C. R. hebd. Séance Acad. Sci. **250** (1960) 3653.

[11] J. H. GREEN, J. Polymer Sci. **34** (1959) 514.

[12] F. WENGER, Preprints Polymer Division **2** (2) (1961) 262.

[13] F. WENGER, Makromolekulare Chem. **36** (1960) 200.

[14] W. BUSHUK and H. BENOIT, Can. J. Chem. **36** (1958) 1616.

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# Solution Properties of Block Copolymers of Styrene and Methyl Methacrylate

## Part. II. Viscosity, Osmotic Pressure, and Light Scattering Studies

by

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From the Department of Physical and Inorganic Chemistry of the University of Adelaide,
South Australia

# Solution Properties of Block Copolymers of Styrene and Methyl Methacrylate

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By J. R. Urwin and J. M. Stearne

(Eingegangen am 18. Februar 1964)

SUMMARY:

The block copolymers, previously described in part I, have been studied to determine their behaviour in solution, using the techniques of viscometry, osmometry, and light scattering. The applicability of these techniques to the study of block copolymers is discussed and evidence for interactions peculiar to block copolymers is presented.

ZUSAMMENFASSUNG:

Mit Hilfe der Viskosimetrie, der Osmometrie und der Lichtstreuung wurde das Lösungsverhalten der in Teil I beschriebenen Blockcopolymeren untersucht. Die Anwendbarkeit dieser Untersuchungsmethoden auf Blockcopolymere wird diskutiert; es ergeben sich Hinweise auf besondere Wechselwirkungen bei Blockcopolymeren.

In the first paper of this series we described the preparation of a number of block copolymers of styrene and methyl methacrylate with both narrow molecular weight distribution and a high degree of homogeneity of composition. In this part of the study we present the results of an examination of the viscosity, osmometry, and light scattering behaviour of solutions of these polymers. In particular we have sought to unfold evidence for the existence of interactions in excess of that which might be expected in simple mixtures or in random copolymers of the same composition.

## *Viscometry*

Viscosities were determined using a suspended level viscometer designed to have a minimum kinetic energy correction. All flow times were in excess of 120 sec. The fractional kinetic energy correction was calculated from the instrument constants[1,2] determined by measuring flow times for water at two temperatures. The values found for toluene ($1.54 \cdot 10^{-4}$) and butanone ($2.80 \cdot 10^{-4}$) were negligible compared with the magnitude of the viscosities measured and, therefore, a correction was not applied to the limiting viscosity numbers. Temperature was controlled within 0.005 °C. at all times. The alignment of the viscometer was carefully checked and the instrument was not moved until one complete determination was made. Dilutions were conducted in the viscometer with the most concentrated solution being measured first.

The solvent toluene (Analar grade) was dried over sodium wire and the fraction distilling between 110.6 and 110.9 °C. at 760 Torr was used. Carbon tetrachloride was dried over anhydrous calcium chloride and the fraction boiling between 76.2 and 76.6 °C. at 760 Torr collected. Butanone and nitroethane were of laboratory reagent grade, and were dried with anhydrous potassium carbonate and anhydrous calcium sulphate respectively. Both solvents were fractionated through an efficient column and the fractions boiling at 79.2 to 79.8 °C. for butanone and 114.6–114.9 °C. for nitroethane at 760 Torr were collected and used. All solvents were filtered under dry nitrogen to remove dust and all solutions prepared were similarly filtered through a number 3 sintered glass filter. Transfer to the viscometer was made using dust free pipettes. Flow times were measured with a stop watch reading to 0.01 sec. and each point was determined from three successive flow times which did not vary by more than 0.01 sec.

The data could be represented satisfactorily by the equations:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 \qquad (1)$$

and

$$\ln \eta_{rel}/c = [\eta] - k'[\eta]^2 \qquad (2)$$

Limiting viscosity numbers were, therefore, obtained by extrapolation of $\eta_{sp}/c$ or $\ln \eta_{rel}$ *vs.* concentration to infinite dilutions. Both plots were made on the one graph so as to provide a cross-check and the viscosity constants $k_H$ and $k'$, which are related by the equation

$$k_H + k' = 0.5 \qquad (3)$$

Table 1. The viscosity constants (Huggins constants) for the block copolymers in various solvents at 25 °C.

| Polymer | Polystyrene (%) | $k_H$ | | | |
|---|---|---|---|---|---|
| | | Toluene | Butanone | Carbon tetrachloride | Nitroethane |
| P.M.M.A. .... | 0 | 0.38[b] | 0.44[b] | 0.80[c] | 0.35[c] |
| B 4 ........ | 48 | 0.22 | 0.31 | 0.41 | 0.50 |
| B 3 ........ | 62 | 0.24 | 0.33 | 0.40 | 0.52 |
| B 2 ........ | 70 | 0.27 | 0.35 | 0.38 | 0.55 |
| B 1 ........ | 85 | 0.30 | 0.41 | 0.36 | 0.63 |
| Polystyrene . | 100 | 0.35[a] | 0.50[a] | 0.39 | — |

[a] J. H. Green, J. Polymer Sci. **34** (1959) 514.

[b] S. N. Chinai, J. D. Matlak, A. L. Resnick, and R. S. Samuel, J. Polymer Sci. **17** (1955) 391.

[c] T. Alfrey, R. J. Goldberg, and C. C. Price, J. Colloid Sci. **5** (1950) 251.

were obtained from the slopes and checked by the method of least squares. Similar plots were made for the data in butanone, carbon tetrachloride and nitroethane. The HUGGINS constants found in all four solvents are shown in Table 1. The values for the parent polymers are included for easy comparison.

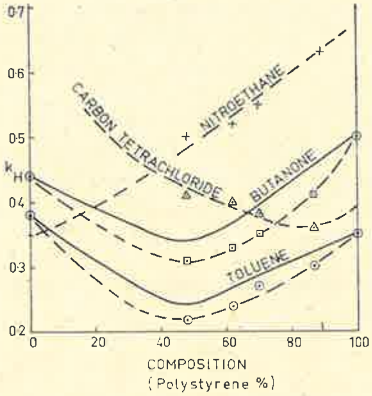

Fig. 1. The viscosity constants (HUGGINS constants $k_H$) as a function of composition

The HUGGINS constants are plotted as a function of the composition of the polymer in several solvents in Fig. 1. It can be seen that, in solvents which are good solvents for both parent polymers, the viscosity constants pass through a minimum at about 50% polystyrene. Since the viscosity constants are indicative of variation in intermolecular forces, as distinct from the limiting viscosity number which reflects variation in intramolecular forces, the implication is that there is greater repulsion in the block copolymer molecules than is to be found in either polystyrene or polymethyl methacrylate. This supports the finding of BURNETT, MEARES, and PATON[4]. Similar repulsions have been observed in simple mixtures of molecules[5] and one is tempted to assume that the same behaviour is being observed in the block copolymers. CRAGG and BIGELOW showed that, for simple mixtures of molecules, the constant for the mixture $k'_m$ can be calculated from the expression

$$k'_m = \frac{k'_A[\eta]_A^2 w_A^2 + k'_B[\eta]_B^2 w_B^2 + 2\,k'_A k'_B[\eta]_A[\eta]_B w_A w_B}{([\eta]_A w_A + [\eta]_B w_B)^2} \qquad (4)$$

where $k'_A$, $k'_B$, $[\eta]_A$, $[\eta]_B$ represent the HUGGINS constants and limiting viscosity number for polymer A and B respectively and $w_A$, $w_B$ represent the respective weight fractions of each block present. The calculated values for the Huggins constants are shown for mixtures of polystyrene and polymethyl methacrylate (full lines) in butanone and toluene. In both cases the experimental values follows the same general pattern as the mixtures but the values obtained are smaller indicating repulsions greater than those found between molecules in a mechanical mixture. The greater negative deviation can only mean that considerable overlap of the domain occupied by each block in the copolymer must exist.

In the solvent carbon tetrachloride the polymethyl methacrylate blocks which are attached to each end of the centre block of polystyrene will occupy a minimum hydro dynamic volume. The centre block on the other hand should be extended and, therefore, the block copolymer molecule behaves like polystyrene homopolymer. The Huggins constants are seen to be roughly constant in the region investigated. It seems likely that k′ drops rapidly with increasing polystyrene content to a constant value equal to that of polystyrene.

In nitroethane which is a non-solvent for polystyrene, the polystyrene block will be in a state of aggregation prior to precipitation so that as the polystyrene content increases the copolymer approaches a point at which it is insoluble in nitroethane above a limiting composition. The experimental values of k′ show an almost linear increase with increasing polystyrene content over the range of composition investigated.

Evidence of strong thermodynamic interaction is clearly shown by the viscosity data. However, the data must be interpreted with some caution, as the error involved in determination of a value for k′ can be as high as 5%. Nevertheless the negative deviations are too consistent to be discounted.

Although the molecular weight range is rather small for the block copolymers examined, we have found that the data can be fitted by a Kuhn-Houwink type equation for the limiting viscosity number as a function of molecular weight.

$$[\eta] = KM^{\nu} \qquad (5)$$

A plot of log $[\eta]$ against log $\overline{M}_W$ using values of $\overline{M}_W$ obtained from light scattering is shown in Fig. 2 for viscosities in toluene. It will be observed that the slope and, therefore, $\nu$ is the same as for polystyrene using the equation of Green[6] and polymethyl methacrylate using the equation of Chinai and co-workers, and that for any given molecular weight the L.V.N. is greater for the block copolymer than for either homopolymer. Stockmayer and co-workers have found that random copolymers of styrene and methyl methacrylate can be represented by a Kuhn-Houwink equation also. However, in accepting this interpretation, the spread of composition should be born in mind.

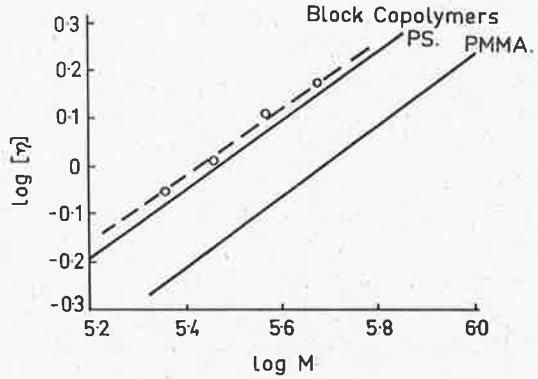

Fig. 2. log [η] *vs.* log M for the block copolymers in toluene

### *Osmometry*

Four osmometers of the Pinner Stabin type[7)] were used for this investigation. Osmometers of this design reach static equilibrium rapidly due to a large membrane area and the relatively small volume employed.

The osmometers may be filled easily without removal from the thermostat so that thermal equilibrium is attained almost immediately. A rotating mounting was constructed to hold all four osmometers with provision for alignment of the capillaries. Reference and solution capillaries were checked to ensure they were matched pairs by adding solvent in the outer jacket and observing the level of the solvent rise in both capillaries. The cathetometer was capable of measuring to 0.001 cm.When the osmometers were assembled to a leak free condition, they were checked by measuring the osmotic pressure developed using the same solution for all four osmometers.

Membranes used were PECEL 600 grade cellulose supplied by Polymer Consultants Ltd., England, which were packed in aqueous acetone. The membranes were conditioned to toluene before use by transferring them at 24 hourly intervals to 75% acetone/water, pure acetone (twice), 75% acetone/toluene, 50% acetone/toluene, 25% acetone/toluene and finally to pure toluene for 48 hrs. Some membranes exhibited a positive osmotic pressure, possibly due to surface inequalities, but which did not exceed 0.05 cm. Where this pressure remained constant a correction was applied to the measured values. Membranes which did not exhibit a reproducible pressure were discarded.

Densities of the block copolymer solutions were based on the values of Matheson and co-workers, assuming a linear relation between density and composition. The densities of one block copolymer (B 4) were calculated at 15 and 50 °C. assuming a linear relationship for density as a function of temperature. Corrections for surface tension effects were deemed negligible. The thermostat was maintained to within ± 0.005 °C., using a thyratron relay and toluene regulator.

The osmotic pressure in dilute solution can be represented by any one of the following three forms:

$$\pi/c = RT/M + Bc + Cc^2 + \ldots\ldots\ldots\ldots \tag{6}$$

$$\pi/c = RT(1/M + A_2c + A_3c^2 + \ldots\ldots\ldots\ldots) \tag{7}$$

$$\pi/c = (\pi/c)_0\,(1 + \Gamma_2c + \Gamma_3c^2 + \ldots\ldots\ldots\ldots) \tag{8}$$

where the constants B, C, $A_2$, $A_3$, $\Gamma_2$, $\Gamma_3$ are all referred to as the virial coefficients. At high dilution Eq. (8) can usually be rewritten in the form:

$$\pi/c = RT/M\,[1 + \Gamma_2c + g\Gamma_2^2c^2] \tag{9}$$

since powers greater than $c^2$ can generally be ignored at high dilution. In this expression

$$\Gamma_3 = g\Gamma_2^2 \tag{10}$$

where g is found experimentally to be equal to $^1/_4$ in good solvents although $g = {}^5/_8$ is the theoretical upper limit for non-interpenetrating spheres. On substituting $g = {}^1/_4$ into (9) we get

$$[\pi/cRT]^{1/2} = M^{-1/2}(1 + {}^1/_2\Gamma_2 \cdot c) \tag{11}$$

Table 2. Osmotic virial coefficients for the block copolymers, measured in toluene at various temperatures

| Polymer | Composition % P.S. | Temp. (°C.) | $\overline{M}_n \cdot 10^{-5}$ | $A_2 \cdot 10^3$ (ccm.·g$^{-1}$) |
|---|---|---|---|---|
| B 1 ........... | 85 | 25 | 3.90 | 0.30 |
| B 2 ........... | 70 | 25 | 3.02 | 0.32 |
| B 3 ........... | 62 | 25 | 2.25 | 0.36 |
| B 4 ........... | 48 | 15 | 1.87 | 0.34 |
| | | 25 | 1.87 | 0.39 |
| | | 50 | 1.87 | 0.51 |

Table 3. Osmotic virial coefficients for the polystyrenes measured in toluene of 25 °C.

| Polymer | $\overline{M}_n \cdot 10^{-5}$ | $A_2 \cdot 10^3$ (ccm. g$^{-1}$) |
|---|---|---|
| P.S. 1 ............................ | 3.42 | 0.31 |
| P.S. 2 ............................ | 2.12 | 0.34 |
| P.S. 3 ............................ | 1.40 | 0.37 |
| P.S. 4 ............................ | 0.90 | 0.42 |

so that $[\pi/cRT]^{1/2}$ is a linear function of the concentration; the intercept yields the number average molecular weight of the polymer. The second virial coefficient can then be found from the slope. Burnett, Meares and Paton[9] found that a value of g equal to or greater than $^5/_8$ was required to fit the data obtained from the block copolymers examined by them. In this work, a value of g equal to $^1/_4$ provided a satisfactory fit as is shown by the linearity of the plot of $[\pi/cRT]^{1/2}$ *vs.* concentration (Fig. 3) for the block B4 measured in toluene at two temperatures. The parent polystyrenes were examined also, and failed to give a linear plot.

The second virial coefficients $A_2$ and the number average molecular weight $\overline{M}_n$ for the block copolymers are given in Table 2, and the corresponding values for the polystyrenes in Table 3. It can be seen that the virial coefficients increase with decreasing molecular weight in both cases. This contrasts with the almost constant value found by Burnett *et al.*, which quantity they assume to be independent of the block copolymer composition. This is based on the assumption that the $A_2$ values for a polystyrene and a polymethyl methacrylate are almost the same for a polymer of comparable molecular weight. Using the same value of $A_2$ quoted by Burnett from the data of Schulz and Doll ($0.33 \cdot 10^{-3}$ at 27 °C. for a molecular weight $1.28 \cdot 10^5$) we estimate from our data for polystyrene the value of $A_2$ for a comparable molecular weight of about $0.4 \cdot 10^{-3}$ (ccm.$\cdot$g$^{-1}$). Consequently, we could expect that increased polystyrene content would yield a higher value of $A_2$ in the block. On the other hand, the effect of increased molecular weight reduces the value of $A_2$ in the polystyrenes so that a similar trend would be expected in the

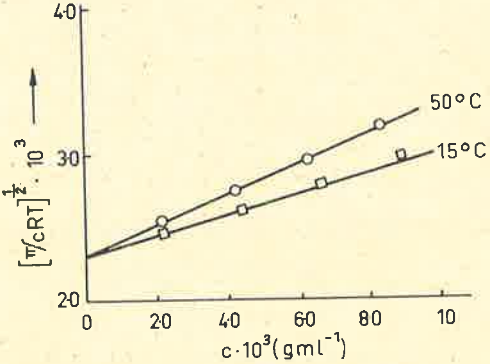

Fig. 3. Plot of $[\pi/cRT]^{1/2}$ *vs.* concentration for the block copolymer B 4 in toluene at 15 and 50 °C.

blocks. It must, therefore, be concluded that molecular weight and composition have a partial cancelling effect on the values of $A_2$ for the block copolymers examined.

## *Light Scattering*

The light scattering instrument was a P.C.L. Peaker supplied by Polymer Consultants Ltd., which had been modified to eliminate the fluctuations due to "hot spotting" of the mercury arc lamp. The cell was fabricated from glass of dimensions 4 mm. · 33 mm. · 46 mm. (depth) rectangular in shape and an outer cell of brass, blackened to absorb stray radiation. The scattered light is observed through a semi circular glass window cemented to the outer cell, and filled with a liquid of the same refractive index as glass, in this case, benzene. Readings can be made over the range 27 to 140°C. with negligible FRESNEL correction.

Calibration of the symmetry of the system was effected by measuring the fluorescence from sodium dichlorofluoresceinate solutions using a yellow filter (Ilford 109 delta chromatic 3, deep yellow) to eliminate scattered light. The value of $r(\Theta) \sin \Theta$, where $r(\Theta)$ is the ratio of the photo current due to scattered and incident light at the angle $\Theta$ showed a slight dependence on $\Theta$. The values were reproducible and, therefore, used to derive a correction factor $\chi(\Theta)$. Calibration of $R_{90}$ was carried out using purified, dust free benzene [$R_{90}$ for benzene[10) was taken as $16.4 \cdot 10^{-6}$] at 5460 Å. The reduced intensity $R(\Theta)$ for unknown solutions was determined from the equation

$$R(\Theta) = K' \cdot n_0^2 \cdot r(\Theta) \cdot \chi(\Theta) \; \frac{\sin \Theta}{1 + \cos^2 \Theta} \tag{12}$$

where $K'$ is the calibration constant, $n_0$ is the refraction index of the solvent and $(r(\Theta) \cdot \chi(\Theta) \cdot \sin \Theta)/(1 + \cos^2 \Theta)$ is the corrected ratio of photo currents at the angle $\Theta$.

All measurements were made in toluene which had been dried over sodium and fractionated through an efficient column. The fraction boiling in the range 110.7–110.9 °C. at 760 Torr was collected, redistilled under nitrogen, and filtered through a number 5 porosity glass filter and centrifuged at 20,000 g. in stainless steel test tubes using a Servall SS-1 angle head centrifuge. Solutions were filtered through a number 4 sintered glass filter using dry nitrogen and finally centrifuged for 1 hr. at 20,000 g. The pipette and cell were rinsed with clarified solvent. The presence of large particles of dust could be detected by visual inspection at low scattering angles. The specific refractive index increments were determined using a double prism refractometer similar to the type described by CECIL and OGSTON[11) calibrated with solutions of sodium chloride. The standard deviation was $4 \cdot 10^{-6}$ and the values of the specific refractive index increments measured at $\lambda = 5460$ Å. were found to be independent of the polymer concentration in the range studied. The refractive index increments for the block copolymers were determined from values obtained for pure polystyrene and pure polymethyl methacrylate assuming a linear relationship between refractive index and the composition of the block copolymer.

The application of light scattering to block copolymers has received some attention particularly in recent years. STOCKMAYER *et al.*[12) derived an equation for the scattering from solutions of block copolymers in which the intensity of light scattered is dependent upon the composition of the block as well as the usual factors. More recent work of BUSHUK and BENOIT 14) and KRAUSE 15) has confirmed this prediction. On consideration it must be obvious that there are two or more scattering elements depending upon the number of monomers used to prepare the polymer: Assuming that the refractive index increment is proportional to its composition, STOCKMAYER and co-workers derive the expression 12)

$$\left(\frac{I(\Theta)}{K'c}\right)_{\substack{c\,=\,0\\ \Theta\,=\,0}} = \left(\frac{dn}{dc}\right)_0^2 \overline{M}_w + 2b\left(\frac{dn}{dc}\right)_0 (M\Delta x) + b^2 < M(\Delta x)^2 > \tag{13}$$

where $I(\Theta)$ is the ratio of the intensity of scattered light at an angle $\Theta$ at a fixed distance from the scattering volume to the intensity of the incident light, c is the concentration of the polymer solution and $(dn/dc)_0$ is the measured refractive index increment and $K' = 2\pi^2 n_0^2\ K/\lambda_0^4\ N$ where $n_0$ is the refractive index of the solvent for light of wavelength $\lambda_0$ in vacuo, N is AVOGADRO's number and K is a function of $\Theta$ which includes the instrument calibration constant. The function b in the expression is equal to the difference in refractive index increment between the segments comprising the polymer chain:

$$b = \left(\frac{dn}{dc}\right)_A - \left(\frac{dn}{dc)}\right)_B \tag{14}$$

where A and B refer to the parent homopolymers. The scattering is dependent upon the composition distribution of the copolymer by the relations

$$(M\Delta x) = w_i M_i (\Delta x)_i \tag{15}$$

$$M(\Delta x)^2 = w_i M_i (\Delta x_i)^2 \tag{16}$$

where $w_i$ is the weight fraction of the molecules in the sample with molecular weight $M_i$ and composition $x_i$ with $(\Delta x)_i = (x_i - x_0)$, where $x_0$ is the average composition of the copolymer sample. An apparent value of the molecular weight is, therefore, found for block copolymers, after extrapolation to zero scattering angle and to infinite dilution. Since the scattering equation of STOCKMAYER *et al.*, contains three unknowns, $\overline{M}_w$, $M\Delta x$, $M(\Delta x)^2$ then these quantities should be obtained from measurements of the light scattering and $(dn/dc)_0$ measurements in three different solvents. KRAUSE 15) has demonstrated the applicability of this approach using data from light scattering in six different solvents. However, if the copolymer molecules are uniform in composition, the molecular weight obtained from light scattering will be independent of the refractive index increment[13, 14]. Block copolymers prepared by the anionic technique are reasonably uniform in composition as well as chain length and, therefore, it is to be expected that under these circumstances M(apparent) = $M_W$ and the normal procedure for determining molecular weight of extrapolation to zero concentration and infinite dilution can be adopted.

The light scattering data has been treated according to the method of ZIMM[16]. A plot of $\left(\frac{Kc}{R(\Theta)}\right)\cdot 10^6$ *vs.* $(\sin^2 \Theta/_2 + 20c)$ for sample B 3 in toluene is shown in Fig. 4. The molecular weight was determined according to the equation:

$$\frac{Kc}{R(\Theta)} = \frac{1}{M_w P(\Theta)} + 2A_2c + \cdots\cdots \tag{17}$$

where $P(\Theta)$ is the particle scattering factor and $A_2$ is the 2nd virial coefficient. The particle scattering factor is unity at $\Theta = 0$ and, therefore, extrapolation of $Kc/R(\Theta)$ to zero angle and then to zero concentration yields the molecular weight. The second virial coefficient $A_2$ was determined from the plot of $\left(\frac{Kc}{R(\Theta)}\right)_{\Theta=0}$ *vs.* c. Linear plots were obtained for all four blocks as can be seen in Fig. 5. The z average mean square radius of gyration $R_{Gz}$ was determined from the ratio of the initial slope to intercept from the plot of $\left(\frac{Kc}{R(\Theta)}\right)_{\Theta=0}$ *vs.* $\sin^2 \Theta/2$ using the relation[17],

$$\frac{\text{Initial slope}}{\text{Intercept}} = 16\,\pi^2(R_{Gz})^2/3\lambda^2 \tag{18}$$

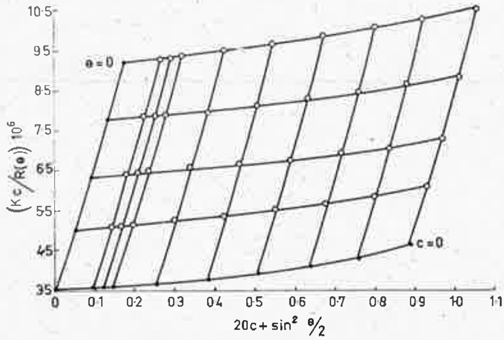

Fig. 4. ZIMM plot for the block copolymer sample B 3 in toluene

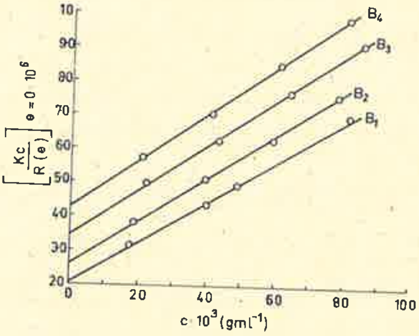

Fig. 5. Plot of $\left(\frac{Kc}{R(\Theta)}\right)_{\Theta = 0}$ *vs.* concentration for the block copolymers

Table 4. The molecular weights, radius of gyration, virial coefficients and heterogeneity ratio for the block copolymers in toluene at 25 °C.

| Polymer | P.S. (%) | $\overline{M}_w \cdot 10^{-5}$ | $\overline{M}_n \cdot 10^{-5}$ | $R_{Gz}$ (A.U.) | $A_2 \cdot 10^3$ (ccm.g$^{-1}$) | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|
| B 1 | 85 | 4.70 | 3.90 | 287 | 0.301 | 1.21 |
| B 2 | 70 | 3.70 | 3.02 | 253 | 0.317 | 1.23 |
| B 3 | 62 | 2.66 | 2.25 | 216 | 0.324 | 1.27 |
| B 4 | 48 | 2.30 | 1.87 | 190 | 0.346 | 1.22 |

The weight average molecular weight, virial coefficient and radius of gyration for the four block copolymers in toluene are shown in Table 4. The heterogeneity ratio $\overline{M}_w/\overline{M}_n$ is shown and indicates that the blocks are somewhat broader in distribution than the parent polystyrenes. However, it is probable that the ratio is smaller than that given in view of the apparent $\overline{M}_w$ being used which could be too high by a factor of 1.1.

The virial coefficients show the same trend as those obtained by osmotic pressure measurements, in that the values of $A_2$ show a slight increase with decreasing molecular weight. However, all values of $A_2$ measured by light scattering are slightly lower than the corresponding values from osmotic pressure data.

We wish to thank Professor D. O. Jordan for helpful discussions and one of us (J.M.S.) wishes to record his thanks for the award of a Commonwealth Post Graduate Research Scholarship.

[1] P. F. ONYON, Techniques of Polymer Characterization, Ed. P. W. ALLEN, Butterworths, London 1959, p. 181.

[2] O. E. ÖHRN, Ark. Kemi **12** (1958) 397.

[3] M. L. HUGGINS, J. Amer. chem. Soc. **64** (1942) 2176.

[4] G. M. BURNETT, P. MEARES, and C. PATON, Trans. Faraday Soc. **58** (1962) 737.

[5] L. H. CRAGG and C. C. BIGELOW, J. Polymer Sci. **16** (1955) 177.

[6] J. H. GREEN, J. Polymer Sci. **34** (1959) 514.

[7] S. H. PINNER and J. V. STABIN, J. Polymer Sci. **9** (1952) 575.

[8] M. S. MATHESON, E. E. AUER, E. B. BEVALAQUA, and E. J. HART, J. Amer. chem. Soc. **71** (1949) 2610; **73** (1951) 1700.

[9] Ref. [4].

[10] P. DOTY and R. F. STEINER, J. chem. Physics **18** (1950) 1211.

[11] R. CECIL and A. G. OGSTON, J. sci. Instruments **28** (1951) 253.

[12] W. H. STOCKMAYER, L. D. MOORE, M. FIXMAN, and B. N. EPSTEIN, J. Polymer Sci. **16** (1955) 517.

[13] W. BUSHUK and H. BENOIT, C. R. hebd. Séances Acad. Sci. **246** (1958) 3167.

[14] W. BUSHUK and H. BENOIT, Canad. J. Chem. **36** (1958) 1616.

[15] S. KRAUSE, J. physic. Chem. **65** (1961) 1618.

[16] B. H. ZIMM, J. chem. Physics **16** (1948) 1099.

[17] K. A. STACEY, Light Scattering in Physical Chemistry, Butterworths, London 1956.

European Polymer Journal, 1965, Vol. 1, pp. 227–234. Pergamon Press Ltd. Printed in England.

# SOLUTION PROPERTIES OF BLOCK COPOLYMERS OF STYRENE AND METHYLMETHACRYLATE—III*

## CONFIGURATIONAL AND THERMODYNAMIC PARAMETERS

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**Abstract**—Thermodynamic and configurational parameters have been derived from data published previously and from some viscosity data presented here. There is evidence to suggest that the block copolymer molecule in dilute solution may be considered as a random coil and therefore that the usual dilute solution theories are applicable. Extra interactions in excess of those found in homopolymers are present and appear to be a function of the number of contacts between chemically different segments in the chain and the solvent used in the investigation. Intramolecular phase separation appears to exist in the unsolvated molecule, possibly as microcrystalline regions. This situation might also persist even in dilute solution with some solvents, but probably vanishes in good solvents for both types of segments.

## INTRODUCTION

In a previous publication[(1)] we presented details of viscosity, osmotic pressure and light scattering studies on four well characterized block copolymers of styrene and methyl methacrylate. All the polymers examined were reasonably monodisperse and unfractionated. Turbidimetric titrations showed the complete absence of any homopolymer and that the copolymer consisted entirely of the triple block species. In this paper we derive the configurational and thermodynamic parameters with the primary object of obtaining information on the extent of interactions between segments of the polystyrene and polymethyl methacrylate chains in dilute solutions. Finally we discuss the possible configuration of block copolymers in dilute solutions.

### *Configurational parameters*

The second virial coefficient which appears in the series expansion of the osmotic pressure for a polymer solution is expressed by the following higher approximation equation of Orofino and Flory[(2)] for the whole range of polymer solvent interaction,

$$A_2 = (16\pi N_A/3^{3/2})\,[\langle \bar{S}^2\rangle^{3/2}/\bar{M}_W^2]\ln[1+(\pi^{1/2}/2)(\alpha^2-1)] \qquad (1)$$

or in the alternative form,

$$A_2 = (2^{5/2}\pi N_A/3^3\Phi)([\eta]/\bar{M}_W)\ln[1+(\pi^{1/2}/2)(\alpha^2-1)] \qquad (2)$$

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* Parts I and II, see Ref. 1

where $\langle \bar{S}^2 \rangle$ is the mean square radius of gyration,
$\bar{M}_W$ the weight average molecular weight,
$[\eta]$ the limiting viscosity number or intrinsic viscosity,
$\alpha$ the Flory expansion factor defined by the ratio

$$\alpha = \langle \bar{r}^2 \rangle^{1/2} / \langle \bar{r}_0^2 \rangle^{1/2} \tag{3}$$

of the root mean square end to end distance in a particular solvent to the corresponding unperturbed values, and $\Phi$ is the universal constant in the Flory–Fox viscosity equation.(3) The value used in this work, $\Phi = 2{\cdot}0 \times 10^{21}$, was the average value found for the block copolymers by substituting the intrinsic viscosity, $\bar{M}_W$ and $\langle \bar{r}^2 \rangle$ into the equation, uncorrected for polydispersity. Actually, little variation was found in the values of $\Phi$ for each block by constrast with the results of Krause(14) on the same system.

We have computed the expansion factor $\alpha$ from both Eqns. (1) and (2) in toluene. The first of these equations combines the osmotic pressure and light scattering data and the second equation osmotic pressure and viscosity data. The values computed from Eqns. (1) and (2) were almost identical. Values of $\alpha$ in other solvents could then be found from the relation

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\alpha_1^3}{\alpha_2^3} \tag{4}$$

where the subscripts represent solvent (1) and solvent (2) respectively. This is valid since the remaining parameters in the viscosity relation(4)

$$[\eta] = \Phi(\langle \bar{r}_0^2 \rangle M)^{3/2} \alpha^3 M^{1/2} \tag{5}$$

remain constant. The use of a lower power of $\alpha$ in Eqn. (5) has been recommended(5) in order to take better account of the non-Gaussian character of chains with excluded volume. However, Fox(6) reports that the use of the amended form is not warranted in the case of methyl methacrylate at least. The use of the higher power in $\alpha$ has been adopted in calculations reported herein.

TABLE 1. CONFIGURATIONAL PARAMETERS FOR BLOCK COPOLYMERS OF STYRENE AND METHYL METHACRYLATE IN TOLUENE AT 25°

| Polymer | Composition % P.S. | $M_W \times 10^{-5}$ | $A_2$ (OSM) | $\alpha$ from Eqn. (1) | $\langle \bar{S}_0^2 \rangle^{1/2}$ Å | $\langle \bar{r}_0^2 \rangle^{1/2}$ Å | $\left(\frac{\langle \bar{r}_0^2 \rangle}{Z}\right)^{1/2}$ cm × $10^8$ | $\frac{\langle \bar{r}_0^2 \rangle^{1/2}}{\langle \bar{r}_{0f}^2 \rangle^{1/2}}$ |
|---|---|---|---|---|---|---|---|---|
| P.S. | 100 | 3·83 | 0·307 | 1·293 | — | — | 5·30(*a*) | 2·44(*b*) |
| $B_1$ | 85 | 4·70 | 0·295 | 1·297 | 221 | 542 | 5·67 | 2·59 |
| $B_2$ | 70 | 3·70 | 0·324 | 1·295 | 196 | 478 | 5·65 | 2·57 |
| $B_3$ | 62 | 2·86 | 0·362 | 1·318 | 163 | 401 | 5·36 | 2·44 |
| $B_4$ | 48 | 2·30 | 0·394 | 1·330 | 143 | 350 | 5·21 | 2·38 |
| P.M.M.A. | 0 | 3·08 | — | 1·282 | — | — | 4·65(*a*) | 2·20(*b*) |

(*a*) T. G. Fox, *Polymer*, **3**, 111 (1962).
(*b*) Flory, Principles of Polymer Chemistry, Cornell University Press, p. 618 (1953).

A knowledge of the expansion factors enables one to calculate a number of configurational parameters useful in an attempt to elucidate the structure of the block copolymers.

The root mean square unperturbed displacement length is widely used to characterize the spatial dimensions of the polymer molecule. The parameter, defined by

$$(\langle \bar{r}_0^2 \rangle / Z)^{1/2} \tag{6}$$

is a constant for the homopolymers and independent of $\bar{Z}$ the average number of bonds in a chain. The displacement length or end-to-end distance is derived from the experimentally determinable quantity, the root mean square radius of gyration $\langle \bar{S}_0^2 \rangle^{1/2}$ by an equation analogous to (3) and from the relation

$$\langle \bar{r}_0^2 \rangle = 6 \langle \bar{S}_0^2 \rangle \tag{7}$$

applicable to a spherically symmetrical molecule with a Gaussian distribution of segments about the centre of mass.(7) The block copolymer molecule probably does not conform closely to such a model but deviation from Gaussian behaviour may not seriously affect the final results.

An indication of the extent of steric interaction can be gained from the comparison of the extent of internal restriction in the block copolymers and the parent homopolymers. The degree of restriction to free rotation is given by the stiffness parameter,(4)

$$\langle \bar{r}_0^2 \rangle^{1/2} / \langle \bar{r}_{0\mathrm{f}}^2 \rangle^{1/2} \tag{8}$$

The value of $\langle \bar{r}_{0\mathrm{f}}^2 \rangle^{1/2}$ is calculated assuming free rotation from the relation

$$\langle \bar{r}_{0\mathrm{f}}^2 \rangle = \bar{Z} l^2 \frac{1 + \operatorname{Cos} \theta}{1 - \operatorname{Cos} \theta} \tag{9}$$

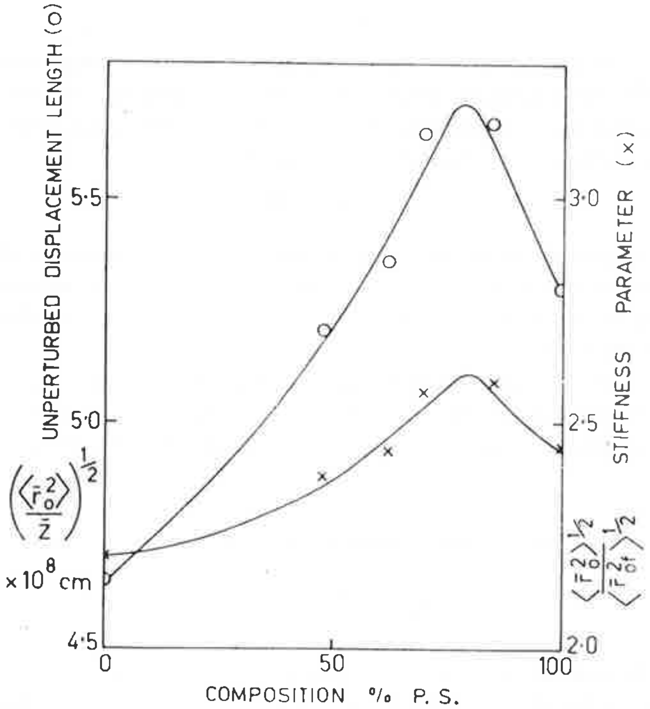
in which $Z$ is the number of bonds in the chain, $l$ is the bond length, and $\theta$ is the angle between successive bonds. Assuming $l = 1{\cdot}54$ Å for the carbon–carbon bond and the tetrahedral angle 109° 28′ the *stiffness* parameter has been calculated for the four block copolymers. These values are shown in Table 1 where they may be compared with values obtained for the homopolymers.

Included in the table are the expansion factors ($\alpha$), the unperturbed displacement lengths, radius of gyration and the parameter $(\langle \bar{r}_0^2 \rangle / \bar{Z})^{1/2}$. The expansion factor for polystyrene was calculated from equation (2), using an average value of the product of

$$\frac{A_2 \bar{M}_W}{[\eta]} \tag{10}$$

appearing in the equation from data on the parent polystyrenes. The corresponding value for methyl methacrylate was calculated from the viscosity data of Fox.(6) Extrapolating the intrinsic viscosities in toluene at various temperatures, we find $[\eta]_{25^\circ} = 0{\cdot}562$ for $\bar{M}_v = 308 \times 10^3$ and using $K = 4{\cdot}8 \times 10^{-4}$ we calculate $\alpha_{25^\circ} = 1{\cdot}282$. The values of $(\langle \bar{r}_0^2 \rangle / \bar{Z})^{1/2}$ given for polystyrene and polymethyl methacrylate are those reported by Fox(6) in his paper.

The displacement length parameter and the stiffness parameter are both shown in Fig. 1, where it can be seen that there is an obvious maximum at about 80 per cent polystyrene content. This contrasts with the maximum in the analogous parameter $(\langle \bar{r}_0^2 \rangle / M)^{1/2}$ reported by Burnett, Meares and Paton(8) where a sudden transition occurs at about 60 per cent polystyrene content. In our results there appears to be a gradual transition from the values for the homopolymers through a maximum at about 75–80 per cent in the composition scale. The dissymmetry is presumably caused by the difference in the values for the homopolymer. The more expanded form of the polymer occurring at the maximum is reflected in the increased restriction to free rotation.



### *The excluded volume effect*

The binary cluster integral $\beta$ correlates the excluded volume effect with the second virial coefficient, although as Zimm, Stockmayer and Fixman⁽⁹⁾ observe the physical interpretation of $\beta$ as an excluded volume should not be taken too literally in all circumstances. The values of $\beta$ for each block copolymer in the several solvents may be computed from the expression derived by Kurata, Stockmayer and Roig,⁽⁵⁾

$$(\alpha^3-\alpha)/N^{1/2} = \{(1+\tfrac{1}{3}\alpha^{-2})^{-3/2}\}^{-1}\,(4/3)^{5/2}\,(3/2\pi)^{3/2}\,(\beta/a^3) \tag{11}$$

where $N$ is the number of segments in the chain and the parameter $a$ is the effective bond length. These authors consider the preferred statistical chain to be the most appropriate choice for the equivalent random chain⁽¹⁰⁾ required for the evaluation of $\beta$ from solution properties. The effective bond length is thus defined by

$$a^2 = \langle \bar{r}^2\rangle/\bar{Z} \tag{12}$$

where $\bar{Z}$ is the average number of bonds in the chain. $\langle \bar{r}^2\rangle$ may be obtained from the viscosities using the relation

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\langle \bar{r}^2\rangle_1^{3/2}}{\langle \bar{r}^2\rangle_2^{3/2}} \tag{13}$$

for solvents other than toluene.

TABLE 2. THE INTRINSIC VISCOSITIES, EXPANSION FACTORS AND BINARY CLUSTER INTEGRALS IN (1) TOLUENE, (2) BUTANONE, (3) CARBON TETRACHLORIDE AND (4) NITROETHANE AT 25°

| | Intrinsic Viscosities [$\eta$] at 25° | | | | Expansion Factors $\alpha$ | | | | Binary Cluster Integrals $\beta$ CCS × $10^{24}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Polymer | (1) | (2) | (3) | (4) | (1) | (2) | (3) | (4) | (1) | (2) | (3) | (4) |
| $B_1$ | 1·496 | 0·904 | 1·170 | 0·198 | 1·297 | 1·097 | 1·196 | 0·661 | 10·2 | 1·71 | 3·49 | −6·6 |
| $B_2$ | 1·274 | 0·773 | 1·059 | 0·345 | 1·295 | 1·097 | 1·218 | 0·838 | 11·0 | 1·87 | 5·00 | −4·6 |
| $B_3$ | 1·038 | 0·641 | 0·860 | 0·462 | 1·318 | 1·122 | 1·238 | 1·006 | 12·5 | 2·51 | 6·45 | 3·2 |
| $B_4$ | 0·887 | 0·545 | 0·732 | 0·531 | 1·330 | 1·130 | 1·247 | 1·120 | 13·6 | 2·38 | 7·93 | 12·1 |

In Table 2 the intrinsic viscosities, expansion factors and the binary cluster integrals in the several solvents and for each block copolymer are tabulated. The expansion factors and the values of $\beta$ all show an increase towards the middle of the composition scale.

### *Thermodynamic parameters*

The thermodynamic parameters are computed from the temperature dependence of the second virial coefficient which is expressed by the relation,(11)

$$A_2 = (\bar{v}_2^2/V_1)\psi_1(1-\theta/T)F(X) \tag{13}$$

where $\bar{v}_2$ is the specific volume of the polymer, $V_1$ is the molar volume of the solvent, $\psi_1$ the entropy of dilution parameter, related to the partial molar entropy of dilution $\bar{S}_1$ by

$$\psi_1 = \Delta\bar{S}_1/Rv_2^2 \tag{14}$$

at a fixed volume fraction $v_2$. $\theta$ is the Flory temperature and $F(X)$ is a function of $\alpha$ which becomes unity at $T = \theta$.(11)

The block copolymer $B_4$ was examined at three temperatures and a plot of the second virial coefficient as a function of temperature is shown in Fig. 2.

We have calculated values for $\bar{v}_2$ and $V_1$ from the data of Fox and Loshaek(12) on polystyrene and methyl methacrylate assuming volume additivity. The value of $F(X) = 0{\cdot}82$ has been computed from an average value of $\alpha = 1{\cdot}3$ in toluene, neglecting all terms beyond the square term in

$$F(X) = 1 - X/2!\,2^{3/2} + X^2/3!\,3^{3/2} - X^3/4!\,4^{3/2} \tag{15}$$

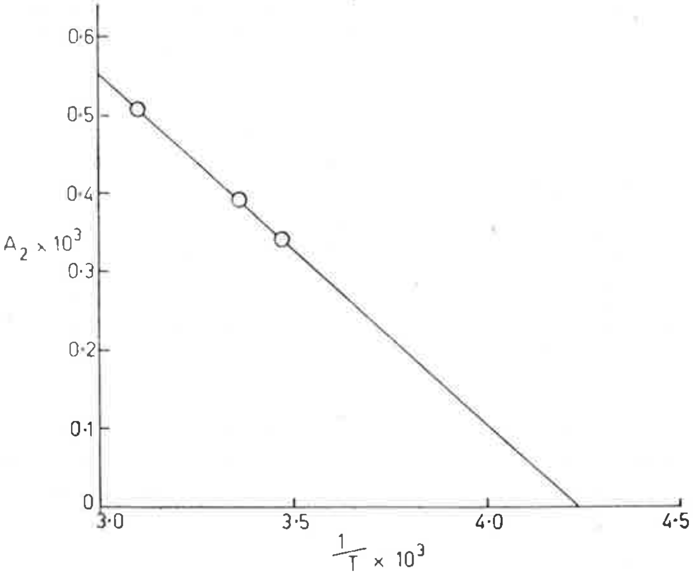
The entropy of dilution parameter is obtained from the slope of the plot of $A_2$ versus $1/T$. The intercept at $A_2 = 0$ is the Flory temperature $\theta$.

The heat of dilution parameter may be computed from the relation(11)

$$\kappa_1 = \frac{\theta}{T}\psi_1 \tag{16}$$

and the interaction parameter $\chi$ from the expression

$$\chi = \tfrac{1}{2} - (\psi_1 - \kappa_1) \tag{17}$$



using the values for $\psi_1$ and $\kappa_1$ previously found. The heat of dilution parameter is related to the partial molar heat of dilution in a manner analogous to the relation between the entropy term, and the molar entropy of dilution thus,

$$\kappa_1 = \Delta \bar{H}_1 / RT v_2^2 \tag{18}$$

Values obtained for $\theta$, $\kappa_1$, $\psi_1$, $\chi$ for the block $B_4$ and values reported previously for polystyrene and polymethyl methacrylate are all shown in Table 3. It is obvious on inspection that whilst the interaction parameter remains apparently unchanged, the heat and entropy of dilution parameters are much larger than the values published for the parent homopolymers. Similar results have been reported by Burnett, Meares and Paton(8) for a series of block copolymers of styrene and methyl methacrylate obtained by fractionation. In the paper by these authors and in this work the critical solution temperature is shown to be greater than the values obtained for the homopolymers indicating extra interactions from the chemically different segments in the copolymer molecule.

Of course, $\theta$ determined experimentally is an average value only and represents the point at which positive and negative contributions to the excluded volume cancel.

TABLE 3. THERMODYNAMIC PARAMETERS

| Polymer | $\theta$°K | $\kappa_1$ | $\psi_1$ | $\chi_1$ |
|---|---|---|---|---|
| P.S. | 160 | 0·06 | 0·11 | 0·452 |
| $B_4$ | 235 | 0·254 | 0·322 | 0·432 |
| P.M.M.A. | 208 | 0·076 | 0·11 | 0·466 |

## DISCUSSION

The thermodynamic parameters shown in Table 3 for the block copolymer $B_4$ reveal larger heat and entropy of dilution parameters than has been observed for either of the parent homopolymers. An increase in interactions between chemically different segments within the polymer must be concluded. Repulsive interactions between chemically different molecules have been observed in the case of mixtures and random copolymers(13) and it is, therefore, to be expected that similar interactions will be observed for block copolymers. The larger entropy of dilution parameter has been interpreted by Burnett, Meares and Paton(8) to imply that a greater degree of configurational restriction exists in the unsolvated block which is progressively relieved as the molecule imbibes solvent. These authors observed a maximum in $\theta$, $\kappa_1$, and $\psi_1$ which occurs at the middle of the composition scale.

Looking at the problem another way the high entropy of dilution may also be due to greater order in the "dry" block. That is, microcrystalline regions might exist which are randomized as the molecule becomes increasingly solvated. Thus as the solution becomes increasingly concentrated the repulsions due to chemically different segments cause "intramolecular phase separation". This situation may even persist in dilute solution to some degree.

The configurational parameters give support to the contention that repulsive interactions exist within the block copolymer molecule. The more expanded configuration of the copolymer and the restriction to free rotation are shown in Table 1 and the first figure. However, in this work there appears to be a smooth transition from one pure homopolymer to the other passing through a maximum at about 80 per cent polystyrene content rather than the "sudden transition" observed by Burnett *et al.* and contrasting with the somewhat lower values reported by Krause.(14)

The final evidence for increased interactions and possible phase separation is to be found in the excluded volume effect. The binary cluster integrals which are an average value of the contributions from the chemically different segments in the chain all show an increase in the middle of the composition scale where the greatest number of contacts between chemically different segments is to be expected.

In a good solvent for both polymers the random coiling of the polymer chain is almost complete in dilute solution, and therefore the maximum number of repulsion contacts occur. In such a solvent $\beta$ is large due to the large contribution from chemically different segments.

In nitroethane, the negative values of $\beta$ indicate that the molecule is close to precipitation. The solvent is a non-solvent for polystyrene and therefore the polystyrene block is collapsed. It must be observed that in this case the single contact approximation is probably inapplicable, since it seems likely that most contacts will be ternary or even greater due to the absence of solvent from the styrene segments, Even so, it seems likely that when the molecule contains one type of segment mainly, then separation into chemically different domains is almost complete. Carbontetrachloride by contrast is a good solvent for polystyrene but a poor solvent for polymethyl methacrylate. Here again, whilst there is no collapsed molecule, multiple contacts are ensured by the exclusion of solvent from the domain of the polymethyl methacrylate and allowing a greater number of contacts between chemically different segments.

There seems every indication that, in dilute solution, the random coil model is applicable to a block copolymer and therefore that the assumption of a Gaussian distribution of segments is a reasonable one. The application of the usual theories of dilute solution is therefore valid. However, only an average value of the contributions from the chemically different segments within the chain is obtained experimentally and since the contribution to solution properties in excess of those found for the homopolymers is small for block copolymers, considerable care must be exercised both in obtaining these values and in the preparation of samples to be investigated.

*Acknowledgement*—The authors wish to thank Dr. T. Kurucsev for helpful suggestions.

## REFERENCES

(1) J. R. Urwin and J. M. Stearne, *Makromolek. Chem.* **78**, 194, 204 (1964).
(2) T. A. Orofino and P. J. Flory, *J. chem. Phys.* **26**, 1067 (1957).
(3) P. J. Flory and T. G. Fox, *J. Am. chem. Soc.* **73**, 1904 (1951).
(4) P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Chap. XIV, p. 612 (1953).
(5) M. Kurata, W. H. Stockmayer and A. Roig, *J. chem. Phys.* **33**, 151 (1960).
(6) T. G. Fox, *Polymer*, **3** 111 (1962).
(7) Ref. (4) Chap. X.
(8) G. M. Burnett, P. Meares and C. Paton, *Trans. Faraday Soc* **.58**, 737 (1962).
(9) B. Zimm, W. H. Stockmayer and M. Fixman, *J. chem. Phys.* **21**, 1716 (1953).
(10) H. Tompa, *Polymer Solutions*, p. 246, Butterworth (1956).
(11) Ref. (4) Chap. XII.
(12) T. G. Fox and S. Loshaek, *J. Polym. Sci.* **15**, 371 (1955).
(13) References are given in the paper of Burnett *et al.*
(14) S. Krause, *J. phys. Chem.*, Ithaca, **68**, 1948 (1964).

**Résumé**—Des paramètres thermodynamiques et configurationnels ont été dérivés de données précédemment publiées et de certaines données sur la viscosité, ci-présentées. Certaines preuves suggèrent que le bloc molécule co-polymère, dans une solution diluée, peut être considéré en tant que formation accidentelle et par conséquent les théories habituelles concernant une solution diluée s'appliquent. Des réactions supplémentaires surpassant celles trouvées dans les homopolymères sont présentes et semblent être en fonction du nombre de contacts entre des segments chimiquement différents du point de vue de la chaîne et du solvant employés pour l'investigation. Une séparation de phase intramoléculaire semble exister dans la molécule insolvatisée, possiblement sous forme de régions microcrystallines. Cette situation pourrait même persister dans une solution diluée avec quelques solvants, mais disparait probablement dans les bons solvants pour les deux types de segments.

**Sommario**—Dei parametri termodinamici e configurazionali sono stati derivati da data precedentemente pubblicate e da alcune altre appresso presentate sulla viscosità. Ci sono delle prove da suggerire che il blocco molecola co-polimere in soluzione diluita può essere considerato pari a una formazione casuale e quindi le solite teorie riguardanti una soluzione diluita, sono applicabili. Delle reazioni estra che superano quelle che si trovano in omopolimeri sono presenti e sembrano essere in funzione al numero di contatti fra segmenti chimicamente diversi nella catena e nel solvente adoperati per l'investigazione. Una separazione di fase intramolecolare sembra esistere nella molecola insolvatizzata, forse pari a delle regioni microcristalline. Tale situazione potrebbe persistere anche in soluzione diluita con alcuni solventi, ma probabilmente svanisce in solventi buoni per entrambi tipi di segmenti.

**Zusammenfassung**—Thermodynamische und configurationale Ergebnisse wurden von früheren und von einigen hier gegebenen Viscositäts-angaben hergeleitet. Es besteht Grund zur Annahme, dass das Block-co-polymere Molekül in verdünnter Lösung als Zufallsprodukt angesehen werden kann und dass deshalb die üblichen Theorien über verdünnte Lösungen anwendbar sind. Weitere Wechselwirkungen neben solchen, die man in Homopolymeren findet, sind vorhanden und erscheinen eine Funktion der Anzahl von Kontakten zwischen den verschiedenen Segmenten in der Kette und dem Lösungsmittel, das für die Untersuchung benutzt wurde, zu sein.

Intramolekuläre Phasentrennung scheint im ungelösten Molekül vorhanden zy sein, möglicherweise als mikro-krystallinische Regionen. Diese Situation kann möglicherweise auch sogar in verdünnten Lösungen mit gewissen Lösungsmitteln weiterbestehen, verschwindet aber wahrscheinlich in guten Lösungsmitteln für beide Segmenttypen.

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# THE KINETIC CHARACTERIZATION OF THE POLYMERIZATION OF ISOPRENE IN BENZENE INITIATED BY BUTYL LITHIUM AS A FIRST STEP IN THE SYNTHESIS OF BLOCK COPOLYMERS

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**Abstract**—The kinetics of the initiation and propagation steps in the polymerization of isoprene in benzene, initiated by butyl lithium as a first step in the synthesis of block copolymers has been examined. The rate of initiation is first order with respect to butyl lithium. A slow initial reaction is followed by an acceleration of the rate as polymer is generated. The sigmoidal rate curve appears to be characteristic of the initiation step and not due to termination products. The rate of propagation is shown to be a half order with respect to the concentration of growing chains, indicating a dimeric association of the polymer.

## INTRODUCTION

STUDIES on the solution properties of block copolymers have demonstrated the desirability of developing better synthetic methods if these investigations are to be worthwhile.(1) The strict tolerances imposed on homogeneity of the product, in molecular weight, composition, absence of extraneous homopolymer, and possibly even micro structure, place very high demands on skill and technical ingenuity.

Certain essential conditions must be observed in the two stages of the preparation. Firstly, all of the monomer in the first stage must have been consumed before the second monomer can be added. Secondly, the initiation step must be fast compared with the propagation step if the molecular weight distribution is not to be broad. Alternatively, a polymer seed of low molecular weight may be prepared and then added to the bulk of the monomer for the propagation step. This method still requires a fast initiation in order that all of the initiator be consumed. It may be possible to add small amounts of polar substances such as tetrahydrofuran since Worsfold and Bywater(2) have found that these substances cause a large increase in initiation with little increase in propagation. The third condition is that impurities which will cause initiator destruction or the destruction of growing chains must be reduced to negligible proportions. The problem reaches significant proportions when high molecular weight products are desired since the initiator concentrations employed are of the order of $10^{-4}$ molar and spurious termination must be at least two orders smaller than this. Finally, in the second stage of the polymerization the second monomer must be added without the addition of terminating material to avoid contamination of the product with homopolymer from the first step.

In this study the solvent benzene was chosen because of the stereospecificity of the polymer formed when isoprene is polymerized by lithium alkyls in benzene.(3, 4) The configuration of the polymer product is mainly *cis* 1,4 although the exact proportion of the micro-structure so far reported appears to be in poor agreement. This is probably due, in part, to the different methods of analysis employed.(4) The lack of published data in this solvent led us to examine both the initiation and progapation steps. The concentration of polyisoprenyl lithium was determined spectrophotometrically in the visible range and was based on determinations of "living ends" using the Volhard methyl iodide analysis. End points were detected both colorimetrically and by the more direct electrometric method. Consumption of monomer was followed by dilatometry.

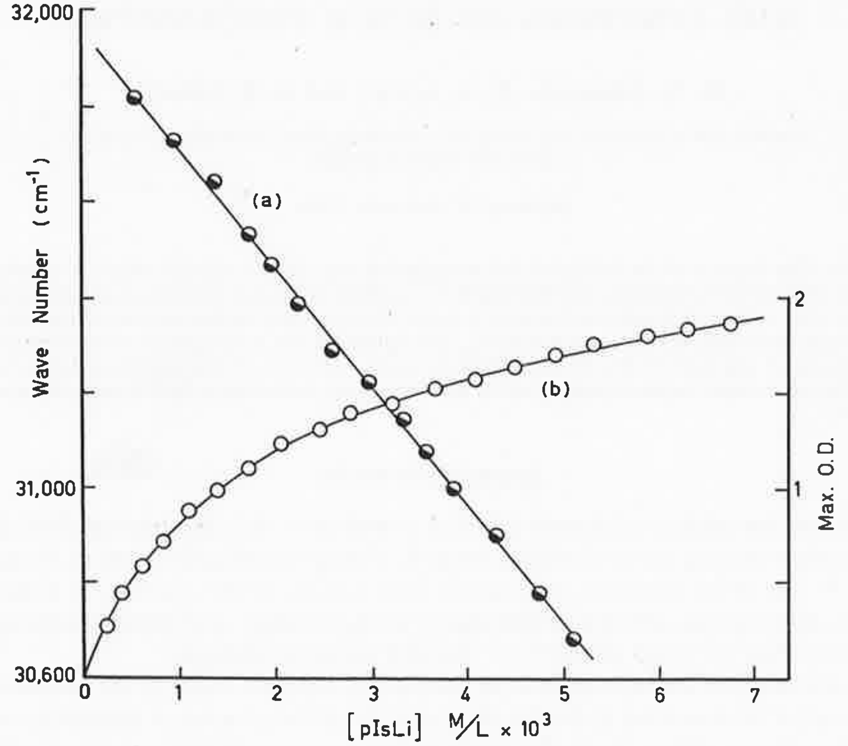

FIG. 1.(a). Frequency of the absorption maximum vs. the concentration of polyisoprenyl lithium.
(b). The optical density of the absorption maximum vs. the concentration of polyisoprenyl lithium.

Spectrophotometric studies of the coloured polyisoprenyl lithium showed a hypsochromic shift of the maximum absorption on dilution. Within the range of concentrations measured ($5 \times 10^{-4}$ M–$5 \times 10^{-3}$ M) the drift was linear [Fig. 1.(a)]. This concentration dependence rather suggests that a whole spectrum of polymerization intermediates, complexed with the solvent, is involved. The extinction coefficients ranged from $\epsilon = 500$ at low concentrations (up to $2{\cdot}5 \times 10^{-3}$ M) to $\epsilon = 280$ at the highest concentration $1{\cdot}0 \times 10^{-2}$ M. Comparing these data with the kinetic results, the average association number for the growing chain appears to change from the dimeric form in dilute solution to trimer or tetramer in more concentrated solution. Sinn has reported the existence of the monomer form at very low concentrations and an even higher association number in concentrated solutions of n-heptane. Conductivity studies in these solutions indicate the virtual absence of free ions.(5) A calibration curve [Fig. (1b)] was constructed from the observed O.D. at the maximum at various concentrations and the concentrations of polyisoprenyl lithium were computed from the maxima observed at each stage of the polymerization.

## EXPERIMENTAL

Benzene (Univar A.R. grade) was dried over sodium wire, refluxed over calcium hydride and fractionally distilled. After degassing on the vacuum line a quantity of butyl lithium was added and styrene distilled into the vessel. The characteristic red colour developed after termination of adventitious material. Benzene for use as solvent was flash distilled from this reservoir.

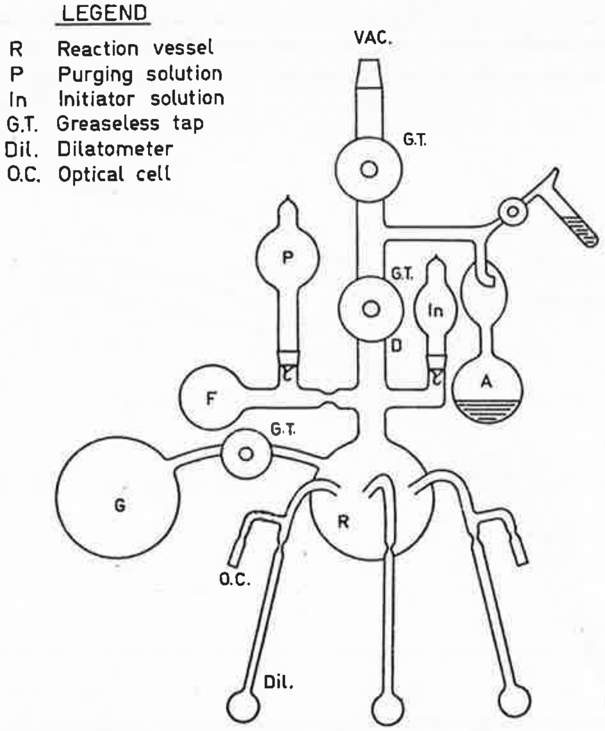

FIG. 2. The reaction vessel.

Monomers were dried over calcium hydride, degassed and distilled. The middle fraction was distilled on to fresh calcium hydride and allowed to stand for 24 hr. The process was repeated three times and finally stored at −10° in the dark. Methyl iodide was subjected to the same procedure before use.

Purging solutions were prepared from styrene and butyl lithium in benzene and stored in 50-ml ampoules with twist break seals ready for use. Butyl lithium was prepared by slow addition of a solution of butyl chloride in benzene to lithium shavings in benzene in an atmosphere of oxygen free nitrogen. After 12 hr the concentrated butyl lithium solution was decanted into a retort fitted with a greaseless tap. Ampoules of butyl lithium were sealed off at this stage for use in determining the initiation rate. Polyisoprenyl lithium "seed" was prepared using this butyl lithium. After degassing, a calculated quantity of isoprene was added and the formation of isoprenyl lithium followed spectrophotometrically in sealed optical cells. Having determined the concentration of the initiator "seed", predetermined volumes were sealed off in ampoules. The initiator seed prepared had an average molecular weight of about 3000 when all butyl lithium had been consumed. Analysis of the concentration of "seed" was effected by adding methyl iodide and determining the concentration of lithium iodide resulting. The solutions were titrated with excess silver nitrate and back titration with ammonium thiocyanate or more commonly a potentiometric titration was employed by titrating the silver nitrate against the lithium iodide directly. This method proved to have the greater accuracy.

Propagation was followed by dilatometry. The solutions were prepared in the vessel shown in Fig. 2 which allowed the purging of the apparatus including dilatometers and spectrophotometer cells. The partially spent purging solution was tipped into bulb F and the vessel removed from the apparatus. Monomer and solvent were flash distilled into A and purging solution added through a greaseless tap until a permanent colour persisted. The solution was washed around the upper part of the vessel and then tipped back into A. Monomer and solvent were then distilled into the reaction flask, the large greaseless tap at D closed and initiator seed added. Samples for dilatometry and spectrophotometry were then sealed off. The reaction mixture was isolated in bulb G for the second stage of the preparation.

## RESULTS

A preliminary examination of this system indicated that initiation was complete when an average of 40 monomer units had been consumed for each molecule of butyl lithium, a value which is much smaller than the several hundred units found in cyclohexane by Worsfold and Bywater.(2) This value is simply the ratio of the total monomer consumed at complete initiation to the total initiator generated. The polymerization was followed spectrophotometrically and by dilatometry simultaneously. These values lead to a considerable improvement in homogeneity over the reaction in cyclohexane, nevertheless a reduction in monomer consumed during initiation is desirable.

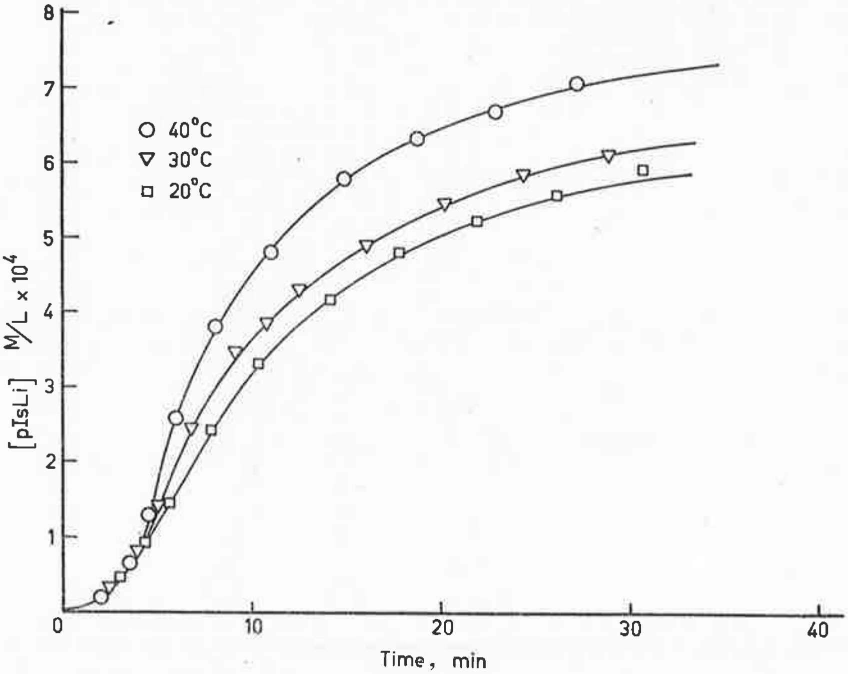

FIG. 3. Initiator conversion–time curves for the formation of polyisoprenyl lithium at several temperatures.

The initiator time–conversion curves (Fig. 3) are sigmoidal due to an initial induction period which is followed by an acceleration of the rate. The butyl lithium initially added to the system was found to correspond with the final concentration of polyisoprenyl lithium and therefore it must be concluded that the induction period is characteristic of the initiation step.

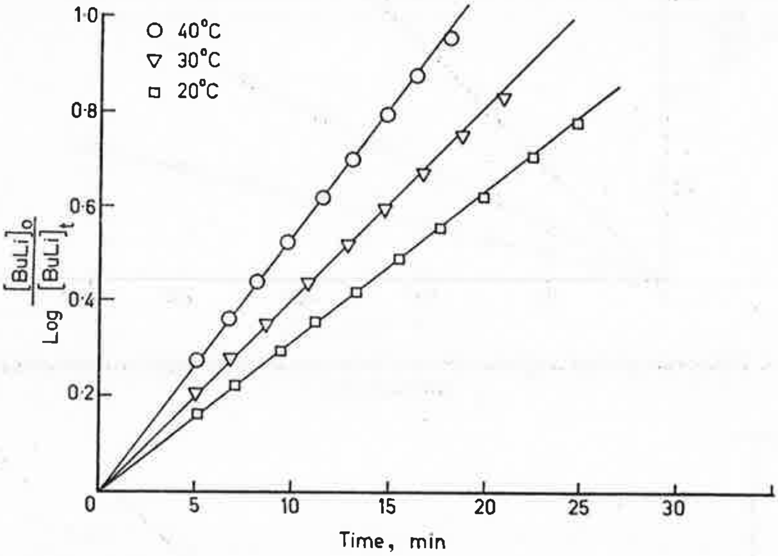

FIG. 4. First-order plots of the conversion of butyl lithium to polyisoprenyl lithium at several temperatures.

Excellent first-order plots of the initiation rate after the induction period were obtained (Fig. 4). The energy of activation and pre-exponential factor were obtained from the temperature dependence of the rate of initiation and the apparent rate constant for initiation is then

$$k_1 = 10^{2\cdot 0} \exp - \frac{4\cdot 300}{RT}$$

and at 30° is $8{\cdot}04 \times 10^{-2}$ litre $\text{mole}^{-1}$ $\text{min}^{-1}$. Worsfold and Bywater$^{(2)}$ have proposed that a complex of the polyisoprenyl lithium and butyl lithium is an active polymerization agent. The low pre-exponential factor observed here is consistent with the large negative entropy to be associated with formation of such a complex. It seems plausible that the ion pairs $\text{Bu}^-\text{Li}^+$ may begin the initial slow reaction which is rapidly catalyzed by the complex being formed.

The rate of propagation was followed by dilatometry after all of the butyl lithium was consumed and the optical density of the solution remained constant. Good first-order plots were obtained for the consumption of monomer over at least four half-life times (Fig. 5). The rate of propagation is therefore

$$-\frac{d[M]}{dt} = k_2\ [\text{polyisoprenyl lithium}]^n[\text{isoprene}]^{1\cdot 0}$$

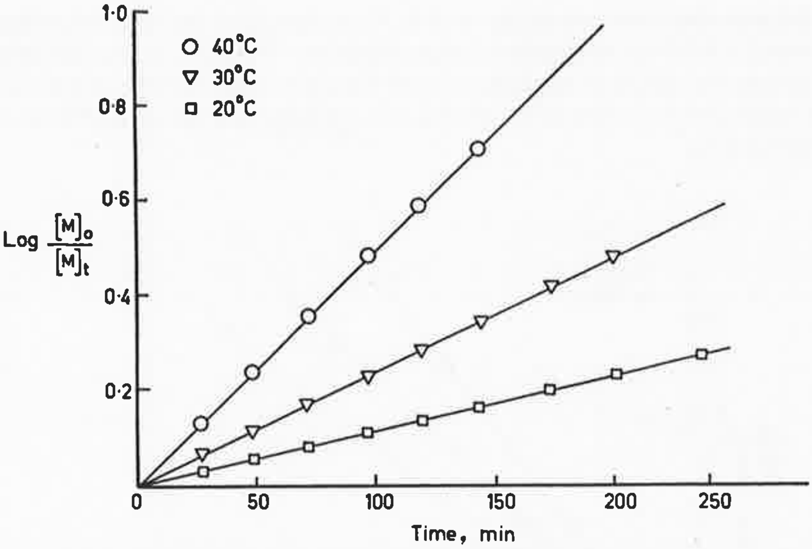

FIG. 5. First-order plots of the consumption of monomer in the propagation reaction at several temperatures.

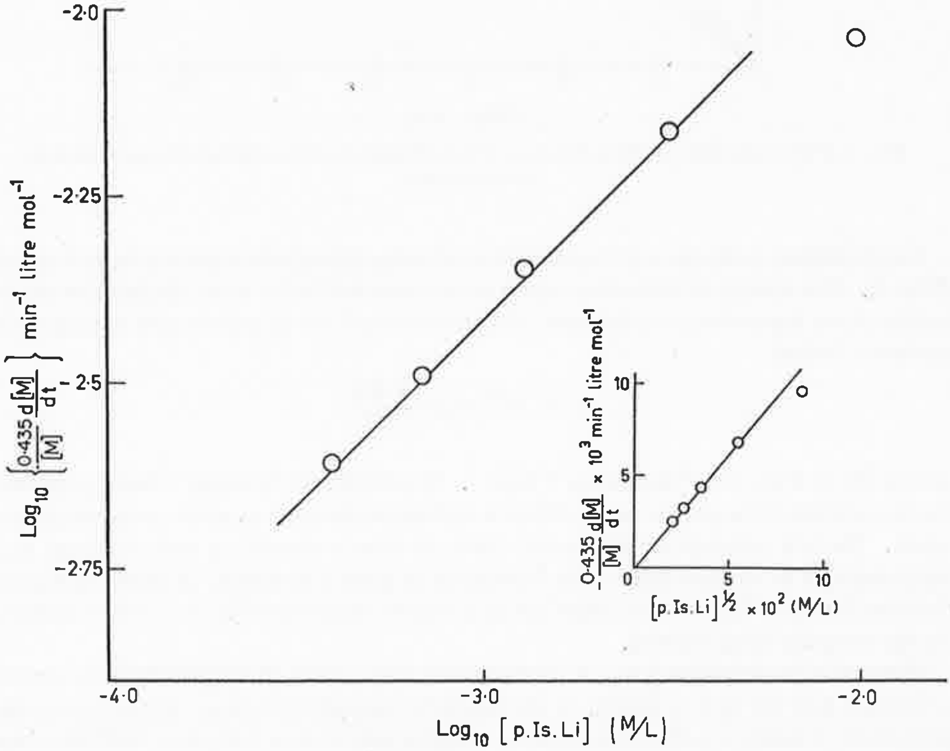

FIG. 6. $\log_{10}\left[-\frac{0\cdot435}{[M]}\frac{d[M]}{dt}\right]$ vs. $\log_{10}$ [polyisoprenyl lithium].

Inset: $-\frac{0\cdot435}{[M]}\frac{d[M]}{dt}$ vs. [polyisoprenyl lithium]$^{\frac{1}{2}}$.

in accordance with the mechanism

$$[\mathrm{Bu}(M)_x\mathrm{Li}]_n \rightleftarrows n\mathrm{Bu}(M)_x\mathrm{Li} \qquad K_2$$

$$\mathrm{Bu}(M)_x\mathrm{Li} + \mathrm{M} \rightarrow \mathrm{Bu}(M)_{x+1}\mathrm{Li} \qquad k_p$$

in which the growing chain is assumed to be strongly associated. The apparent rate constant is therefore a function of the equilibrium constant. In Fig. 6 a plot of $\log_{10} - (1/[M])/(\mathrm{d}[M]/\mathrm{d}t)$ vs. $\log_{10}[\mathrm{p{\cdot}Is{\cdot}Li}]$ has been constructed. The slope of the line drawn through the experimental points is 0·5 corresponding to a half order with respect to polyisoprenyl lithium. The points suggest that a change in slope at higher concentrations might be expected but the data are inconclusive and further study is under way to examine the kinetics in this system.

The Arrhenius constants have been determined from the temperature dependence of the rates and the apparent rate constant for propagation is:

$$k_2 = 10^{9\cdot 0}\exp - \frac{13{,}300}{RT}$$

and at 30° the experimental value is $7{\cdot}7 \times 10^{-2}$ litre $\mathrm{mole}^{-1}$ $\mathrm{min}^{-1}$.

Inset is the plot of $-(1/[M])/(\mathrm{d}[M]/\mathrm{d}t)$ vs. $[\text{polyisoprenyl lithium}]^{\frac{1}{2}}$ which demonstrates the absence of adventitious termination.

## DISCUSSION

Efforts to determine the absolute rate constants in anionic polymerization have been aggravated by the existence of complex association equilibria, and work done on this problem has been reviewed recently by Bywater.(4) Whilst little data have been published on initiation, several attempts have been made to evaluate $k_p$. Two lines of approach have been used. Sinn(7, 8) has worked at low concentration and assumed that only the unassociated form of the growing chain exists. Morton(9,19) has attempted to determine the equilibrium constant $K_2$ by an independent method. Bywater concludes that, despite the ingenuity shown by these workers, no accurate value for $k_p$ has yet been obtained. Despite this handicap, it is instructive to determine the apparent rate constants in a given system in order that $k_1$ and $k_2$ may be compared.

It is seen from the measured rate constants at 30° that the rates of initiation and propagation are approximately equal and the Arrhenius factors show that polymerization at lower temperatures improves the ratio in favour of initiation. The addition of small amounts of polar substances such as T.H.F. has been shown to increase initiation with little change in propagation. This might be used to advantage in providing a narrower molecular weight distribution, however the resulting change in microstructure may be a disadvantage when examining solution properties.

It can be concluded from this study that the system investigated will provide a satisfactory first stage for the synthesis of homogeneous block copolymers of predictable molecular weight, composition and purity. The second stage is now being investigated.

## REFERENCES

(1) J. R. Urwin and J. M. Stearne, *Europ. Polym. J.* **1**, 227 (1965).
(2) D. J. Worsfold and S. Bywater, *Can. J. Chem.* **42**, 2884 (1965).
(3) H. Morita and A. V. Tobolsky, *J. Am. chem. Soc.* **79**, 5853 (1957); A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.* **40**, 73 (1959); other Refs. in Bywater review, Ref. 4.

(4) S. Bywater, *Advances in Polymer Science* **4**, 66 (1965).
(5) H. Sinn, Preprint P.575 *I.U.P.A.C. International Symposium on Macromolecular Chemistry, Prague* 1965.
(6) A. F. Johnson and D. J. Worsfold, *J. Polym. Sci.* **A3**, 449 (1965).
(7) H. Sinn and O. T. Onsager, *Makromolek. Chem.* **55**, 167 (1962).
(8) H. Sinn and F. Patat, *Angew. Chem.* **75**, 805 (1963).
(9) M. Morton, L. J. Fetters and E. E. Bostick, *J. Polym. Sci.* **C1**, 311 (1963).
(10) M. Morton and L. J. Fetters, *J. Polym. Sci.* **A2**, 3311 (1964).

**Résumé**—La cinétique des mesures d'initiation et de propagation dans la polymérisation de l'isoprène en benzène, a débuté par le butyllithium comme première mesure dans la synthèse de blocs de copolymères, et a été examinée. Le taux d'initiation est de premier ordre en ce qui concerne le butyllithium. Une réaction initiale lente est suivie par une acceleration du taux à mesure que le polymère est généré. Le taux de courbe sigmoidale semble être caractéristique des mesure d'initiation, et non pas dû à des produits de terminaison. Le taux de propagation est démontré comme étant d'un ordre moyen par rapport à la concentration de chaînes en croissance, indiquant une association dimérique du polymère.

**Sommario**—La cinetica del progresso dell'iniziazione e propagazione nella polimerizzazione di isoprino nella benzina, iniziata da bitillutio come primo passo nella sintesi di copolimeri in blocco, è stata-esaminata. La quantità di iniziazione è di primo ordine rispetto al bitillutio. Una leggera iniziale reazione è seguita da una accelerazione della quantità quando il polimero è generato. La curva della quantità sigmoidale appare caratteristica del passo di iniziazione e non dovuta a prodotti di terminazione. La quantità di propagazione dimostra di essere di ordine dimezzato rispetto alla concentrazione di catene crescenti, indicando un'associazione dimerica del polimero.

**Zussammenfassung**—Die kinetische Theorie der Einleitungs und Ausbreitungsstufen der Polymerisation von Isopren in Benzol, welche von Butyllithium als eine erste Stufe in der Synthese von Block-Mischpolymerisation eingeleitet ist, wurde untersucht. Die Einleitungsgeschwindigkeit ist mit Hinsicht zu Butyllithium, von der ersten Ordnung. Eine langsame Anfangsreaktion wird als Polymer erzeugt, gefolgt bei einer Beschleunigung der Geschwindigkeit. Die sigmaförmige Geschwindigkeitskurve scheint eine Charakteristik der Einleitungsstufe zu sein und wird nicht von Endprodukten veranlasst. Es wird gezeigt, das die Ausbreitungsgeschwindigkeit von halber Ordnung, in Hinsicht zu der Konzentration von wachsenden Ketten, ist, welche eine dimerische Zuordnung des Polymers anzeigt.

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# THE SYNTHESIS OF MODEL BLOCK COPOLYMERS OF POLY(*cis*-1,4-ISOPRENE : STYRENE)

By D. N. Cramond* and J. R. Urwin*

[*Manuscript received February* 26, 1968]

## *Summary*

The synthesis of model block copolymers of poly(*cis*-1,4-isoprene : styrene) initiated by butyllithium in the solvent benzene is described in detail, and the analysis of the microstructure of the polyisoprene sequence discussed. The copolymers were found to be of narrow distribution in molecular size and composition and the microstructure was close to that expected from previously published results on the synthesis of polyisoprenes.

## Introduction

Theories of the statistical thermodynamics of polymers in solution are based on molecular models that are idealized homogeneous systems. The effect of heterogeneity in molecular weight on the various parameters is not well understood, which leads to ambiguity when applied to heterogeneous systems.[1] Attempts to achieve systems approaching the idealized systems have led to only slight improvement in agreement between theory and practice. However, since the experimental errors in the determination of parameters such as the second virial coefficient are never less than 5% at best[2] it can be assumed that reasonably good fractionation can eliminate the effects of heterogeneity for all practical purposes, at least for a single polymer fraction. Extension of these ideas to copolymers is unhappily far from satisfactory despite the efforts of many investigators in this field.[3] This is all the more regrettable since it is to the copolymers that we look for the increased diversification in properties, being demanded by modern technology, rather than from new homopolymers. The subject has been reviewed recently[3] with particular reference to the problems which remain unsolved and the efforts that have been made to bridge the gaps in our knowledge. Some of the abnormal properties of copolymers are also discussed qualitatively.

Copolymers, whether graft, block, or statistical are generally more heterogeneous than their homopolymer counterparts. It has been shown that the fractionation of copolymers can lead to fractions which are more heterogeneous than the original product since fractionation is according to molecular weight and composition unless special precautions are taken and suitable solvent–non-solvent systems found.[3] It is most likely that earlier studies on fractionated copolymers will be distorted due to the variation in distribution throughout the series of fractions measured. Thus considerable caution should be observed when comparing results obtained on

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[1] Stockmayer, W., *Makromolek. Chem.*, 1960, **35**, 54, 63.

[2] Cassassa, E. F., *Polymer*, 1962, **3**, 625.

[3] Benoit, H., *Ber. Bunsenges. phys. Chem.*, 1966, **70**, 286.

*Aust. J. Chem.*, 1968, **21**, 1835–43

homopolymer fractions with those obtained on copolymer fractions unless it has been established that the same distributions are to be found throughout the samples measured.

The alternative to fractionation procedures is, of course, the synthesis of well characterized whole polymers, particularly those synthesized by employing anionic techniques. Under these circumstances narrow distributions in both molecular weight and in composition are feasible. This approach is more tedious, more time-consuming, and requires special apparatus, but one must admit that the end justifies the means. In this work a number of polymers have been prepared using a method based on an earlier investigation of the kinetics of the polymerization of polyisoprene in benzene initiated by butyllithium.[4] These polymers consist of a two-sequence block copolymer with one end the rubber *cis*-1,4-polyisoprene (or mainly so) and the second sequence the glassy syndiotactic polystyrene. The microstructure of the polyisoprene has been shown to depend on the initiator, the solvent used, and to some extent the amounts of certain impurities found in the initiator.[5,6] This certainly limits the choice of solvent and initiator that can be used. The main requirements for synthesis of this type are a good high vacuum system, all-glass apparatus employing break-seals rather than stopcocks, the prepurging of all materials and glassware prior to use, and careful attention to kinetics to ensure conditions under which narrow distributions ensue; also homopolymer should be present in negligible quantity.

In this paper we describe such a synthesis of a series of block copolymers and the analysis by i.r. and n.m.r. spectroscopy of the microstructure of the polyisoprene sequence in the blocks, and as a check the analysis of a sample of polyisoprene prepared in the same way. The analysis of the breadth of distribution and average molecular weights of these samples by gel permeation chromatography (g.p.c.) has been reported elsewhere.[7]

## EXPERIMENTAL

### *The Vacuum System*

A very simple, yet highly efficient, system was constructed by eliminating all but essential stopcocks and joints and by reducing the volume of the system to the minimum possible. The aim was to obtain working pressures of the order of $10^{-5}$–$10^{-6}$ torr as rapidly as possible, thereby reducing the time that monomers were left on the vacuum line at room temperature. In this system, a pressure of $10^{-4}$ torr was achieved in about 15 minutes and $10^{-5}$–$10^{-6}$ torr in about one hour. The unit was constructed from a 3-stage stainless steel Speedivac mercury 2M3D pump attached to a stainless steel liquid-air trap leading to a single all-glass trap and finally to a take-off manifold with only two outlets. One of these was in the form of a double outlet with a single stopcock. A Metrovac VC9 ionization gauge measured the pressure at the head (29D2) attached to the manifold. High-vacuum Apiezon T grease was used, degassed before use.

### *Initiator Preparation*

Chips of lithium were placed in benzene in the vessel *1* (Fig. 1) through the side; the vessel was stoppered, degassed three times, and butyl chloride distilled in from a vacuum measuring

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[4] Cramond, D. N., Lawry, P. S., and Urwin, J. R., *Eur. Polym. J.*, 1966, **2**, 107.

[5] Cubbon, R. C. P., and Margerison, D., *Prog. Reaction Kinet.*, 1965, **3**, 9.

[6] Bywater, S., *Adv. Polym. Sci.*, 1965, **4**, 66.

[7] Cramond, D. N., Hamond, M. J., and Urwin, J. R., *Eur. Polym. J.*, in press.

cylinder on the line. The reaction was allowed to proceed at 0° (ice-bath) for about 12 hr. Any unchanged butyl chloride was then removed and the vessel sealed from the line under vacuum. The mixture was then filtered into the side vessel and finally sealed off from the main vessel at the restriction R. The concentrated solution was diluted in the second vessel (*2* in Fig. 1) by simply distilling benzene from a reservoir on the line, in which the benzene was stored over "living ends" of polystyrene, and breaking in the concentrated solution. The samples were then at a concentration of about $10^{-2}$M. The concentration of BuLi was determined as previously described[4] and one of these samples was diluted to the correct concentration for polymerization using the same type of vessel as before. Various amounts of the dilute solution in break-seal ampoules were stored under refrigeration for use when required.

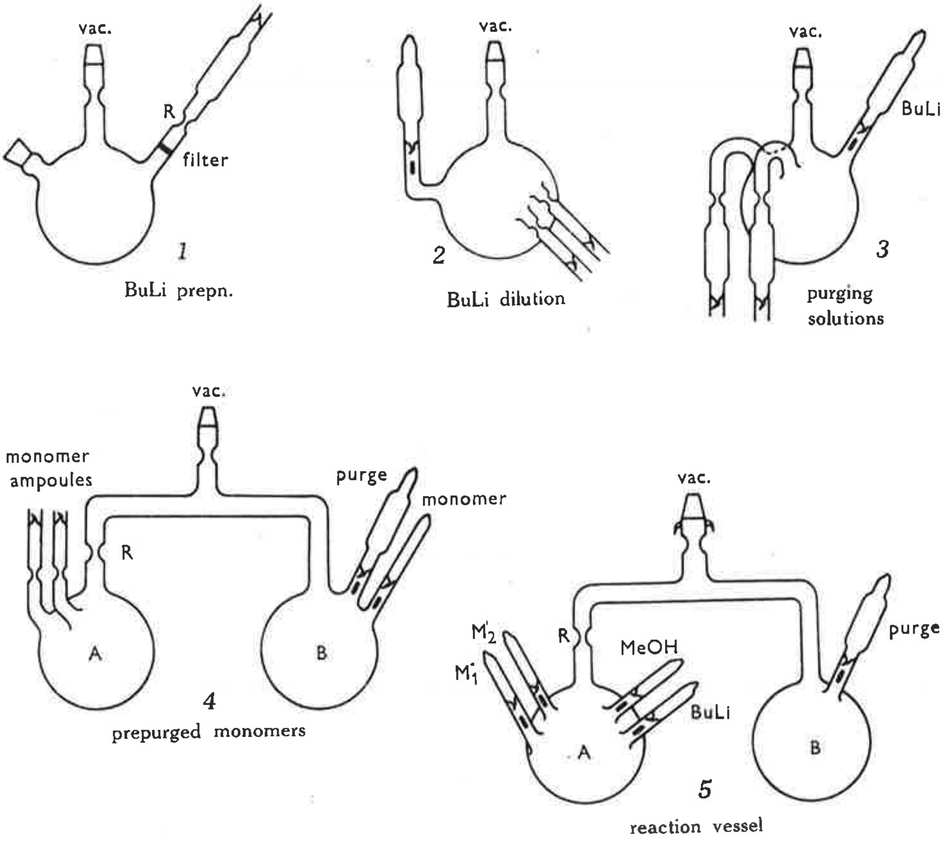

Fig. 1.—Glass apparatus used in the synthesis of block copolymers.

### *Solvent Benzene*

A.R. Benzene was dried over calcium hydride until effervescence ceased, refluxed over the reagent for 6 hr, and then distilled through a 3-ft column of stainless steel wire. The solvent was degassed on the vacuum line, in a flask to which a break-seal ampoule of BuLi was attached. A small volume of styrene was distilled in from the dried monomer, the initiator was broken in, and after all terminating material had been removed a deep red colour persisted. Excess BuLi present ensured the absence of styrene monomer. All benzene used elsewhere in this synthesis was distilled from this reservoir or another like it.

### *Purging Solution*

Benzene and monomer from over $CaH_2$ were distilled into vessel *3* and sealed off from the line. Butyllithium was added from the break-seal ampoule and after the production of "living ends" the solution was poured into the side ampoules and sealed off. Again excess BuLi ensured that no styrene monomer remained. These solutions were re-used several times, or at least until the colour had faded, by pouring off after purging into another vessel fitted with a break-seal.

### *Monomers*

All monomer samples were prepurged in vessel *4* (Fig. 1). The monomer was first dried over $CaH_2$ several times and distilled into a break-seal ampoule. Purging solution and monomer were attached to bulb B. Solvent was distilled into the vessel and it was then removed from the line. Purging solution was broken in and the vessel washed thoroughly, particularly the bulb A carrying up to 10 break-seal ampoules. Finally, after 2–3 hr, the apparatus was washed with solvent until all living ends were poured back into side B. The monomer was broken in to the living ends solution, mixed well for 5 min, and then monomer and solvent flash-distilled into side A. After sealing off at R, various volumes of the solution were tipped into the previously marked side ampoules. The concentration of monomer was known approximately from the total volume in side A. Ampoules were kept in the dark under refrigeration ($-10°$) until required.

### *Preparation of the Copolymers*

The reaction vessel 5 was assembled as quickly as possible. Ampoules of the two monomers, initiator, purging solution, and terminating material (methanol) were sealed on, the whole apparatus evacuated to $10^{-6}$ torr and sealed off from the line. Purging solution was introduced and the whole apparatus washed thoroughly for several hours in an air-conditioned room to avoid loss of monomer. The reaction vessel was then washed by distilling solvent from the living ends in B and returning it to B after washing. This was repeated several times. Finally, when the side A was clean and free of coloured living ends, solvent was distilled back into bulb A which was sealed off at the restriction R. Monomer 1 (isoprene) was broken in, followed by the initiator, and reaction allowed to proceed at about 5° for 4 hr. This allows complete initiation with a minimum of propagation as has already been discussed.[4] The second monomer was kept at ice temperature by use of an ice-filled plastic bag wrapped around the ampoule. This was done to avoid loss of monomer on standing. In a preliminary investigation, Lawry[8] found the kinetics of the cross-propagation reaction of styrene with polyisoprenyllithium to be similar to initiation which means that, at low temperatures, cross-propagation can proceed with the minimum of propagation of the second monomer. Thus after allowing the propagation of isoprene to go to completion at room temperature, monomer 2 (styrene) was added and the temperature was again lowered to 5° for a further 4 hr. Finally, on raising to ambient temperature and allowing the reaction to proceed for about 12 hr the methanol was broken in and the reaction terminated. The terminated polymer was precipitated in a large volume of cold methanol with rapid stirring. The polymer was filtered off, dried under vacuum, and stored at room temperature, under vacuum and in the dark. The latter precaution was found to be necessary in order to prevent oxidative degradation without resort to antioxidants. Some samples which were to be used in glass transition studies were precipitated from chloroform solution containing 1% of antioxidant before storage. Actually, solutions of the polymer in tetrahydrofuran were found to be quite stable for periods of a month or more provided they were kept in the dark and under refrigeration.

Under the conditions of the preparation, a product could be expected which would be free from parent homopolymers (polystyrene and polyisoprene), of narrow molecular weight distribution and narrow composition distribution, and which would be essentially of the *cis*-1,4 isomer in the polyisoprene sequence. Molecular weight and composition were controlled by manipulation of the volumes of monomers and initiator introduced. After some initial problems with degradation which resulted in discarding one series of polymers entirely, a series of block copolymers was synthesized along with a random copolymer formed by adding both monomers simultaneously.

[8] Lawry, P. S., Ph.D. Thesis, University of Adelaide, 1966.

Two samples of polyisoprene were also synthesized to allow a check to be made on the results of the investigation into microstructure of the blocks.

## THE MICROSTRUCTURE

Proton magnetic resonance spectroscopy was performed on a Varian DP60 n.m.r. spectrometer using the HA60 probe at 30°. Solutions (5%) of polyisoprene and the block copolymer were investigated in benzene, chloroform, and carbon tetrachloride to establish the most satisfactory solvent for the analysis. It can be seen that the peaks 5a and 5b are well defined in the benzene solutions (Fig. 3 below). Comparison of the several spectra showed that the best resolution could be achieved in this solvent and therefore all analyses were made in benzene. Infrared spectra were obtained using a Perkin–Elmer 21 double-beam recording spectrometer. All measurements were made on 5% chloroform solutions in 1-mm sodium chloride cells.

Infrared analyses have been widely used for the determination of the microstructure of dienes, but difficulty is experienced in distinguishing the *cis* and *trans* isomers since the out-of-plane C–H vibration bands are weak and of almost the same frequency. More recently a combination of i.r. and n.m.r. spectra has been employed in the analysis; however, it is also possible to obtain an answer using n.m.r. alone. Examination of the block copolymers presents a further problem in that the polystyrene sequence contributes to the spectrum in both i.r. and n.m.r. in the region of interest. It is possible to attempt a correction to the n.m.r. by making an estimate of the contribution from the polystyrene and subtracting from the integrated curve, but the accuracy leaves much to be desired. Fortunately there are no peaks in the i.r. due to polystyrene at the frequencies used in the analysis; that is, the background contribution is roughly constant.

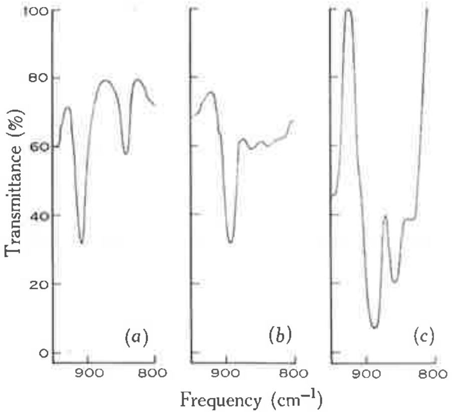

Fig. 2.—I.r. spectra of
(*a*) polystyrene;
(*b*) BCP1;
(*c*) polyisoprene.

Two methods of analysis were adopted. In the first, the total of the 1,4 structures, the 3,4 and 1,2 content were evaluated from i.r. spectra. Inspection of the i.r. spectrum in Figure 2 indicates the absence of 1,2 isomer at 909 cm$^{-1}$. In view of the high extinction reported (Table 1), any peak at this frequency will be almost entirely due to this isomer and should be easily detected. If the complete absence of the 1,2 structure can be inferred, the analysis for total 1,4 and 3,4 may be made by measuring the optical densities $D$ at 888 and 858 cm$^{-1}$ and substituting the extinctions reported by Richardson and Sacher[9] (Table 1) into the usual equations for a mixture, which yields

$$D_{888} = 159c_{3,4}+7\cdot 82c_{1,4}$$

$$D_{858} = 3\cdot 87c_{3,4}+16\cdot 12c_{1,4}$$

TABLE 1

EXTINCTION COEFFICIENTS FOR THE VARIOUS ISOMERS OF POLYISOPRENE AT VARIOUS FREQUENCIES ACCORDING TO RICHARDSON AND SACHER[9]

| Isomer | Extinctions at | | | | |
|---|---|---|---|---|---|
| | 815·5 cm$^{-1}$ | 843·0 cm$^{-1}$ | 857·5 cm$^{-1}$ | 887·5 cm$^{-1}$ | 909 cm$^{-1}$ |
| 1,2 | 0·31 | 0·62 | 1·02 | 5·73 | 149 |
| 3,4 | 0·69 | 1·80 | 3·87 | 159 | 7·48 |
| *cis*-1,4 | 6·78 | 19·2 | 8·06 | 4·56 | 2·72 |
| *trans*-1,4 | 6·78 | 11·3 | 8·06 | 3·26 | 2·40 |

Solving for the concentrations of the two structures we have 89% 1,4; 11% 3,4. The ratio of *cis* to *trans* may then be found from the n.m.r. peaks 5a and 5b shown in Figure 3.

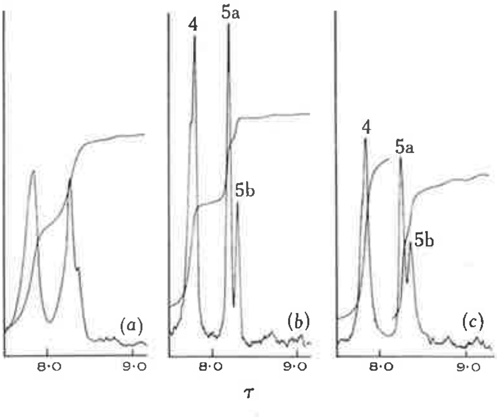

Fig. 3.—N.m.r. spectra of (*a*) polyisoprene, mol.wt. 145,000; (*b*) polyisoprene, mol.wt. 10,000; (*c*) block copolymer.

The proton resonance frequencies in the various structural environments are shown in Figure 4. The peaks at 8·33 $\tau$ and 8·41 $\tau$, that is 5a and 5b according to Chen's assignment,[10] may be used to separate the *cis* and *trans* isomers. The percentage *cis*-1,4 in the polyisoprene is given by the ratio of the area under peak 5a to the total area of 5a and 5b. Combined with the 3,4 content from the i.r. spectra the analysis yields the result: 74% *cis*-1,4; 15% *trans*-1,4; 11% 3,4. These figures are shown in brackets in Table 2.

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[9] Richardson, W. S., and Sacher, A., *J. Polym. Sci.*, 1953, **10**, 353.

[10] Chen, H. Y., *Analyt. Chem.*, 1962, **34**, 1793.

The complete analysis may also be obtained from the p.m.r. spectrum alone. Several combinations may be used but we have chosen to use peaks 4, 5, and 7 corresponding to the methylene protons in the 1,4 structures (a total of 4 protons) and the single proton in the 3,4 isomer, all of which have a resonance frequency at 802 $cm^{-1}$. Actually, the four protons in the 1,4 structures are not identical and inspection of the peak in benzene indicates a double peak. Nevertheless, peak 4 corresponds to 1,4 and 3,4 structures in the ratio 4 : 1. Peak 5 is due to three protons in each of the 1,4 and 3,4 structures. If we let $a = 1,2$; $b = 3,4$; and $c = 1,4$ (total) then the integrated peaks are related according to the equations:

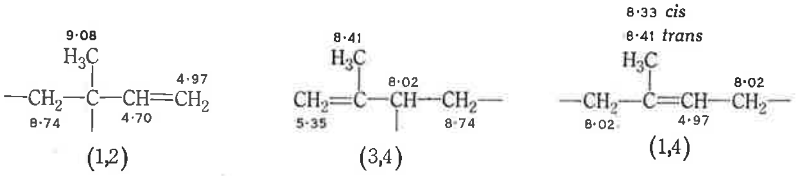

Fig. 4.—N.m.r. frequencies ($\tau$) of polyisoprene.

$$\text{peak } 4 = 4c+1b \tag{1}$$

$$\text{peak } 5 = 3c+3b \tag{2}$$

$$\text{peak } 7 = 3a \tag{3}$$

Finally, the *cis* and *trans* isomers are separated as before. The results are given in Table 2.

TABLE 2

THE MICROSTRUCTURE OF THE BLOCK COPOLYMER BCP1 AND TWO SAMPLES OF ISOPRENE PREPARED BY THE SAME METHOD

(Values in brackets are for combined i.r. and n.m.r. analysis)

| Polymer | *cis*-1,4 | *trans*-1,4 | 1,2 | 3,4 |
|---|---|---|---|---|
| P1 (low mol. wt.) | 77 | 13 | 10 | 0 |
| P1 (high mol. wt.) | 74 (77) | 20 (15) | 2 (0) | 4 (11) |
| BCP1 uncorr. | 68 | 22 | 3 | 6 |
| BCP1 corr. | 72 | 18 | 3 | 6 |

In the case of the block copolymers, the area under peak 5 is enhanced by the presence of a broad peak due to polystyrene. It is difficult to make an appropriate correction. We estimate that peak 5 integral is about 10% too large but this is very approximate. The corrected value is, however, close to the values obtained for the high molecular weight polyisoprene.

### *Predictability of Molecular Weight and Composition*

It is important that the molecular weight of the sample be predictable in order that samples may be prepared with the molecular weights which will be in the most convenient range. For example, the molecular weight should not greatly exceed $5 \times 10^5$ for osmometry or be much less than $5 \times 10^4$ for light-scattering studies. By predictability we mean that the actual molecular weights should conform closely to the simple relation:

$$\text{mol. wt.} = (\text{g of monomer})/(\text{moles of initiator}) \tag{4}$$

for initiation by lithium alkyls. The predicted molecular weights for the series of block copolymers and statistical copolymer are shown in Table 3. The degree of polydispersity according to the ratio $\bar{M}_W/\bar{M}_N$ from g.p.c. is also included in the table. The composition predicted by assuming no loss of monomers during preparation of samples is shown in Table 3 with that found by u.v. spectra. Obviously some monomer is lost by polymerization before the final preparation of the prepurged samples.

Table 3

PREDICTED MOLECULAR WEIGHTS AND DEGREE OF POLYDISPERSITY (P.S.)

| Polymer | Mol. Wt. Eqn. (4) | $\bar{M}_W$[a] from g.p.c. | $\bar{M}_N$[a] from g.p.c. | $\bar{M}_W/\bar{M}_N$ | Predicted P.S. (%) | Found P.S. (%) |
|---|---|---|---|---|---|---|
| BCP1 | $2 \cdot 4 \times 10^5$ | $2 \cdot 48 \times 10^5$ | $2 \cdot 17 \times 10^5$ | 1·15 | 30 | 33 |
| BCP2 | $2 \cdot 4 \times 10^5$ | $2 \cdot 80 \times 10^5$ | $2 \cdot 51 \times 10^5$ | 1·12 | 50 | 59 |
| BCP3 | $2 \cdot 4 \times 10^5$ | $3 \cdot 57 \times 10^5$ | $3 \cdot 18 \times 10^5$ | 1·12 | 70 | 78 |
| RCP1 | $3 \cdot 0 \times 10^5$ | $3 \cdot 82 \times 10^5$ | $3 \cdot 29 \times 10^5$ | 1·16 | 50 | 56 |

[a] Estimated error for all values is ±0·20.

## Discussion

The method of synthesis described in this paper allows the preparation of polymers which are reasonably homogeneous in both molecular weight and in composition. The distributions are narrower than is usually obtained by the fractionation of homopolymers, which meets one of the main requirements for polymer samples suitable for physicochemical studies. The predictability of molecular weight is good; in the present example, in the case of the block copolymers the actual molecular weights are within 20% of the predicted values based on the amount of initiator and monomer present. Possibly, the actual and predicted values might be closer if an improved method of analysis of initiator was used. The complete absence of homopolymer shown by g.p.c. studies is also worth noting.

The method is clearly satisfactory since the polymers produced require no further working after the initial precipitation and drying. This can be an important factor where the polymers are prone to degradation during handling. Our experience has been that attempts to reprecipitate by freeze-drying, etc., can lead to rapid degradation of the polyisoprene sequences unless large amounts of antioxidant are added. This is rather undesirable for studies such as osmometry, although satisfactory for glass transition studies.

The microstructure analysis reveals that the polyisoprene is reasonably homogeneous and certainly corresponds to the analyses reported by Worsfold and Bywater[11]

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[11] Worsfold, D. J., and Bywater, S., *Can. J. Chem.*, 1964, **42**, 2884.

although lower than some other values reported. Analyses using i.r. alone seem to underestimate the *trans*-1,4 content.[12] On the other hand, the purity of the lithium used in preparing BuLi may be a factor in increasing the *trans*-1,4 content at the expense of the *cis*-1,4. It would appear that the best approach to analysis of the microstructure of polyisoprene sequences in block copolymers is to synthesize samples of polyisoprene separately using the same method as is used in the block synthesis and make an analysis of this material. Analysis of the copolymers with high styrene content seems out of the question.

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[12] Tobolsky, A. V., and Rogers, C. E., *J. Polym. Sci.*, 1959, **40**, 73.

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# THE ANALYSIS OF BUTYLLITHIUM AT CONCENTRATIONS USED IN THE INITIATION OF POLYMERIZATION

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## SUMMARY

An NMR method devised for analysis of n-butyllithium solutions is acceptably accurate down to concentrations of 0.1 *M*. An ultraviolet method, involving calibration with solutions analyzed by the NMR technique, is accurate to within ±5% down to concentrations of $10^{-3}$ *M*.

Lithium alkyls and in particular butyllithium are currently used in many studies of the reaction mechanism in anionic polymerization[1,2]. Much interest centres around the kinetics of the initiation step, particularly at low concentrations of initiator. The accuracy of these experiments depends to a marked degree upon an accurate determination of the initiator concentration. Statistical analyses on results at these low concentrations show that the reliability of data leaves much to be desired[3] and emphasizes the need for better methods of analysis.

A number of methods for the determination of n-butyllithium (BuLi) solutions are currently in use, almost all of which involve analysis by titration. Perhaps the best known of these techniques is that due to Gilman and co-workers[5,6] which employs a double titration to determine the concentration of n-butyllithium in the presence of lithium butoxide and lithium hydroxide. Recent work[7-10] however, has demonstrated certain unsatisfactory features in the technique concerning the interference by lithium butoxide.

In the single titration technique devised by Eppley and Dixon[10], it was established that butoxide does not interfere with the procedure. The presence of hydroxide however, seems to have been ignored in this technique.

Several other techniques have been proposed[7,11,12] each of which, it is claimed, is comparable to or better than the double titration method. Perhaps the most suitable standard previously devised is the thermometric titration[12] in which butyllithium is titrated against a standard n-butanol solution. However, rather elaborate equipment is required which is not generally available.

It is clear that all of these methods have certain shortcomings, not the least of which is their inability to accurately measure the low concentrations required for high polymer synthesis (*viz.* $10^{-2}$–$10^{-4}$ *M*)[4]. The determination of the metal alkyl at high concentrations by one of the methods described, followed by dilution, even with the greatest care, does not overcome the problem since a proportion of the initiator is always destroyed in the process of dilution and sampling. It was with this in mind that we set out to improve on the generally accepted methods of analysis of lithium alkyls.

## EXPERIMENTAL

The NMR spectrum of n-butyllithium in benzene (Fig. 1) showed a triplet 48 cps upfield from tetramethylsilane (TMS) due to the methylene protons adjacent to the lithium. This triplet can be integrated and compared with the integrated spectrum of a suitable reference liquid. All that is required is to mix a carefully measured volume of the reference liquid with a given volume of the lithium alkyl solution. In this way NMR gives a direct measure of the carbon-bound lithium content. The reference substance should have a large and preferably single peak which does not overlap with the spectrum of butyllithium. A low vapour pressure is preferable since the integrated peak is a measure of the reference in the liquid phase. In this study, mesitylene was chosen as the reference since its NMR spectrum consists of a nine proton singlet 132 cps downfield from TMS (Fig. 1) giving therefore a large separation of reference and n-butyllithium peaks. Furthermore its vapour pressure at 20° (the temperature at which all experimental measurements were recorded) is negligible.

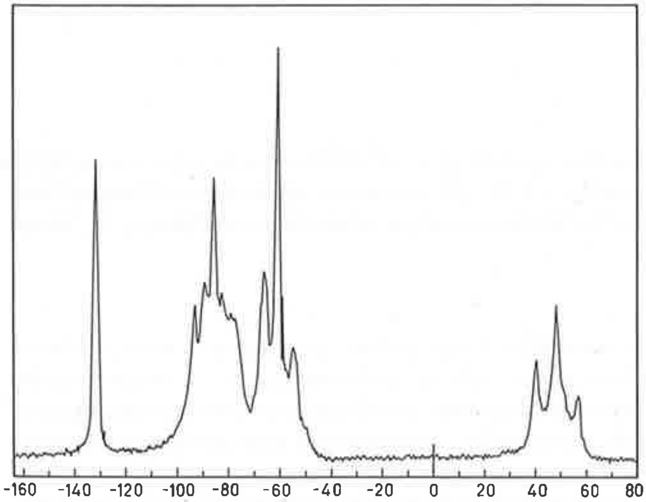

Fig. 1. Nuclear magnetic resonance spectrum at 20° of butyllithium in benzene with mesitylene as reference. Chemical shifts (in cps) are referred to the resonance position of tetramethylsilane.

The NMR method is clearly suitable for analysis down to concentrations where the integrated signal can be estimated with reasonable accuracy, that is in the range above $10^{-1}$ $M$, and is free from the objections raised against the titration techniques. The extension of any of these methods to the range of initiator concentrations used in high polymer synthesis demands that a dilution procedure be adopted. As previously stated, the disadvantage of sampling followed by dilution lies in the loss of initiator by adventitious termination, particularly when more than one dilution is necessary. An alternative is the measurement of optical densities in the ultraviolet at the final concentration to be used. However, to achieve this, the extinction coefficient must be accurately known and one of the titration methods or the NMR technique must be used to calibrate. Again, the dilution procedure is required in any case. We have therefore adopted the procedure whereby the extinction coefficient is determined from optical density measurements on diluted solutions calibrated by NMR which directly measures the carbon-bound lithium content. The problem was then to design suitable glass apparatus which would connect the two physical methods and such that adventitious termination could be eliminated by prepurging with polystyryllithium within a closed system.

Butyllithium solutions were prepared under vacuum as previously described[4]. An ampoule containing the butyllithium in benzene was attached to a U-shaped vessel with a bulb on each arm so constructed that the BuLi/benzene solution could be broken in through a break seal into the bulb on one side. Several NMR tubes and sampling ampoules were attached to the second bulb. The purpose of this apparatus was to ensure that the sample of BuLi to be used for the actual analyses was sufficiently concentrated to give a large integrated α-methylene peak. Preliminary determinations of the NMR peak were the only way to achieve this. The vessel was flamed out, evacuated to $10^{-5}$ mm and sealed off from the line. The BuLi solution was broken into the apparatus and solvent was distilled from the main bulk until an NMR determination showed the integration peak to be large. Samples were then sealed off in break seal ampoules. This method provided about ten 10 ml samples, which were stored in a refrigerator.

The mesitylene to be used as reference was thoroughly dried by refluxing over calcium hydride for several hours and then fractionally distilled. The purity was checked by means of vapour phase chromatography (VPC). Samples of the mesitylene were prepared in break seal ampoules which had previously been accurately calibrated. The ampoules were attached to a vessel similar to the one just described. An ampoule of polystyryllithium in benzene was also attached to the vessel. This was broken in and the benzene was distilled off. A small quantity of mesitylene was distilled on to the remaining living ends. The apparatus was sealed from the vacuum line and purged with the polystyryllithium mesitylene solution.

The vessel was rinsed with the pure solvent distilled from over the living ends (which had been returned to the first bulb), to ensure complete removal of the purging material from the main vessel. The mesitylene was then carefully distilled into the ampoules and sealed off ready for use. A further check by VPC showed the absence of

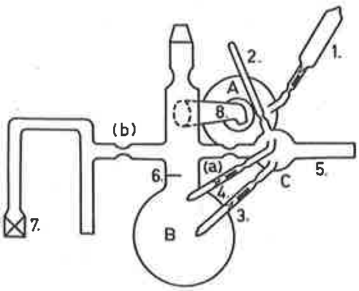

Fig. 2. Apparatus used. 1, Purging solution; 2, NMR tube; 3, BuLi/benzene; 4, mesitylene; 5, 10 ml calibrated tube; 6, 150 ml graduation mark; 7, optical cell; 8, splash head.

impurity in the mesitylene. It was estimated that the volume of mesitylene was known to within 1%.

The design of the apparatus used for the analysis is shown in Fig. 2. Before use, the bulb C and the calibrated tube 5 were thoroughly cleaned to ensure free draining of the BuLi/benzene solution. The vessel was evacuated to $10^{-5}$ mm and sealed off from the vacuum line. The whole apparatus was thoroughly purged with a benzene/polystyryllithium solution 1 and the solution returned to A. Pure solvent was distilled from this solution to other parts of the vessel and after rinsing poured back into A. The splash head 8 was required to avoid bumping. The rinsing process was performed several times until it was considered that all purging solution had been removed. When it was certain that all purging solution had been returned to A the 10 ml sample of BuLi in benzene was broken into the calibrated tube. After allowing sufficient draining time the liquid level was read using a cathetometer. Approximately half the BuLi/benzene solution (5 ml) was carefully tipped into B, and the liquid level in 5 was read again with the cathetometer. The calibrated tube and its contents were then sealed off at (a), and the known volume of mesitylene broken in and thoroughly mixed with the BuLi solution. A small quantity of the mixture was poured into the NMR tube 2 which was sealed off for measurement in the Varian 60 Mcps NMR spectrometer. The integrated NMR peaks of BuLi and mesitylene were compared giving the concentration of the BuLi solution in bulb B. Benzene over the living ends in A was then distilled into B to make the solution up to an accurate 150 ml graduation mark. An error of 0.5 ml in 150 ml is estimated at this point. A known volume of the BuLi solution was run off into a dilution vessel and sealed off at (b).

The optical density of the BuLi solution was measured in the optical cell attached to the dilution vessel. This cell was constructed from rectangular quartz tubing and attached to the glass vessel through a graded seal. A series of dilutions were made by pouring a small quantity of the BuLi solution into the optical cell, noting its volume and distilling benzene from the main bulk followed by careful mixing. Both side arms of the vessel were calibrated for volume which allowed by a simple calculation the determination of the new concentration. Optical densities were determined on a Gilford model 2000 UV spectrophotometer. The path length of the quartz cell was determined by internal calipers in the region of the light path. The error in this measurement is estimated to be less than 1%.

## RESULTS AND DISCUSSION

The optical density over the range 275 m$\mu$ to 305 m$\mu$ was measured for a series of butyllithium concentrations from $6 \times 10^{-3}$ to $3.1 \times 10^{-2}$ moles/litre. The maximum absorption shifted from 278 m$\mu$ at the lowest concentration to 282 m$\mu$ at the highest and changed monotonically with concentration. The reasons for the shift are not clear at this stage and are at present being investigated. Nevertheless at 285 m$\mu$ Beer's Law was obeyed and an extinction coefficient of 91 $\text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ was calculated at this wavelength.

Concentrations of approximately $10^{-3}$ moles/litre in butyllithium have been used in this laboratory to initiate high molecular weight polymers. Further dilutions in the dilution vessel and the use of larger cell path lengths should allow concentrations of this order to be satisfactorily reached. This is being further studied as is the estimation of a concentration limit for this particular system. However over the concentration range studied and at least to $10^{-3}$ $M$ it is felt that butyl lithium can be determined to within 5% using the combined NMR-UV techniques.

No direct comparison was made between the standard titration techniques and our NMR method in estimating butyllithium, however a check on the accuracy of the NMR result was nevertheless made. A sample of butyllithium/benzene was hydrolysed with water and titrated against standard hydrochloric acid. The titre results were consistently 2–3% higher than the NMR analysis. This is expected since titration gives the total lithium content comprising butyllithium, butoxide and hydroxide. The reproducibility of NMR integrals was also checked. Spectra for each tube were integrated in triplicate and excellent reproducibility was obtained. A further check was made for the absence of polystyryllithium by examining the absorption at 334 mμ. No absorption was found indicating that no detectable amounts of living ends from the purging process remained after the washing procedure. Furthermore this precluded possible association between butyllithium and polystyryllithium, a condition which would yield an erroneous butyllithium absorption in the ultraviolet.

From the brief studies performed so far we believe that our main purpose, to establish that the ultraviolet method employing calibration by NMR is feasible, has been achieved and that accurate estimations of butyllithium at the low concentrations required for the synthesis and kinetic studies in high polymers seem possible. The practicability of such a method is clear. Knowledge of an extinction coefficient over a certain concentration range makes the determination of initiator by measurement of its optical absorption relatively simple. Further studies involving comparisons with standard techniques, simpler apparatus design and extensions to other solvents and initiators are now in progress.

## REFERENCES

1 S. Bywater, *Advan. Polymer Sci.*, 4 (1965) 66.
2 R. C. P. Cubbin and D. Margerison, *Progr. Reaction Kinetics*, 3 (1965) 9.
3 D. Margerison, *Trans. Faraday Soc.*, to be published.
4 D. N. Cramond and J. R. Urwin, *Austral. J. Chem.*, 21 (1968) 1835.
5 H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, 66 (1944) 1515.
6 H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
7 P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellestad, *Anal. Chem.*, 33 (1961) 468.
8 C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, 25 (1960) 115.
9 K. C. Eberly, *J. Org. Chem.*, 26 (1961) 1309.
10 R. L. Eppley and J. A. Dixon, *J. Organometal. Chem.*, 8 (1967) 178.
11 A. F. Clifford and R. R. Olsen, *Anal. Chem.*, 32 (1960) 544.
12 W. L. Everson, *Anal. Chem.*, 36 (1964) 854.

European Polymer Journal, 1968, Vol. 4, pp. 451–456. Pergamon Press. Printed in England.

# MOLECULAR WEIGHT DISTRIBUTIONS OF BLOCK COPOLYMERS OF POLY(ISOPRENE:STYRENE) BY GEL PERMEATION CHROMATOGRAPHY

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**Abstract**—Gel permeation chromatograms of block copolymers of *cis* 1:4 polyisoprene and polystyrene with narrow molecular weight and composition distributions have been examined by the normal – probability plot method. The parameters $\bar{M}_w$, $\bar{M}_n$ and standard deviation $\sigma$ have been evaluated and the results compared with $\bar{M}_N$ obtained by high speed osmometry. Fractionation appears to be achieved according to chain length for a particular composition.

## INTRODUCTION

THE INTRODUCTION of the technique of 'gel permeation chromatography'(1) has given new impetus to attempts to obtain molecular weight distributions. The earlier methods were generally tedious, time consuming and often, as in the case of Turbidimetric Titrations,(2, 3) it was difficult to find suitable analytical expressions to describe the distribution. Usually, experimenters avoid the determination of the distribution and simply report two averages from $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$. The ratio of any two such as $\bar{M}_w/\bar{M}_n$ is a measure of the width of the distribution. The problem here is that the ratio $\bar{M}_w/\bar{M}_n$ determined from light scattering and osmometry measurements is not a very accurate quantity since the absolute accuracy obtainable is never better than 10–20 per cent even under the best of conditions.(4) This problem is even further aggravated in the case of co-polymers by the necessity to make determinations in three solvents at least for the evaluation of $\bar{M}_w$(5,6) making the experimental determination of this parameter quite unreliable.

Gel permeation chromatography gives a type of differential molecular weight distribution curve directly. Resolution is not unlimited(7) but the method is generally accepted as a rapid, reproducible and reasonably accurate technique for the determination of size distributions in polymeric compounds. The chromatogram is a composite curve of the Gaussian distribution of its components. The height of the curve does not represent the relative abundance of a particular component since it is influenced by the abundance of neighbouring species. This is of course not a problem peculiar to GPC. At either end of the chromatogram, there are regions which are partly determined by the rate of flow through the column and the concentration of polymer introduced.(8) Further, the column does not resolve broad and narrow distribution polymers equally. However, other studies(8) have shown that optimum working conditions can be easily established. Gel permeation chromatographic distributions err on the high side in contradistinction to fractional precipitation methods in which low molecular weight material may not precipitate. This means that distributions obtained from GPC tend to be broader than they should be.(7) Better resolution can

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be obtained by the choice of the number and permeability of columns used. GPC studies have an important advantage over the more usual description in terms of $\bar{M}_w$ and $\bar{M}_n$ in that the existence of more than one species of polymer is clearly shown. This is important particularly in investigations of block and graft copolymers where extraneous homopolymer may always be present and may interfere with studies of solution properties.

In the present work, several block-copolymers and a random copolymer were examined; the materials were considered, on the basis of the method of synthesis and kinetic studies, to be of narrow distribution and free from homopolymer. Calibrations of the columns were based on narrow distribution polystyrenes and a sample of polyisoprene prepared by the same method as was used for the block-copolymers.

## EXPERIMENTAL

Synthesis of model block copolymers suitable for solution property studies must be made with considerable care if the measurements are to be meaningful. An important requirement is that the copolymers be free from homopolymer. Such material is easily introduced by adventitious termination at initiation and cross propagation. Narrow distributions in molecular weight and composition, particularly the latter, are highly desirable. Gel permeation chromatography provides a rapid method of examination for the presence of more than one species as well as providing a check on size distributions.

Three block copolymers of polyisoprene and polystyrene of the simple AB type were prepared under rigorous conditions of high vacuum ($10^{-5}$–$10^{-6}$ torr). Apparatus was all glass with break seals. The apparatus and all materials were prepurged. Solvents and monomers were flash distilled into pre-purged ampoules or into the reaction vessel and then purged. The vessel was then sealed off from the vacuum line and all subsequent operations carried out without further contact with the atmosphere. Particular attention was paid to the kinetics to ensure narrow distribution and the absence of adventitious terminating material. The polymerization was initiated by butyl lithium in benzene at low temperature as described in a previous publication.(9) Cross propagation was treated similarly since Lawry(10) had found that the temperature dependence followed closely that observed for initiation. These precautions allow initiation and cross propagation to proceed with a minimum propagation which is necessary for a narrow distribution. A fourth polymer, prepared in the same manner except that both monomers were present has been called random copolymer although longer sequences are likely to be present.(11, 12)

A high *cis* 1:4 content was expected from this method of synthesis and the block copolymers were analysed by NMR and i.r. absorption spectroscopy to determine their microstructure. A polyisoprene sample prepared in the same manner as above was also analysed as a check on possible interference from the styrene sequence. All polymers show much the same microstructure. The structural composition was 75% *cis* 1:4 14% *trans* 1:4 and 11% 3:4 isomer. There appeared to be little or no 1:2 isomer present. This analysis compares favourably with that found by Worsfold and Bywater.(13) The compositions of the block and random copolymer were determined by measuring the polystyrene content from the optical density at 269 mμ in the u.v. region of the spectrum.

Gel permeation chromatograph curves were obtained on a Waters Associates instrument containing one each of a $10^4$ A.U. and $10^5$ A.U. columns. Calibration was effected by determining peak counts of a series of narrow distribution polystyrenes supplied by the manufacturers. Peak molecular weights and values of $\bar{M}_w$ and $\bar{M}_n$ were supplied with the samples. The flow rate recommended by the manufacturer was reduced from 1·0 ml/min to 0·51 ml/min to achieve a better resolution. A small shift in peak was observed on flow rate reduction and a smaller change was found when the concentration injected was changed to 0·5% in 60 sec, that is 2·5 mg of polymer injected into the column. Similar preliminary measurements were made on the copolymers and the sample of isoprene.

Number average molecular weights were measured on a Mechrolab high speed osmometer from solutions of polymers and copolymers in toluene at 30°.

## RESULTS

Chromatograms of the copolymers, the isoprene sample and one of the polystyrenes are shown in Fig. 1. Inspection of the curves shows that all polymers may be considered

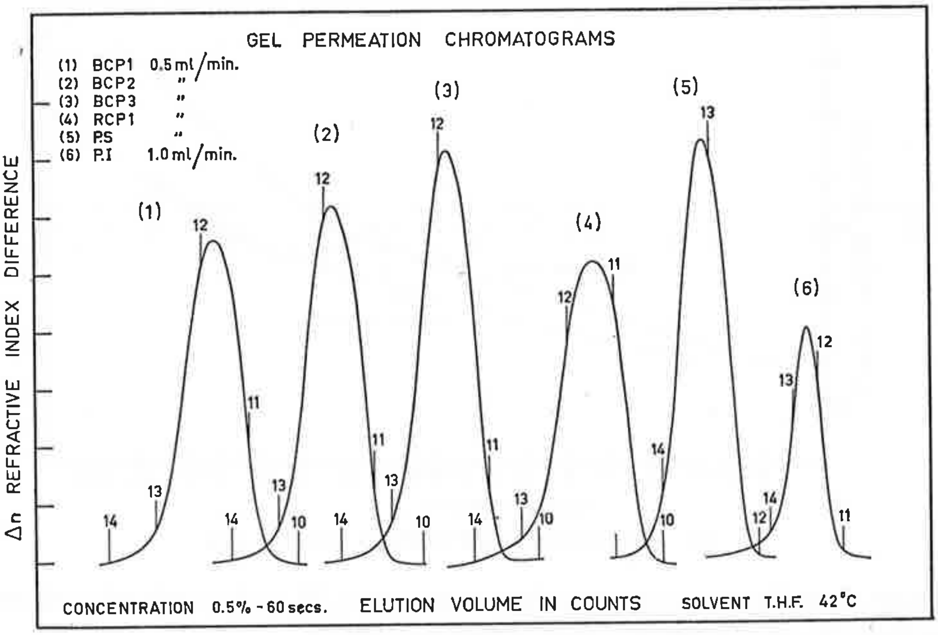

FIG. 1. Chromatograms. BCP = block copolymer
RCP = random copolymer
PS = polystyrene
PI = polyisoprene

to be of narrow distribution and free from extraneous homopolymer in the case of the copolymers. It would appear that the random copolymer has a somewhat broader distribution than the rest. Solutions were tested for degradation which might have occurred but after storage for four weeks identical curves were obtained.

In view of the range of compositions in the block and random copolymers, it was decided to look for evidence of separation by composition as well as size. Samples were collected at each count and analysed for composition in the u.v. at 269 m$\mu$. The method is only qualitative, however, because of the low concentration but comparison of the two counts at 12 and 13 which contain the bulk of the material and assuming the areas under each count correspond to the relative weights of material in the sample the concentrations measured differed by less than 5 per cent which seems satisfactory in view of the method.

The chromatograms were analysed at each half-count by both planimetry and by tracing the curve onto paper, cutting to $\frac{1}{2}$ count sections and weighing. From these data, a cumulative weight curve is easily constructed. The cumulative weight data were plotted on normal-probability paper as shown in Fig. 2. It will be observed that at the slower flow rate a linear plot is obtained over 95 per cent of the chromatogram and we assume that the distribution is Gaussian over this region.

The standard deviation in counts $\sigma_c$ is determined from the difference in counts at the 50 per cent and the 16 per cent mark. To convert this to the molecular weight scale, $\sigma_c$ must be divided by $k$ the slope of the calibration curve. The molecular

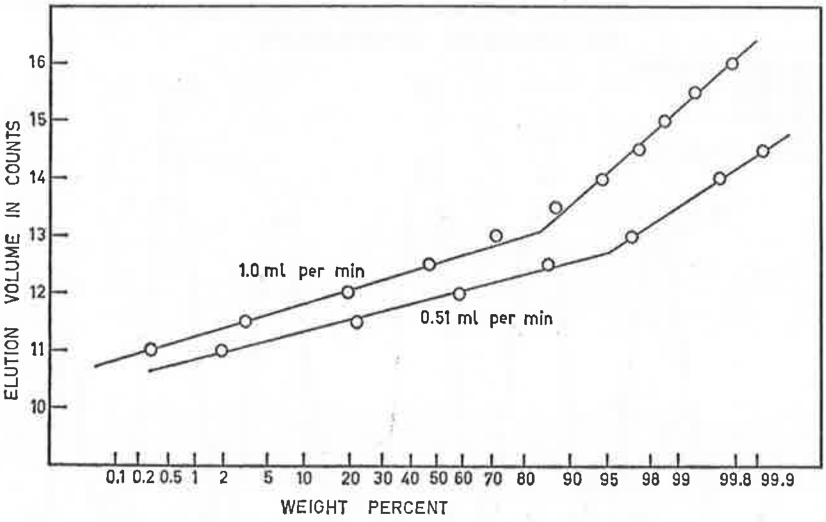

FIG. 2. Cumulative weight curves for two flow rates.

weight at the 50 per cent mark is the geometric mean $\bar{M}_{w(g)}$⁽¹⁴⁾ and therefore the two averages $\bar{M}_w$ and $\bar{M}_n$ may be evaluated from the relations

$$\bar{M}_w = \bar{M}_{w(g)} \exp(\tfrac{1}{2}\sigma^2)$$
$$\bar{M}_w/\bar{M}_n = \exp \sigma^2$$
$$\sigma = \sigma_c/k$$

The molecular weights of the copolymers were evaluated on the basis that the peak count corresponds to the molecular weight at the position corresponding to the weight fraction of polystyrene on a vertical line drawn through the polystyrene and polyisoprene calibration curves. The polyisoprene calibration curve was drawn parallel to polystyrene and through the peak count found for the polyisoprene sample. This was considered satisfactory in view of the small range of molecular weights in the copolymers. The results are set out in Table 1 in which values of $\bar{M}_n$ obtained by osmometry are included for comparison.

TABLE 1. MOLECULAR WEIGHT AVERAGES AND STANDARD DEVIATIONS OBTAINED FROM NORMAL-PROBABILITY PLOTS OF GPC DISTRIBUTION CURVES FOR A SERIES OF COPOLYMERS OF STYRENE AND ISOPRENE

| Polymer | Composition (%P.S.) | From GPC $\bar{M}_w \times 10^{-5}$ $\pm 0{\cdot}20$ | From GPC $\bar{M}_n \times 10^{-5}$ $\pm 0{\cdot}20$ | From osm. $\bar{M}_n \times 10^{-5}$ $\pm 0{\cdot}20$ | $\sigma$ | GPC $\bar{M}_w/\bar{M}_n$ | Peak count |
|---|---|---|---|---|---|---|---|
| Polystyrene* | 100 | 1·73 | 1·64 | | | 1·05 | 13·15 |
| BCP 1 | 33 | 2·48 | 2·17 | 2·47 | 0·370 | 1·15 | 11·70 |
| BCP 2 | 59 | 2·80 | 2·51 | 2·12 | 0·333 | 1·12 | 11·80 |
| BCP 3 | 78 | 3·57 | 3·18 | 2·49 | 0·341 | 1·12 | 11·85 |
| RCP 1 | 56 | 3·82 | 3·29 | 3·53 | 0·385 | 1·16 | 11·50 |
| Polyisoprene | 0 | 1·45† | — | — | | | 12·10 |

* Supplied by Waters Associates.

† Determined by viscometry.

## DISCUSSION

There are several ways of dealing with the experimental data. Tung(7) has proposed two practicable solutions to the problem of relating the gel permeation chromatogram to the true molecular weight distribution function; however, both require a computer to handle the calculations. A much simpler method which involves representing the cumulative curve as a straight line on a normal-probability graph seems to have much to recommend it. One advantage of the latter is that the usual averages $\bar{M}_w$ and $\bar{M}_n$ may be derived from the geometrical mean and standard deviation and compared with more conventional methods of obtaining these parameters. In this study we have employed the normal-probability plot since this seemed the most convenient way of displaying the results.

Billmeyer(4) has discussed the accuracy usually attained in determinations of $\bar{M}_w$ and $\bar{M}_n$ for homopolymers and it would seem that either parameter would be suitable to test the fractionation by GPC columns. Billmeyer also points out that the usual spread of molecular sizes described by the ratio $\bar{M}_w/\bar{M}_n$ is rather inaccurate, an error of 10–20 per cent must be expected. Unfortunately, copolymers of the block and graft type cannot be treated in the same way. Molecular weight determination by Light Scattering yields only an apparent value when the procedure applied to homopolymers is used to determine $\bar{M}_w$ of block and graft copolymers. To obtain the true molecular weight, measurements must be made in three different solvents with differing refractive indices. It is then necessary to solve for the true $\bar{M}_w$ by interposing the data so obtained into three simultaneous equations representing the apparent molecular weights in each solvent. This makes the error in the determination of weight average molecular weight of the copolymers even greater and the determination of the ratio $\bar{M}_w/\bar{M}_n$ rather uncertain. However, Benoit(15) has observed that the number average molecular weight given by the usual expression

$$\bar{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

is unambiguous for homopolymers and copolymers alike. In view of this, we have compared the number average molecular weight $\bar{M}_n$ obtained from GPC data with that obtained from Osmometry as a test of the efficiency of fractionation.

The mode of fractionation achieved by GPC is considered to be due to the depth to which each species is able to diffuse into the gel, that is the fractionation is according to the hydrodynamic volume and therefore, in the case of copolymers, where two distributions can result from the different distributions of chain length and composition, deviations from the usual shape of the curve might result. A mixture of two or more normal curves plotted on probability paper will usually show a double inflection; however, when the difference between the two means is small a single inflection will be observed. The plots for all copolymers used in this study showed no evidence of a double inflection and we must conclude that GPC cannot resolve narrow distributions of the type found in these polymers. The 5 per cent difference in composition found in successive counts therefore must be due to inaccuracies of measurement at low optical densities. It seems that we can safely assume that the distributions follow a Gaussian law at least over the linear part of the curve.

Some evidence of tailing of high molecular weight material has been reported(8) so that, even under ideal conditions, some high molecular weight material which should have appeared earlier will be 'seen' by the refractometer later in the chromatogram. This effect is ignored by the probability plot since it would occur in the last few per cent of the curve; if, however, the effect was real and the tailing was due to low molecular weight material it would greatly alter the number average molecular weight found by osmometry. The results shown in Table 1 indicate a very close agreement between the two values of $\bar{M}_n$ obtained separately from GPC and osmometry. From these results we conclude that the polymers are of narrow distribution in both chain length and composition and that the values obtained for the parameters $\bar{M}_w$ and $\bar{M}_n$ are close to the true values. The use of a linear relation for the effect of composition on peak position may only be satisfactory when the range of molecular weights is small. Further work on a series of polymers with a much wider range of chain lengths is necessary to confirm this assumption.

*Acknowledgement*—We are indebted to the Weapons Research Establishment, Salisbury, South Australia and to Dr. W. G. P. Robertson for permission to use the Waters GPC instrument.

## REFERENCES

(1) J. C. Moore, *J. Polym. Sci.* **A2,** 835 (1964).
(2) F. Rodriguez, R. A. Kulakowski and O. K. Clark, *Ind. engng Chem.* (*Prod. Res. Dev.*) **5,** 121 (1966).
(3) J. R. Urwin, J. M. Stearne, D. O. Jordan and R. A. Mills, *Makromolek. Chem.* **72,** 53 (1964).
(4) F. W. Billmeyer, Jr., *J. Polym. Sci.* **C8,** 161 (1965).
(5) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman and B. N. Epstein, *J. Polym. Sci.* **16,** 517 (1955).
(6) W. Bushuk and H. Benoit, *Can. J. Chem.* **36,** 1616 (1958).
(7) L. H. Tung, *J. Polym. Sci.* **61,** 449 (1962).
(8) H. E. Adams, K. Farhat and B. L. Johnson, *Ind. engng Chem.* (*Prod. Res. Dev.*) **5,** 126 (1966).
(9) D. N. Cramond, P. S. Lawry and J. R. Urwin, *Europ. Polym. J.* **2,** 107 (1966).
(10) P. S. Lawry, Ph.D. Thesis, University of Adelaide (1966).
(11) S. Bywater, *Adv. Polym. Sci.* **4,** 66 (1965). Ref. p. 97.
(12) R. C. P. Cubbon and D. Margerison, *Progr. Reaction Kinetics* **3,** 9 (1965). Ref. p. 440.
(13) D. J. Worsfold and S. Bywater, *Can. J. Chem.* **42,** 2884 (1964).
(14) G. Herdan, *Small particle statistics*, p. 95, 2nd Edn., Butterworths London (1960).
(15) H. Benoit, *Ber. BunsenGes. phys. Chem.* **70,** 286 (1966).

**Résumé**—On a étudié par la méthode de représentation des probabilités normales les chromatogrammes par perméation de gel de copolymères séquences polyisoprène 1-4, polystyrène ayant des distributions étroites en masses moléculaire et en composition. On a évalué les paramètres $\bar{M}_w$,$\bar{M}_n$ et la déviation standard $\sigma$ et on a comparé les résultats avec les $\bar{M}_n$ obtenus par osmométrie ultra-rapide. Il semble que le fractionnement se fait, pour une composition particulière, d'après la longueur des chaînes.

**Sommario**—I cromatogrammi "gel permeation" di copolimeri ad innesto del *cis* 1–4 poliisoprene e del polistirene con intervallo ristretto di peso molecolare e composizione sono stati studiati col metodo del grafico delle probabilità normali. Sono stati ricavati i parametri $\bar{M}_w$, $\bar{M}_n$ e la deviazione standard $\sigma$ e i risultati sono stati confrontati con i valori $\bar{M}_n$ ottenuti con osmometria ad alta velocità. Si vede che, per una particolare composizione si ottiene un frazionamento a secondo della lunghezza della catena.

**Zusammenfassung**—Gelpermeationschromatogramme von Block-Copolymeren aus *cis* 1,4-Polyisopren und Polystyrol mit engen Verteilungen in Bezug auf Molekulargewicht und Zusammensetzung wurden mit Hilfe der Methode der Normal-Wahrscheinlichkeitsauftragung untersucht. Die Parameter für $\bar{M}_w$,$\bar{M}_n$ und für die Standard-abweichung $\sigma$ wurden ermittelt und verglichen mit Werten für $\bar{M}_n$, die mit einem Schnell-Osmometer erhalten wurden. Die Fraktionierung scheint für eine bestimmte Zusammensetzung nach Maßgabe der Kettenlänge zu erfolgen.

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# THE EFFECT OF HETEROGENEITY IN COMPOSITION ON THE DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION OF BLOCK COPOLYMERS BY GEL PERMEATION CHROMATOGRAPHY

By J. R. URWIN* and D. N. CRAMOND*†

[Manuscript received October 2, 1968]

### *Summary*

The molecular weight of samples of block copolymers of poly(isoprene : styrene) determined by gel permeation chromatography (g.p.c.) are found to deviate from the values obtained by light scattering and osmometry. The extent of the deviation depends on composition, and comparision of (g.p.c.) values with osmometry ($\bar{M}_N$) can be interpreted if account is taken of the effect of heterogeneity. The drift in composition with molecular weight calculated from light scattering data can be used to predict the direction of the deviation, at least qualitatively.

## INTRODUCTION

The chromatogram of a polymer obtained by the method of gel permeation chromatography (g.p.c.) is a composite of the Gaussian curves of all the species in the sample. The total area under the curve is proportional to the concentration although the height of the curve at a given eluent volume is not proportional to the relative abundance of a particular component.[1] This applies equally to copolymers as well as homopolymers. The maximum in the curve obtained by plotting the cumulative weight against the eluent volume, is used to determine the molecular weight of the sample. However, a problem arises in the case of copolymers which are not monodisperse. The usual method for determining the weight of material corresponding to a particular eluent volume is differential refractometry, and when the refractive index increment is different for the two kinds of segments comprising the copolymer, as it usually is, the refractometer will give a reading too high or too low, depending upon whichever type of segment is in excess of the average composition at a particular eluent volume. An indication of the direction of the drift in composition with molecular weight is obtained from light scattering studies,[2] although a reasonably accurate quantitative assessment, which would enable a correction to be made, is not so readily obtained.

The theory of fractionation by g.p.c. is still a highly speculative subject, but factors which affect the fractionation are becoming increasingly evident. Recently, it was reported[3] that a universal calibration curve can be constructed for any par-

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[1] Tung, L. H., *J. appl. Polym. Sci.*, 1966, **10**, 375.

[2] Bushuk, W., and Benoit, H., *Can. J. Chem.*, 1958, **36**, 1616.

[3] Grubisic, Z., Rempp, P., and Benoit, H., *Polym. Lett.*, 1967, **5**, 735.

*Aust. J. Chem.*, 1969, **22**, 543–8

ticular arrangement of g.p.c. columns by plotting the hydrodynamic volume or its equivalent determined from viscosity studies against the peak count, that is, the elution volume corresponding to the maximum of the g.p.c. curve. Calibration of a simple homopolymer is generally effected by measuring the peak count against elution volume for a series of well-characterized polymers. For calibration of copolymers, the plots of peak count against elution volume for both homopolymers, of which the copolymer is comprised, are required. The molecular weight can then be determined by extrapolation assuming a linear relation in terms of composition by weight.

The procedure outlined above is valid if it can be assumed that the refractive index increment is independent of molecular weight and that the copolymer sample is monodisperse in molecular weight and composition. Some doubt has been raised with regard to the former assumption[4] although the work referred to states, rather cautiously, that the effect observed may only apply to a particular method of synthesis. Nevertheless, similar behaviour might well be observed with other polymers and other synthetic methods. The latter assumption concerning monodisperse samples is generally not valid. Light scattering studies can provide an indication of the direction of the deviation in composition with molecular weight from the true values, but in view of the very large errors in the determination of this drift it is doubtful whether a meaningful correction could be applied in the present instance. It also raises the question of whether using these methods one can obtain from g.p.c. measurements anything more than a qualitative indication of the breadth of distribution and an approximation of molecular weights.

## EXPERIMENTAL

Three well-characterized block copolymers which have been designated BCP1–3, composed of polyisoprene and polystyrene and synthesized under strictly controlled conditions,[5] using butyllithium initiator in benzene, were examined in a Waters gel permeation chromatograph. The solvent was tetrahydrofuran at 40°. Two columns, one each of $10^5$ Å and $10^4$ Å, were employed with a flow rate of $0\cdot51$ ml per minute. A fourth polymer examined and designated RCP1 was synthesized by adding both monomers at the same time. This polymer, whilst having a random structure, was expected to contain long sequences and therefore behave, to some extent, like a block copolymer. Calibration was achieved using polystyrenes supplied by the instrument manufacturer and a sample of polyisoprene prepared in these laboratories by the same method as was used in the first step of the synthesis of the block copolymers. It could be reasonably assumed that the slope of the polyisoprene calibration line was parallel to that of the polystyrene.

Light scattering results were obtained on a Sofica light scattering apparatus using the unpolarized 546-mm mercury line, in three solvents (toluene, cyclohexane, and methyl isobutyl ketone). Results were both hand-calculated and, in part, computed on the C.D.C. 6400 computer at the University of Adelaide. $\partial n/\partial c$ values were calculated from a least-squares plot of published values of natural rubber and polystyrene over a wide range of solvents and assuming a linear relation with composition to hold.

Viscometry data were obtained on a semi-automatic viscometer of the suspended level type constructed in these laboratories. All flow times were in excess of 200 sec and a crystal timer enabled measurement to be made to $0\cdot01$ sec at $30\pm0\cdot01°$.

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[4] Barrall, E. M., Cantow, M. J. R., and Johnson, J. F., *J. appl. Polym. Sci.*, 1968, **12**, 1373.

[5] Cramond, D. N., and Urwin, J. R., *Aust. J. Chem.*, 1968, **21**, 1835.

## RESULTS

The cumulative weight at half-count intervals against elution volume was plotted on normal probability graph paper. The plots given here in full detail (Fig. 1) show that for each block copolymer a linear plot was obtained over 95% of the chromatogram, as we indicated in a preliminary report,[6] and to 90% for RCP1. It is therefore established that the distribution is Gaussian, or at least it can be assumed to be so over this region. The standard deviation $\sigma_c$ determined from the difference in counts at the 50% and 16% marks is converted to molecular weight by the slope of the calibration curve $k$. The weight average and number average moleculer weights are then calculated from the relations[7]

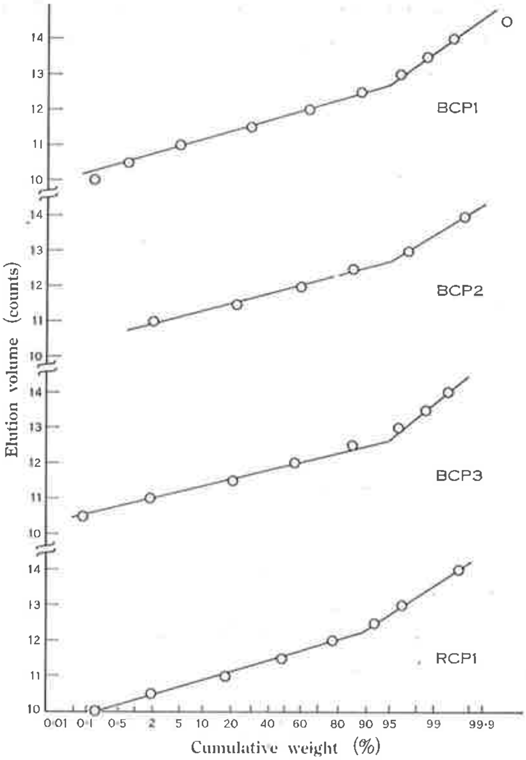

Fig. 1—Cumulative weight plotted on normal probability paper against elution volume in counts for the series of copolymers.

$$\bar{M}_W = \bar{M}_W(g)\exp(\tfrac{1}{2}\sigma^2) \tag{1}$$

$$\bar{M}_W/\bar{M}_N = \exp(\sigma^2) \tag{2}$$

$$\sigma = \sigma_c/k \tag{3}$$

where $\bar{M}_W(g)$ is the geometric mean, and $\bar{M}_W$ and $\bar{M}_N$ have their usual meaning.

[6] Cramond, D. N., Hammond, J. M., and Urwin, J. R., *Eur. Polym. J.*, 1968, **4**, 451.

[7] Herdan, G., "Small Particle Statistics." p. 83. (Butterworths: London 1960.)

A universal calibration curve was constructed from a plot of $\log[\eta]M$ against the peak count. Viscosity data in tetrahydrofuran were not possible due to lack of polymer, but data in toluene, a thermodynamically similar solvent, which should be a satisfactory alternative, were employed in this test. The plot was found to be reasonably linear, although a better fit was obtained when the peak count was replaced by the elution volume corresponding to the geometric mean (Fig. 2). All points fall on a straight line which also passed through points corresponding to the polystyrenes and the polyisoprene sample used in the calibration.

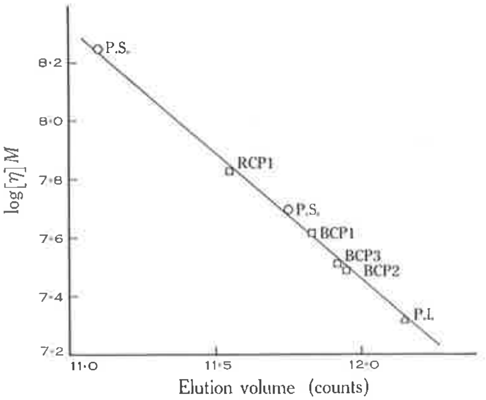

Fig. 2.—Logarithm of the product of the limiting viscosity number and molecular weight against the peak count.

## Discussion

The chromatogram for a multicomponent system can be represented by an equation expressing its Gaussian shape which has the form:[1]

$$F(v) = \int_{v_a}^{v_b} W(y)\,(h/\pi)^{\frac{1}{2}} \exp\{-h(v-y)^2\}\,dy \tag{4}$$

where $F(v)$ represents the chromatogram, $v_a$ and $v_b$ are the initial and final eluent volumes for the chromatogram, $h$ is the resolution factor, $y$ is the peak eluent volume, and $W(y)$ is a distribution function used to denote the relative abundance of the components of the system. A log-normal distribution is often assumed for the molecular weight distribution which has the form

$$w(M) = \beta^{-1}\pi^{-\frac{1}{2}}M^{-1}\exp\{-\beta^{-2}\ln^2(M/M_0)\} \tag{5}$$

where $\beta$ is a parameter denoting the breadth of the distribution. On substitution of (5) into (4) a solution to (4) can be found and then the important parameters $\beta$ and $M_0$ may be obtained from the experimental chromatogram. Alternatively, a graphical procedure may be adopted using normal probability graph paper which gives a linear display of the cumulative weight data. The latter method was adopted in this work. In practice, a differential refractometer is employed to measure the relative weight of components occurring at a particular eluent volume, which is an elegant method in the case of homopolymers provided the refractive index is independent of molecular weight. However, in the case of a copolymer, the different segments which comprise the molecule will have different $\partial n/\partial c$ values and the refractometer will record the relative abundance of the two types of segments occurring at a particular eluent volume. Only in the case of a sample monodisperse in composition will the chromatogram be truly representative of the distribution of molecular weight. In all other cases, the curve will be skewed and the peak count displaced.

The weight average molecular weight as obtained by light scattering is unfortunately subject to rather large errors. This is due to the necessity to employ at least three solvents with different refractive indices which yield three different statements of the usual light scattering equation.[2] Two other parameters are obtained from this data using the now well-known relationship originally proposed by Stockmayer *et al.*:[8]

$$\left[\frac{I_\theta}{K'c}\right]_{\theta\to 0}^{c\to 0} = \left(\frac{\partial n}{\partial c}\right)_0^2 \bar{M}_W + 2b\left(\frac{\partial n}{\partial c}\right)_0 \langle M(\Delta x)\rangle + b^2\langle M(\Delta x)^2\rangle \qquad (6)$$

where $b = (\partial n/\partial c)_A - (\partial n/\partial c)_B$, $(\partial n/\partial c)_0$ is the refractive index increment determined experimentally, and the subscripts A and B refer to the two homopolymers. The parameters $\langle M(\Delta x)\rangle$, $\langle M(\Delta x)^2\rangle$, where $\Delta x$ is the deviation from average composition $x_0$ (i.e. $\Delta x = (x_1 - x_0)$), are interpreted as a measure of the drift in the composition of the copolymer with molecular weight and the width of the composition distribution respectively. The sign of $\langle M(\Delta x)\rangle$ may be either positive or negative depending upon the direction of the drift, but $\langle M(\Delta x)^2\rangle$ should be positive always.

TABLE 1

MOLECULAR WEIGHT PARAMETERS DERIVED FROM G.P.C., LIGHT SCATTERING, AND OSMOMETRY FOR BLOCK COPOLYMERS OF POLYISOPRENE AND POLYSTYRENE

| Parameter | BCP1 | BCP2 | BCP3 | RCP1 |
|---|---|---|---|---|
| Composition wt. % polydispersity | 33 | 59 | 78 | 56 |
| $10^{-5}\bar{M}_W$ from g.p.c. | 2·5 | 2·8 | 3·6 | 3·8 |
| $10^{-5}\bar{M}_N$ from g.p.c. | 2·2 | 2·5 | 3·2 | 3·3 |
| $10^{-5}\bar{M}_N$ from osmometry | 2·4 | 2·1 | 2·5 | 3·5 |
| $10^{-5}M_W$ from light scattering | 2·6 | 2·2 | 2·6 | 3·7 |
| $10^{-5}\langle M(\Delta x)\rangle$ | +0·17 | +0·79 | +0·39 | −0·95 |
| $10^{-5}\langle M(\Delta x)^2\rangle$ | −0·04 | −0·88 | +0·89 | +3·18 |
| $\bar{M}_W/\bar{M}_N$ (g.p.c.) | 1·15 | 1·12 | 1·12 | 1·16 |
| $\bar{M}_W/\bar{M}_N$ (light scattering/osmometry) | 1·08 | 1·05 | 1·04 | 1·06 |

Inspection of the results listed in Table 1 shows that the true block copolymers BCP1–3 display a drift in composition which is in the opposite direction to RCP1. This is interpreted to mean that the molecular weights from g.p.c. will be too high in the case of the block copolymers and too low in the case of RCP1. The two negative values for $\langle M(\Delta x)^2\rangle$ are rather disconcerting since, as has been stated, they should all be positive. Krause[9] has found a similar effect in the case of block copolymers of styrene and methyl methacrylate and has interpreted this to mean that the accumulated

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[8] Stockmayer, W. H., Moore, L. D., Fixman, M., and Epstein, B. N., *J. Polym. Sci.*, 1955, **16**, 517.

[9] Krause, S., *J. phys. Chem.*, 1961, **65** ,1618; 1964, **68**, 1948.

errors in the calculation are numerically large and responsible for the negative values. This, unfortunately, does not inspire confidence in the quantitive aspect of these results and it is therefore doubtful as to whether any useful purpose can be served by applying a correction to the g.p.c. molecular weights based on these results.

Comparison of molecular weights obtained by g.p.c., light scattering, and osmometry is interesting nevertheless. In view of the larger error in light scattering it is certainly more profitable to compare $\bar{M}_{\mathrm{N}}$ values. The deviation between the results of these two methods increases with increasing polystyrene content and it should be noted that the polymer RCP1 shows a slight trend in the opposite direction. This drift is entirely consistent with the direction indicated by the light scattering data from the sign of $\langle M(\Delta x)\rangle$ and we may therefore conclude that the trends in the results agree, at least qualitatively.

The degree of heterogeneity given by $\bar{M}_{\mathrm{W}}/\bar{M}_{\mathrm{N}}$ is broader in the g.p.c. results which is in agreement with the prediction[1] that the log-normal distribution always gives rise to a broadened distribution even though the mean is not displaced. However, here again a word of caution is necessary since the error in $\bar{M}_{\mathrm{W}}$ from light scattering is large which makes the error in the ratio from light scattering and osmometry large as well. The opinion has been expressed that it would be better to compute the results using such numerical solutions for general distributions as Gaussian quadrature or polynomial expansion;[1] always of course provided that a computer is available. This is clearly desirable rather than to sacrifice precision for some simplicity in calculation. Nevertheless, it seems entirely reasonable to use the simple approach when a computer programme is not at hand.

Finally, the excellence of the $\log[\eta]M$ against peak count plot is further confirmation of the view that the method of fractionation is according to the hydrodynamic volume. In this work, the significance of the better fit using the geometric mean may simply be that the plot on normal probability paper corrects the skewing of the curve due to the composition drift.

It seems obvious that the g.p.c. determination of molecular weight distributions must take account of the drift in composition with molecular weight which must always be present and to a much greater extent in more polydisperse polymers than those which have been examined here. The effect can not be counteracted by other analytical techniques although other methods may allow the individual distributions of separate blocks to be analysed. This could also be done using the differential refractometer for a single block by the choice of the appropriate solvent but is generally impossible for both blocks. Clearly much more work is required to achieve similar success in this field with block copolymers as that which has been demonstrated for homopolymers.

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# SOLUTION PROPERTIES OF BLOCK COPOLYMERS OF POLY(ISOPRENE : STYRENE)—I

## MOLECULAR DIMENSIONS BY VISCOSITY AND LIGHT SCATTERING METHODS

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**Abstract**—Viscosity and light scattering data for block copolymers of poly(isoprene : styrene) have been determined in the solvents toluene, cyclohexane and methyl isobutyl ketone. The displacement length parameter $<\bar{r}^2>^{\frac{1}{2}}/Z^{\frac{1}{2}}$ reaches a maximum in the middle of the composition scale. Binary cluster integrals calculated from second virial coefficients show that the magnitude of the volume effect increases over the range of solvents MBK to toluene. An attempt to explain these effects in terms of increased interaction is made here but such an interpretation must be treated with considerable caution.

## INTRODUCTION

THE MOLECULAR dimensions of copolymers have been studied, in general, by the well established techniques of viscometry and light scattering. These methods allow the determination of the parameters which define uniquely the hydrodynamic volume or the end-to-end distance and the radius of gyration, at least when applied to homopolymers. The extrapolation of these ideas to copolymers is usually valid in the first case but presents many difficulties in the second. Nevertheless, it is possible, if one proceeds with caution, to obtain very valuable information on the structure of the copolymers in solution. We begin by briefly discussing some of the difficulties in the interpretation of the light scattering data. For many years now, it has been known that the light scattering equation generally applicable to the analysis of polymers for the determination of the weight average molecular weight yields only an apparent value in the case of copolymers. Many years ago, Stockmayer, Moore, Fixman and Epstein(1) derived an expression for the behaviour of the intensity of light scattered by a copolymer solution and showed that the intensity, after extrapolation to infinite dilution and zero angle, is dependent on the composition distribution of the copolymer sample. Later, Bushuk and Benoit(2) derived these same equations in an entirely equivalent form except that the final equations are arranged in a more useful way. The theory was tested by these authors using both a statistical and a block copolymer. Krause(3) has also demonstrated the validity of these equations on fractionated samples of block copolymers measured in six different solvents having a wide spread of refractive index increments. Several other analyses have been reported over the last few years,(4–7) but the number of studies of block copolymers is still relatively small.

All the scattering elements in a homopolymer scatter in the same manner, whereas in a copolymer there may be two or more scattering elements depending upon the

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number of different kinds of segments making up the polymer. Considering binary copolymers only, the apparent molecular weight $M_{ap}$ is given by

$$M_{ap} = \bar{M}_W + 2P[(\nu_A - \nu_B)/\nu_0] + Q[(\nu_A - \nu_B)/\nu_0]^2 \quad (1)$$

in which $M_W$ is the true weight average molecular weight, $\nu_A$, $\nu_B$ are the refractive index increments of homopolymers $A$ and $B$ respectively and $\nu_0$ the measured refractive index increment of the copolymer solvent system. $P$ and $Q$ are related to the heterogeneity in composition of the sample by the definitions

$$P = \Sigma\gamma_i M_i \delta x_i; \; Q = \Sigma\gamma_i M_i (\delta x_i)^2 \quad (2)$$

in which $\delta x_i = (x_i - x_0)$ and $\delta x_i$ is the deviation in composition of molecules of type $i$ from the average composition $x_0$.

$\gamma_i$ is the weight fraction of the molecules in the copolymer with molecular weight $M_i$ and composition $x_i$. In principle, the true weight average molecular weight may be obtained by measurements in three solvents having different refractive index increments. These measurements provide three independent statements of Eqn. (1) i.e. three simultaneous equations which may be easily solved for the three unknowns $\bar{M}_W$, $P$ and $Q$.

The radius of gyration of a homopolymer is determined from the first term in the expansion of the function $P(\theta)$ as a function of $\sin^2 \theta/2$. Application of this method to the case of a copolymer raises several problems which have not been satisfactorily resolved. The expression for two types of segments only is as follows,⁽⁸⁾

$$R^2_{ap} = \alpha^2 R^2_A + \beta^2 R^2_B + 2\alpha\beta R^2_{AB} \quad (3)$$

where $R_{ap}$ is the apparent radius of gyration of the whole molecule, $R_A$ and $R_B$ are the radii of gyration about the centre of gravity of parts $A$ and $B$ respectively and $R_{AB}$ is defined by

$$R^2_{AB} = \tfrac{1}{2}\{R^2_A + R^2_B + (G_A G_B)^2\} \quad (4)$$

$(G_A G_B)^2$ is the mean square distance of the centres of gravity of parts $A$ and $B$. In principle, one should be able to determine $R^2_A$, $R^2_B$ and $(G_A G_B)^2$ by light scattering measurements in three solvents. Two difficulties arise immediately in that polydispersity affects the results in a complex fashion and the volume effect should be negligible or alternatively the same in the three solvents, which is very difficult to realize. This means that the average value of the radius of gyration obtained by this method is not readily interpreted in a physical sense. However, under certain specific conditions, it may be possible to arrive at a measure of molecular dimensions in a particular solvent. Leng and Benoit⁽⁹⁾ have proposed an alternative use of the light scattering data, using the product of the molecular weight and mean square radius of gyration These authors have shown that under certain circumstances it is possible to distinguish between statistical, block and graft copolymers from the direction of concavity of the parabola formed when the product $M_{ap}. R^2_{ap}$ is plotted as a function of the refractive index increment. It is obvious that there is no well trodden path to obtaining an unambiguous value for the radius of gyration in the case of a block copolymer.

## EXPERIMENTAL

The four samples of copolymer, I.S.1 to I.S.4, were prepared anionically in benzene solution using butyl lithium as initiator. The first three polymers were synthesized by firstly preparing unterminated isoprene and then adding styrene monomer to form block copolymers. I.S.4 was synthesized by adding the initiator to a mixture of both monomers. Details of the synthesis have been described elsewhere.(10) Copolymer I.S.4 is expected, on the basis of the known kinetic mechanism, to be composed largely as a block copolymer with some random copolymer character between the long sequences. The polymers were precipitated in a large excess of methanol, filtered, dried under vacuum and stored *in vacuo* at 20°. The composition of each copolymer was determined by measuring the optical density of chloroform solutions at the polystyrene peaks at 262 mμ and 269 mμ using a Beckmann D.U. spectrophotometer with digital readout and substituting into the equations

$$Ks = \frac{\text{Optical density at } \lambda}{\text{Cell path length (cm)} \times \text{conc. (g/l.)}}, \tag{i}$$

$$K = xK_S + (1 - x)K_I \tag{ii}$$

where $K_S$ and $K_I$ are the specific extinction coefficients, at the particular wave length, of polystyrene and polyisoprene respectively and $K$ is the value for the copolymer. The values determined at both peaks were found to be identical. Microstructure analysis by N.M.R. showed the material to be largely the *cis* 1:4 isomer.(10) Gel permeation chromatographic analysis(11) demonstrated the complete absence of any homopolymer in all copolymer samples and that all samples were of narrow molecular weight distribution. The solvents used in this work were of A.R. grade, dried over calcium hydride, refluxed over the same drying agent for 24 hr, and finally fractionated using a 3 ft column with a 1:10 take-off rate. Before use the solvents were filtered under pressure through a No. 5 porosity glass filter with dry nitrogen. Solutions were prepared by weighing the sample directly into the volumetric flask and dissolving in the dust-free solvent. The concentrated solution thus prepared was then diluted to obtain a range of five solutions. A Beckmann model L centrifuge was employed to dedust solutions for several hours at 30,000 g using a swinging bucket rotor and stainless steel insert tubes. Light scattering cells and pipettes were cleansed in specially constructed washing towers and vacuum dried before use. Solutions were transferred to light scattering cells as soon after centrifuging as possible. The light scattering instrument used in this study was a "Sofica" photogonio diffusometer, model 4200, modified to the extent that the instrument galvanometer was replaced by a Kipp and Zonen Microva linear scale galvanometer to allow easier and more accurate readings to be achieved. The instrument was calibrated using very carefully dedusted pure benzene. Calibration was based on the Rayleigh ratio of benzene $R_{90} = 15{\cdot}8 \times 10^{-6}$ at $\lambda = 546$ mμ and the volume correction sin $\theta$ shown to be satisfactory after allowing for depolarization.(12) All measurements were made at the wavelength $\lambda = 546$ mμ using unpolarized light. As a secondary standard, a special glass provided by the manufacturers, which scatters about 50 per cent more than the benzene, was generally used in place of the benzene. All measurements were made at 30° ± 0·5° in a dust-free, air-conditioned room. The light scattering data were firstly extrapolated to zero scattering angle and then extrapolated to infinite dilution. Values of d$n$/d$c$ were calculated from published data(13, 14) in a number of solvents of different refractive indices for polystyrene and natural rubber. Measurements of d$n$/d$c$ were made on a sample of polyisoprene synthesized by the same method as was used for the copolymers using a Brice–Phoenix differential refractometer. Calculation of d$n$/d$c$ for the copolymers was made by assuming the relation

$$(\mathrm{d}n/\mathrm{d}c)_0 = (\mathrm{d}n/\mathrm{d}c)_{\mathrm{P.S.}} \times + (\mathrm{d}n/\mathrm{d}c)_{\mathrm{Is}}(1 - x)$$

where $(\mathrm{d}n/\mathrm{d}c)_0$, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{P.S.}}$ and $\mathrm{d}n/\mathrm{d}c)_{\mathrm{Is}}$ are the refractive index increments of copolymer, polystyrene and polyisoprene in the particular solvent, respectively, and $x$ is the weight fraction of polystyrene in the copolymer.

An automatic viscometer, constructed in these laboratories according to the design of Steel(15) was used in all measurements of viscometry. Flared capillaries(16) were employed to eliminate the usual kinetic energy corrections. Solvent flow times in excess of 200 sec were reproducible to ±0·01 sec using the photoelectric timing device and crystal actuated timer. The thermostat was controlled to ±0·01° with a thermistor controller designed and constructed in these laboratories.

## RESULTS AND DISCUSSION

The experimental light scattering data, plotted according to the method of Zimm, for the block copolymer I.S.1 in cyclohexane is shown in Fig. 1. The complete absence of the involuted form, typical of incorrect dedusting procedures, can be seen from the figure. Apparent molecular weights in each solvent and the true weight average molecular weight calculated from Eqn. (1) are displayed in Table 1. Comparison of the values obtained in methyl isobutyl ketone (MBK) with the true values shows that the

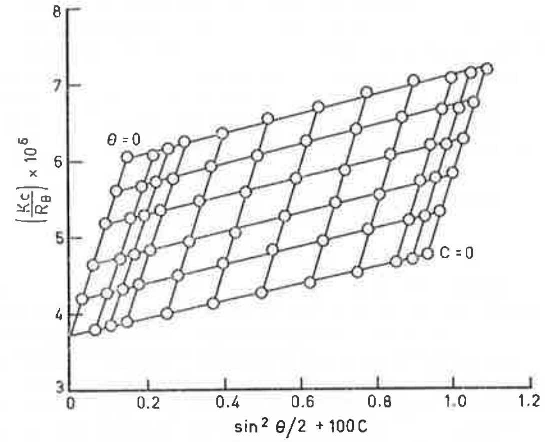

FIG. 1. Zimm plot for the block copolymer I.S.1 in cyclohexane at 30°.

TABLE 1. MOLECULAR WEIGHT AND HETEROGENEITY PARAMETERS FOR THE COPOLYMERS DETERMINED BY LIGHT SCATTERING IN TOLUENE, CYCLOHEXANE AND METHYL ISOBUTYL KETONE AT 30°

| Polymer | Composition (wt. %) | | $M_{ap} \times 10^{-5}$ | | $\bar{M}_w \times 10^{-5}$ | $P/\bar{M}_w$ | $Q/\bar{M}_w$ |
|---|---|---|---|---|---|---|---|
| | | Tol. | c.Hex. | MBK | | | |
| I.S.1 | 33 | 2·93 | 2·68 | 2·63 | 2·56 | +0·07 | −0·01 |
| I.S.2 | 59 | 2·89 | 2·64 | 2·50 | 2·21 | +0·36 | −0·40 |
| I.S.3 | 78 | 3·19 | 2·69 | 2·63 | 2·59 | +0·15 | +0·34 |
| I.S.4 | 56 | 5·20 | 3·42 | 3·44 | 3·70 | −0·26 | +0·86 |

molecular weights measured in a solvent with a high refractive index increment are probably as accurate as those calculated according to Eqn. (1), particularly since the estimated error is so large. The experimental values agree with those obtained by gel permeation chromatography(11) provided account is taken of the effect of heterogeneity in composition on the peak count.(17) The heterogeneity parameters, $P/\bar{M}_W$ and $Q/\bar{M}_W$, given in Table 1 indicate that the polymers are of narrow distribution, although the negative values obtained for $Q/\bar{M}_W$ are disconcerting. Negative values for $Q$ have been reported previously(3) and are attributed to the accumulative errors in the experimental results. In order to minimize the error, it has been suggested that measurements in five to six solvents are required; however lack of sufficient polymer precluded this method. The sign of $P/\bar{M}_W$ may be either positive or negative, the sign signifying whether the composition drift in the polymer sample is to the high or low molecular weight side of the molecular weight distribution. In view of the identical method of synthesis, the positive values for the first three copolymers are, not surprisingly, consistent. The opposite sign shown by I.S.4 is indicative of the different mechanism of synthesis. The results clearly suggest a narrow distribution of molecular weight which is entirely in agreement with G.P.C. results. Copolymer I.S.4 is the most heterogeneous of the series as is to be expected in view of the method of synthesis. This particular polymer is likely to contain long sequences but will have some degree of randomness in the centre of the chain. The root mean square end-to-end distance may be calculated by making use of the viscosity relation

$$[\eta] = \Phi \langle \bar{r}^2 \rangle^{3/2}/\mathrm{M} \qquad (5)$$

and provided the assumption of a gaussian distribution of segments is valid or that the deviation from such a distribution is not too great, we may write

$$\langle \bar{r}^2 \rangle^{1/2} = \langle \bar{s}^2 \rangle^{1/2}/6^{1/2} \qquad (6)$$

and so obtain the radius of gyration.

The Flory constant $\Phi$ was evaluated from Eqn. (5) on substitution of the radius of gyration determined in MBK (Table 2) which was obtained by extrapolating $[Kc/R_\theta]^{c=0}$ vs. $\sin^2 \theta/2$ to zero angle. The value $\Phi$ was found to be constant at $1 \cdot 9 \times 10^{-21}$ for all the copolymers. Using this value and the true weight average molecular weight in conjunction with the limiting viscosity number yields values of $\langle \bar{r}^2 \rangle^{1/2}$ in all three solvents. The limiting viscosity numbers and second virial coefficients determined in the three solvents are shown in Table 2 along with the r.m.s. radius of gyration measured in MBK.

TABLE 2. LIMITING VISCOSITY NUMBERS AND SECOND VIRIAL COEFFICIENTS IN TOLUENE, CYCLOHEXANE AND MBK AT 30° AND THE R.M.S. RADIUS OF GYRATION IN MBK

| Polymer | $[\eta]$ (ml/g) | | | $A_2 \times 10^4$ (cm³ mole g⁻²) | | | $\langle \bar{s}^2 \rangle^{1/2}$ |
|---|---|---|---|---|---|---|---|
| | Tol. | c.Hex. | MBK | Tol. | c.Hex. | MBK | (Å) |
| I.S.1 | 161·1 | 141·0 | 69·5 | 8·10 | 7·66 | 1·38 | 185·5 |
| I.S.2 | 140·3 | 112·5 | 59·9 | 9·04 | 5·51 | 1·25 | 168·0 |
| I.S.3 | 126·8 | 86·3 | 60·2 | 8·78 | 3·48 | 1·60 | 177·4 |
| I.S.4 | 183·0 | 145·7 | 97·0 | 10·2 | 4·40 | 1·74 | 234·3 |

The expansion factor may be defined by either of the usual expressions

$$\alpha = \langle \bar{r}^2 \rangle^{1/2}/\langle \bar{r}_0^2 \rangle^{1/2} \qquad (7)$$

or

$$\alpha = \langle \bar{s}^2 \rangle^{1/2}/\langle \bar{s}_0^2 \rangle^{1/2} \qquad (8)$$

and may be calculated from the viscosity data in conjunction with the second virial coefficients by making use of the expression of Orofino and Flory(18)

$$A_2 = (2^{5/2}\pi N_A/3^3\Phi)([\eta]/\bar{M}_W) \ln [1 + (\sqrt{\pi}/2)(\alpha^2 - 1)]. \qquad (9)$$

The second virial coefficients were obtained by the usual method in light scattering of extrapolating the plot of $[Kc/R_\theta]_{\theta=0}$ to zero concentration. In Table 3 are given the virial coefficients, expansion factors and the parameters $(\langle \bar{r}^2 \rangle/Z)^{1/2}$ and $(\langle \bar{r}_0^2 \rangle/Z^{1/2})$ which characterize the dimensions of the polymer in a particular solvent and the unperturbed dimensions. The value of $Z$ used refers to the number of links in the chain rather than segments since the 1:4 isomer of polyisoprene contains twice as many bonds in the backbone as does polystyrene. The presence of some 3:4 isomer is ignored, as is the presence of the double bond in the 1:4 structures.

TABLE 3. EXPANSION FACTORS AND DISPLACEMENT LENGTH PARAMETERS IN TOLUENE, CYCLOHEXANE AND MBK

| | $\alpha$ | | | $<\bar{r}^2>/Z)^{\frac{1}{2}}$ (Å) | | | $(<\bar{r}_0^2>/Z)^{\frac{1}{2}}$ |
|---|---|---|---|---|---|---|---|
| Polymer | Tol. | c.Hex. | MBK | Tol. | c.Hex. | MBK | (Å) |
| I.S.1 | 1·422 | 1·393 | 1·146 | 5·40 | 5·29 | 4·36 | 3·80 |
| I.S.2 | 1·416 | 1·321 | 1·131 | 6·04 | 5·64 | 4·83 | 4·27 |
| I.S.3 | 1·443 | 1·314 | 1·199 | 6·35 | 5·78 | 5·00 | 4·40 |
| I.S.4 | 1·456 | 1·363 | 1·195 | 6·04 | 5·65 | 4·96 | 4·15 |
| P.Styrene | 1·325 | 1·000 | 1·068 | 6·40† | 4·83† | 5·16† | 4·83† |
| P.Isoprene | 1·414 | 1·440 | 1·036 | 4·72‡ | 4·81‡ | 3·46‡ | 3·34‡ |

† Calculated from Krigbaum and Carpenter, *J. phys. Chem.* **59,** 1166 (1955).
‡ Calculated from Wagner and Flory, *J.A.C.S.* **74,** 195 (1952).

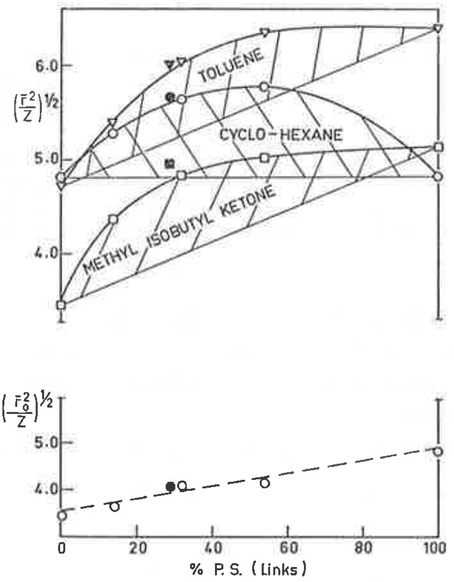

FIG. 2. The unperturbed displacement length parameters and the displacement length parameters in the three solvents.

The unperturbed displacement length parameters and the displacement length parameters in the three solvents are shown in Fig. 2. It can be seen quite clearly that, within the limits of experimental error, the unperturbed dimensions obey the simple relation

$$R^0 = xR_A^0 + (1-x)R_B^0 \tag{10}$$

where $R^0$, $R_A^0$ and $R_B^0$ are the total unperturbed end-to-end distance and that for homopolymer $A$ and $B$, respectively. $R^0$ here is an average value only, and is that dimension which for the given composition yields a zero virial coefficient. It means that the positive contribution from the slightly more expanded than unperturbed part of the chain cancels out the negative contribution from the less expanded than unperturbed portion. The fact that the unperturbed dimension so defined is simply the sum of its parts over the whole composition range suggests that the deviation from unperturbed dimensions may be small for both sequences. The stiffness parameter $<\bar{r}_0^2>^{\frac{1}{2}}/<\bar{r}_{0f}^2>^{\frac{1}{2}}$ which defines the degree of restriction to rotation shows a behaviour similar to the unperturbed displacement length as might be expected. It means that the degree of restriction to rotation varies linearly with composition from polystyrene to polyisoprene.

The parameter $(<\bar{r}^2>/Z)^{\frac{1}{2}}$ shows a maximum in the middle of the composition range in each case. The magnitude of this deviation from linearity appears to be similar for all polymers. Certainly, these results indicate that a more expanded polymer exists at the middle of the composition scale, which one can assume must be due to extra interactions of a repulsive nature. The implication is that, when the chain consists of equal numbers of links, there is the maximum number of hetero-contacts between the different segments of the chain. It also implies that there is at least some region where the segments are sufficiently mixed to give rise to the extra repulsions. Superficially, it is tempting to deduce from this argument that the molecular conformation is that of a "pseudo gaussian" coil. However, the real criterion is the extent to which mixing occurs. It is of interest to note that the copolymer I.S.4 shows similar behaviour to the true block copolymers. This indicates that the copolymer is very largely composed of long sequences and may be considered as a block copolymer.

Another approach to this problem is to consider the binary cluster integrals which may be taken to represent the excluded volume of a pair of segments. The ternary and higher order clusters may safely be disregarded in dilute solutions. Employing the equation derived by Kurata, Stockmayer and Roig(19)

$$(\alpha^3 - \alpha)/N^{\frac{1}{2}} = \{(1 + 1/3\alpha^{-2})^{-3/2}\}^{-1}\,(4/3)^{5/2}(3/2\pi)^{3/2}(\beta/a^3) \qquad (11)$$

where $N$ may be the number of segments or links (in our case links) and $a$ is the effective bond length defined by

$$a^2 = <\bar{r}^2>/Z \qquad (12)$$

we have calculated the values of $\beta$ for all the copolymers in the three solvents. The binary cluster integrals show a greater interaction in toluene than in MBK (Fig. 3) which, on the face of it, suggests greater interaction in the good solvent for both polymer segments than in the poor solvent for both types of segments. However, as has been observed previously(20) it is all too easy to forget that the pair potential

$$w(r) = -kT \ln g^*(r) \qquad (13)$$

which represents the potential energy for solute–solute interactions in the definition of the binary cluster integral

$$\beta = \int_0^\infty [1 - g^*(r)]4\pi r^2 \mathrm{d}r \qquad (14)$$

depends intimately on the solvent–solute and solvent–solvent interactions as well. Consequently, it would be all too easy to exaggerate the significance of the binary cluster data whereas it may simply be that again there is evidence of maximum inter-

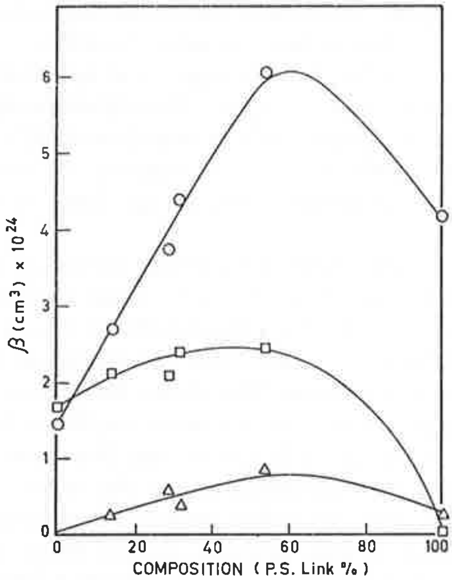

FIG. 3. Binary cluster integrals for the copolymers in toluene, cyclohexane and MBK at 30°.
○ Toluene □ Cyclohexane △ MBK

action near the middle range of composition. The actual position of the maximum depends on the magnitude of $\beta$ for the parent homopolymers.

It would seem then that these results, at least within the framework of the qualifications previously outlined, favour a random coil structure with a more expanded conformation due to extra repulsions rather than the segregated structure which results from intramolecular phase separation. However, it must be admitted that the evidence obtained so far is inconclusive and a cautious approach to the interpretation of these results should be adopted at this stage.

*Acknowledgements*—One of us (D.N.C.) thanks I.C.I.A.N.Z. for the award of a research fellowship. We thank the Australian Research Grants Committee for permission to use the Sofica light scattering apparatus and differential refractometer.

## REFERENCES

(1) W. H. Stockmayer, L. D. Moore, M. Fixman and B. N. Epstein, *J. Polym. Sci.* **16,** 517 (1955).
(2) W. Bushuk and H. Benoit, *Can. J. Chem.* **36,** 1616 (1958).
(3) S. Krause, *J. phys. Chem.* **65,** 1618 (1961).
(4) H. Benoit, *Ber der Bunsen,* **70,** 286 (1966), (see references in this review).
(5) H. Inagaki and T. Miyamoto, *Makromolek. Chem.* **87,** 166 (1965).
(6) D. Froelich and H. Benoit, *Makromolek. Chem.* **92,** 224 (1966).
(7) A. Dondas, P. Rempp and H. Benoit, *Europ. Polym. J.* **3,** 657 (1967).
(8) H. Benoit and C. Wippler, *J. Chim. phys.* **57,** 524 (1960).
(9) M. Leng and H. Benoit, *J. Chim. phys.* **58,** 480 (1961).
(10) D. N. Cramond and J. R. Urwin, *Aust. J. Chem.* **21,** 1835 (1968).
(11) D. N. Cramond, J. M. Hammond and J. R. Urwin, *Europ. Polym. J.* **4,** 451 (1968).
(12) D. J. Coumou, *J. Coll. Sci.* **15,** 408 (1960).
(13) Polymer Handbook, Edited by J. Brandup and E. H. Immergut, Interscience (1966).
(14) M. G. Huglin, *J. appl. Polym. Sci.* **9,** 3963 (1965).
(15) B. J. Steel, *J. scient. Instr.* **42,** 751 (1965).
(16) W. A. Caw and R. G. Wylie, *Br. J. appl. Phys.* **12,** 94 (1961).

(17) D. N. Cramond, Thesis, Adelaide (1968).
(18) T. A. Orofino and P. J. Flory, *J. chem. Phys.* **26,** 1067 (1957).
(19) M. Kurata, W. H. Stockmayer and A. Roig, *J. chem. Phys.* **33,** 151 (1960).
(20) W. H. Stockmayer, *Makromolek. chem.* **35,** 54 (1960).

**Résumé**—On a effectué des mesures de viscosité et de diffusion de la lumière sur des copolymères séquencés poly(isoprène: styrène) dans le toluène, le cyclohexane et la méthylisobutylcétone. Le paramètre de déplacement $<\bar{r}^{2\frac{1}{2}}/Z^{\frac{1}{2}}>$ possède une valeur maximale au milieu de l'échelle des compositions. Les intégrales d'amas binaires calculés à partir des seconds coefficients du viriel montrent que l'importance de l'effet de volume croît de la MBC au toluène. On essaye d'expliquer ces effets par une interaction accrue mais cette interprétation doit être considérée avec une prudence extrême.

**Sommario**—Sono stati determinati dati di viscosità e di "light scattering" per copolimeri a blocchi del poli(isoprene: stirene) nei solventi toluene, cicloesano e metil isobutil chetone. Il parametro di spostamento della lunghezza $<\bar{r}^2>^{\frac{1}{2}}/Z^{\frac{1}{2}}$ raggiunge un massimo nel mezzo della scala di composizione. Integrali binari a gruppo calcolati dal secondo coefficiente del viriale mostrano che la grandezza dell'effetto del volume aumenta oltre il campo dei solventi MBK fino al toluene. Si fa qui un tentativo di spiegare questi effetti nei termini di un'interazione aumentata, ma una tale interpretazione, deve essere trattata con considerevole cautela.

**Zusammenfassung**—Für Block-Copolymere von Poly-(isopren : styrol) wurden die Viskositäts- und Streulicht-Daten in den Lösungsmitteln Toluol, Cyclohexan und Methyl-isobutyl-keton bestimmt. Der Parameter der Verschiebungslänge $<\bar{r}^2>^{\frac{1}{2}}/Z^{\frac{1}{2}}$ erreicht ein Maximum bei etwa gleicher Zusammensetzung. Die aus den zweiten Virialkoeffizienten berechneten binären Cluster Integrale zeigen, daß die Größe des Volumeneffekts innerhalb der Lösungsmittelreihe von MBK nach Toluol hin ansteigt. Es wird versucht, diese Effekte als Ausdruck zunehmender Wechselwirkung zu erklären, jedoch muß eine solche Interpretation mit Vorsicht verwendet werden.

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# SOLUTION PROPERTIES OF BLOCK COPOLYMERS OF POLY(ISOPRENE : STYRENE)—II

## THERMODYNAMIC PARAMETERS FROM OSMOTIC DATA

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**Abstract**—Osmotic pressure data, obtained from a study of four block copolymers, have been used to calculate second virial coefficients and number average molecular weights. The virial coefficients were determined over a range of temperatures in toluene and cyclohexane. The theta temperatures, entropy of dilution, heat of dilution and the solvent–solute interaction parameters were derived and their behaviour is discussed.

## INTRODUCTION

THE OSMOTIC pressure, which is directly related to the chemical potential of the solvent in the solution, is derived from the partial differentiation of the free energy of mixing(1)

$$\Pi = -(\mu_1 - \mu_1^{\circ})/V_1 \equiv -(\partial \Delta G_M/\partial V)_{T,P,n_2}. \tag{1}$$

Taking into account the multiple interactions between molecules, the final equation takes the form

$$\Pi/c_2 = RT\,(1/\text{M} + A_2c_2 + A_3cz_2 + \ldots) \tag{2}$$

or

$$\Pi/c_2 = (\Pi/c_2)_0\,(1 + \Gamma_2c_2 + \Gamma_3c_2 + \ldots) \tag{3}$$

where $A_2 = \Gamma_2/\text{M}$ and M is the number average molecular weight ($\bar{\text{M}}_\text{N}$). Generally speaking, for poor solvents, $\bar{\text{M}}_\text{N}$ and the second virial coefficient $A_2$ are obtained from a plot of $\Pi/c_2\ RT$ vs. $c_2$, but in good solvents the third virial coefficient may not vanish when $A_2 = 0$. It is then convenient to assume the relation

$$\Pi/c_2 = (\Pi/c_2)_0\,(1 + \Gamma_2c_2 + g\Gamma_2{}^2c_2{}^2) \tag{4}$$

in which $g$ is a factor equal to 0·25 in most cases. The third term takes account of the curvature of the plot of $\Pi/c_2$ vs. $c_2$. Equation (4) is easily rearranged to(2)

$$(\Pi/c_2)^{\frac{1}{2}} = (\Pi/c_2)_0^{\frac{1}{2}}\,(1 + \Gamma_2/2c_2) \tag{5}$$

and $(\Pi/c_2)^{\frac{1}{2}}$ is plotted against concentration over the range where $\Pi/c_2$ does not exceed $3(\Pi/c_2)_0$. The number average molecular weight and the second virial coefficient are obtained from the intercept and the slope respectively.

### *The thermodynamic interaction parameters*

The chemical potential of the solvent in the solution relative to that in the pure liquid is obtained by differentiation of $\Delta G_M$ with respect to the number of solvent

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molecules. In terms of one mole of solute, the relative partial molar free energy is given by

$$\mu_1 - \mu_1^\circ = RT[\ln(1 - v_2) + (1 - 1/\bar{x}_n)v_2 + \chi_1 v_2^2] \tag{6}$$

in which $v_1$ and $v_2$ are functions of $n_1$ and $\bar{x}_n$ is the number average degree of polymerization. The quantity on the right of this equation may be separated into the relative partial molar configurational entropy of the solvent and the heat of dilution. On substituting Eqn. (1) the relation takes the form

$$\Pi = -(RT/V_1)\,[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2] \tag{7}$$

and on expanding the logarithmic term and neglecting higher powers of $v_2$ yields

$$\Pi = (RT/V_1)\,[v_2/x + (\tfrac{1}{2} - \chi_1)v_2^2 + v_2^3/3 + \ldots]. \tag{8}$$

The parameter $\chi_1$ in these equations is the partial molar enthalpy or heat of dilution defined thus,

$$\Delta\bar{H}_1 = RT\,\chi_1 v_2^2$$

and may possibly contain an entropy contribution. It may readily be shown that the non-ideal terms represent the excess chemical potential, i.e. the chemical potential in excess of the ideal contribution $-RTv_2/\mathrm{M}$. This excess chemical potential may be written in the following manner with complete generality:

$$(\mu_1 - \mu_1^\circ)_{\mathrm{ex.}} = RT(\kappa_1 - \psi_1)v_2^2 \tag{9}$$

where $\kappa$ and $\psi$ are the heat and entropy parameters defined by the relations

$$\Delta\bar{H}_1 = RT\;\kappa_1 v_2^2 \tag{9a}$$

and

$$\Delta\bar{S}_1 = R\,\psi_1 v_2^2. \tag{9b}$$

Equation (9) may also be written in the equivalent form

$$(\mu_1 - \mu_1^\circ)_{\mathrm{ex.}} = -RT\,\psi_1\,(1 - \theta/T)v_2^2 \tag{10}$$

since by comparison of Eqns. (8) and (9)

$$\kappa_1 - \psi_1 = \chi_1 - \tfrac{1}{2} \tag{10a}$$

and also the relation

$$\theta = \kappa T/\psi \tag{10b}$$

may be used to define the parameter $\theta$, the Flory or theta temperature. At the theta temperature, the excess chemical potential is zero and the deviations from ideality vanish.

The thermodynamic interaction parameters $\psi_1$ and $\kappa_1$ or $\psi_1$ and $\theta$ required to characterize the system may be determined directly from the second virial coefficient

$$A_2 = (\bar{v}_2^2/V_1)\,\psi_1\,(1 - \theta/T)\,F(X) \tag{11}$$

where $\bar{v}_2$ is the specific volume of the polymer, $V_1$ is the molar volume of the solvent and $F(X)$ is a function of the degree of expansion of the polymer chain. The theta temperature may be determined from the temperature dependence of the osmotic pressure second virial coefficient by extrapolating a plot of $A_2$ vs. $1/T$ to $A_2 = 0$.

The entropy of dilution parameter $\psi_1$, may then be evaluated from the slope of this plot at $T = 0$ where the slope equals $\psi_1 \theta(\bar{v}_2{}^2/V_1)$. The values of $\bar{v}_2$ may be reasonably approximated from the homopolymers by assuming volume additivity to apply. The heat of dilution parameter $\kappa$ is then calculated from Eqn. (10b) and finally $\chi_1$ with the aid of Eqn. (10b). Although these theories are derived from a consideration of homopolymers, we assume their extrapolation to copolymers without further comment.

## EXPERIMENTAL

All measurements of osmotic pressure were made using a high speed osmometer (Mechrolab 501) Cellulose membranes were carefully conditioned in stages to the solvent to be used. Solvents were prepared in the same manner as those used in the light scattering studies(3) described in the previous paper. It was found necessary to adopt the practice of checking the operation of the osmometer with a solution of polystyrene of known molecular weight before beginning each series of measurements because the presence of leaks or bubbles in the system were not easily detected immediately. Measurements were made in toluene, cyclohexane and methyl isobutyl ketone using $\Pi/c_2$ plotted against concentration for the last two solvents. However, in the case of toluene $(\Pi/c_2)^{\frac{1}{2}}$ vs. $c_2$ was plotted. It was found to be difficult to operate the osmometer below 20° and temperatures above 40° were considered hazardous due to the risk of degradation of the polyisoprene sequences. In this work, the polymer samples were used only once, as earlier studies showed rapid oxidation and chain scission of reprecipitated samples which was made manifest by the broadening of G.P.C. distribution curves.(4) The use of antioxidants was avoided throughout this work. The polymers were measured in toluene and MBK at three temperatures and the second virial coefficients plotted against $1/T$. Extrapolation to $A_2 = 0$ yielded the theta temperatures.

## RESULTS AND DISCUSSION

The second virial coefficients of all polymers in the three solvents at 30° determined by osmometry and by light scattering are presented in Table 1; for the purposes of discussion, the number average molecular weights obtained in MBK are included. The measure of agreement achieved between the two methods in the solvent methyl isobutyl ketone is very satisfactory. It demonstrates that the difference so often observed between light scattering and osmometry data is due, very largely, to heterogeneity of the samples.(5) As has been shown already, the polymers used in this work

TABLE 1. SECOND VIRIAL COEFFICIENTS OBTAINED BY OSMOMETRY AND LIGHT SCATTERING IN TOLUENE, CYCLOHEXANE AND METHYL ISOBUTYL KETONE AT 30°

| Copolymer | $\bar{M}_N \times 10^{-5}$ | $A_2$, cm$^3$ mole g$^{-2}$ $\times 10^4$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | Toluene | | Cyclohexane | | MBK | |
| | | O.P. | L.S. | O.P. | L.S. | O.P. | L.S. |
| I.S.1 | 2·41 | 8·46 | 8·10 | 6·97 | 7·66 | 1·39 | 1·38 |
| I.S.2 | 2·11 | 8·43 | 9·04 | 5·39 | 5·51 | 1·25 | 1·25 |
| I.S.3 | 2·47 | 6·87 | 8·78 | 3·46 | 3·48 | 1·59 | 1·60 |
| I.S.4 | 3·52 | 7·11 | 10·20 | 4·64 | 4·40 | 1·76 | 1·76 |

have quite narrow molecular weight and composition distributions.(6) It seems therefore that we can eliminate heterogeneity as a factor in this discussion. The results in cyclohexane are reasonably satisfactory but those in toluene show a greater divergence than might have been expected. Curiously, greater coincidence emerges when the slopes of the $\Pi/c_2$ vs. $c_2$ are used to calculate $A_2$ for toluene than when $(\Pi/c_2)^{\frac{1}{2}}$ vs. $c$ data is employed. This may simply mean that the use of $g = 0{\cdot}25$ is incorrect and that a larger value for $g$ should be introduced into Eqn. (4). Similar behaviour has been reported by Cooper, Eaves and Vaughan on a series of polyisoprenes.(7) Burnett, Meares and Paton(8) found it necessary to adopt the theoretical value $g = 5/8$ in their study of block copolymers.

In discussing these results, it must be recalled that homopolymers show an increase in $A_2$ with decreasing molecular weight.(9, 10) This is probably the main reason for the larger value for I.S.2 in toluene. The difference observed between I.S.1 and I.S.3 in cyclohexane, in view of the fact that the molecular weight is similar, must be due to solvent effects brought about by the quite different composition of the two polymers. Comparing I.S.2 and I.S.4, we find that the value of $A_2$ for I.S.4 is smallest in both toluene and cyclohexane, which is probably attributable to the high molecular weight of this polymer. The trend observed for values of $A_2$ in MBK is not readily interpreted in this qualitative fashion. However, we note that the effects of heterogeneity in I.S.4 may account for the larger value of $A_2$ for this polymer in a solvent where the virial coefficients are generally small. It appears that the solvent effect far outweighs the effect of chain length in this solvent when one compares I.S.1 and I.S.3. The low $A_2$ value of I.S.2 in this solvent is inexplicable, even qualitatively, from the limited data available.

Values of $A_2$ at the several temperatures in toluene and cyclohexane along with the theta temperatures in those solvents are given in Table 2. Unfortunately, the lack of sufficient polymer precluded a study in methyl isobutyl ketone. The theta temperatures measured in the two solvents are shown graphically in Fig. 1. The values determined in toluene can be seen to pass through a maximum and those measured in cyclohexane show a positive deviation from linearity with composition. This behaviour is similar to that found earlier for a series of block copolymers of styrene and methyl methacrylate.(11) It must be admitted that the extrapolation in the case of toluene gives rise to a large error due to our inability to use a wider range of temperatures and to use

TABLE 2. SECOND VIRIAL COEFFICIENTS AT SEVERAL TEMPERATURES (°C) FROM OSMOTIC DATA IN TOLUENE AND CYCLOHEXANE

| Copolymer | $A_2$, cm$^3$ mole g$^{-2}$ × 10$^4$ | | | | | |
|---|---|---|---|---|---|---|
| | Toluene | | | Cyclohexane | | |
| | 20° | 30° | 40° | 20° | 30° | 40° |
| I.S.1 | 7·70 | 8·46 | 8·58 | 6·40 | 6·97 | 7·19 |
| I.S.2 | 8·26 | 8·43 | 9·27 | 4·39 | 5·39 | 5·99 |
| I.S.3 | 6·34 | 6·87 | 7·01 | 2·19 | 3·46 | 4·64 |
| I.S.4 | 6·97 | 7·11 | 7·96 | 3·92 | 4·64 | 5·40 |

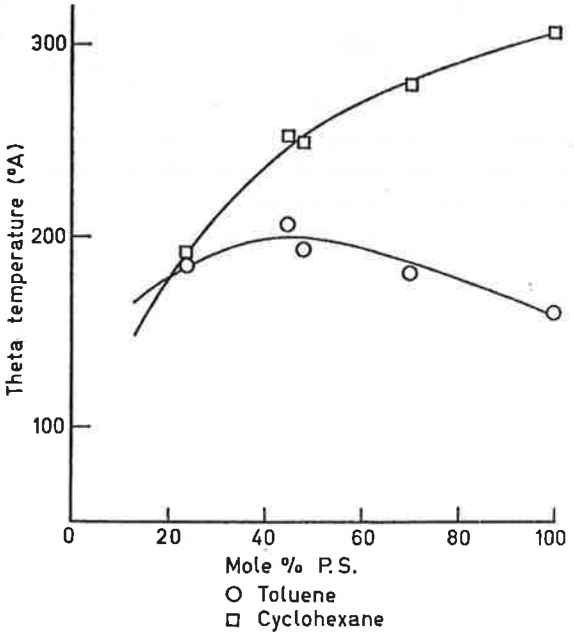

FIG. 1. Theta temperatures vs. composition for the copolymers in toluene and cyclohexane.

temperatures approaching the theta point. However, the values in cyclohexane are reasonably accurate. It seems likely that at least the general trend has been demonstrated in both solvents. Since the theta point is that temperature at which the excess chemical potential due to segment–solvent interactions (and in the case of copolymers, cross interactions as well) becomes zero and deviations from ideality vanish, then the behaviour of $\theta$ with composition is a measure of the extent of cross interaction. We can therefore interpret these results to mean that there is greater interaction near the middle of the composition scale in both solvents.

The entropy of dilution parameters, heat of dilution parameters and the polymer–solvent interaction parameters for the copolymers in toluene and cyclohexane are presented in Table 3. The values of $\chi_1$ show little fluctuation over the composition

TABLE 3. THE ENTROPY AND HEAT OF DILUTION PARAMETERS, POLYMER–SOLVENT INTERACTION PARAMETERS AND THE THETA TEMPERATURES FROM OSMOTIC DATA IN THE SOLVENTS TOLUENE AND CYCLOHEXANE

| Copolymer | Composition, mole% P.S. | Toluene | | | | Cyclohexane | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\psi$ | $\kappa$ | $\chi$ | $\theta$,°K | $\psi$ | $\kappa$ | $\chi$ | $\theta$,°K |
| I.S.1 | 24 | 0·214 | 0·130 | 0·416 | 185 | 0·175 | 0·120 | 0·445 | 192 |
| I.S.2 | 48 | 0·246 | 0·157 | 0·411 | 193 | 0·324 | 0·266 | 0·442 | 249 |
| I.S.3 | 70 | 0·195 | 0·116 | 0·421 | 180 | 0·507 | 0·467 | 0·460 | 279 |
| I.S.4 | 45 | 0·250 | 0·170 | 0·420 | 206 | 0·296 | 0·246 | 0·450 | 252 |

range except that they are lower than those reported for the homopolymers. Since the interaction parameter remains virtually constant, then a change in the entropy parameter is reflected in the heat parameter since $\kappa_1$ is calculated from Eqn. (10b) using the other two quantities $\psi_1$ and $\theta$. The entropy of dilution parameter for the copolymers in toluene appears to go through a maximum in the middle of the composition scale (Fig. 2) as was previously observed for the displacement length in the light scattering results. By contrast, the results for cyclohexane appear to deviate in the opposite fashion, although it must be admitted that a linear relation might fit the data

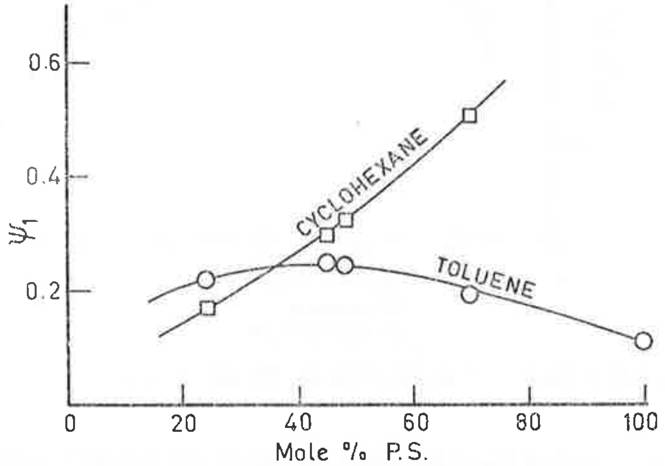

FIG. 2. The entropy of dilution parameters as a function of composition for the copolymers in toluene and cyclohexane.

just as satisfactorily. Extrapolation to pure polystyrene yields a value which does not agree with the value calculated by Flory. It would seem then that either our values of $\psi_1$ for all copolymers are consistently high or the reported value for polystyrene is incorrect. There seems no logical reason to assume a maximum at high concentration. It is interesting to note that the copolymer I.S.4, which has some random character, shows similar behaviour to the block copolymers and must therefore be considered as essentially a block copolymer with some discontinuity in sequences.

Toluene is a good solvent for both polystyrene and polyisoprene. Both sequences of the copolymer are therefore expanded; from the maximum in the plot of $\psi_1$ vs. composition, it would seem that the expansion of the molecule is even greater when the numbers of segments in the chain are equal which occurs in the middle of the composition scale. This increase in the entropy of dilution is due to the greater volume occupied by the molecule, and consequently the greater number of arrangements of the solvent molecules. We repeat that this interpretation is consistent with the increase in molecular dimensions observed previously. Cyclohexane is a poor solvent for polystyrene but a reasonably good solvent for polyisoprene. Here it is difficult to reconcile the increased dimensions of the copolymer with behaviour of the entropy parameter. It is, nevertheless, interesting to speculate on the conformation of the molecule. Since the polystyrene sequence would normally assume unperturbed dimensions in this solvent, then the opportunity for hetero-contacts is increased due to exclusion of solvent molecules from the nearest neighbour region, provided that a random chain is assumed. The additional hetero-contacts would give rise to a more expanded molecule than one in which cross contacts are absent. On the other hand, some degree of phase separation might occur within the molecule and thereby reduce the number of hetero-contacts. This could possibly give rise to a decrease in the total entropy of dilution. The latter effect would arise as a result of the exclusion of solvent from the polystyrene segments in the structure. The true conformation may consist of a combination of these two views; at this juncture, a definitive explanation must await a more detailed study.

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## REFERENCES

(1) P. J. Flory, *Principles of Polymer Chemistry*, Chap XII, Cornell University Press (1953).
(2) U. Berglund-Larsson reported in Flory's book, Chap. VII.
(3) D. N. Cramond, Thesis, University of Adelaide (1968).
(4) D. N. Cramond and J. R. Urwin, *Austral. J. Chem.* **21**, 1835 (1968).
(5) E. F. Casassa, *Polymer* **1**, 169 (1960).
(6) D. N. Cramond and J. R. Urwin, *Europ. Polym. J.* **4**, 451 (1968).
(7) W. Cooper, D. E. Eaves and G. Vaughan, *J. Polym. Sci.* **59**, 241 (1962).
(8) G. M. Burnett, P. Meares and C. Paton, *Trans. Faraday. Soc.* **58**, 737 (1962).
(9) E. F. Casassa, *Polymer* **3**, 625 (1962).
(10) J. R. Urwin and J. M. Stearne, *Makromolek. Chem.* **78**, 204 (1964).
(11) J. R. Urwin and J. M. Stearne, *Europ. Polym. J.* **1**, 227 (1965).
(12) See p. 625 of Ref. 1.

**Résumé**—A partir des données de pression osmotique obtenues pour quatre copolymères séquencés on calcule les seconds coefficients du viriel et les masses moléculaires moyennes en nombre. Les coefficients du viriel sont établis pour toute une gamme de températures dans le toluène et le cyclohexane. On en déduit les températures theta, l'entropie de dilution, la chaleur de dilution et les paramètres d'interaction solvant–soluté. On discute les résultats.

**Sommario**—Dati osmotici di pressione, ottenuti da uno studio di quattro copolimeri a blocchi, sono stati usati per calcolare secondi coefficienti del viriale e il numero medio dei pesi molecolari. I coefficienti del viriale sono stati determinati sul campo delle temperature in toluene e cicloesano. Sono state derivate le temperature teta, l'entropia di diluizione, il calore di diluizione e i parametri di interazione solvente–soluto, edè stato discusso il loro comportamento.

**Zusammenfassung**—Die Daten des osmotischen Drucks, die bei der Untersuchung von vier Block-Copolymeren erhalten wurden, wurden zur Berechnung der zweiten Virialkoeffizienten und des Zahlenmittelwerts der Molekulargewichte herangezogen. Die Viralkoeffizienten wurden über einen Temperaturbereich in Toluol und Cyclohexan bestimmt. Die Theta-Temperaturen, Verdünnungsentropie, Verdünnungswärme und die Parameter der Wechselwirkung zwischen Lösungsmittel und gelöster Substanz wurden abgeleitet und ihr Verhalten diskutiert.

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**AUSTRALIAN JOURNAL OF CHEMISTRY**

# INTERACTIONS IN BLOCK COPOLYMERS IN SOLUTION: THE EFFECT OF HETERO-CONTACTS ON THE SEGMENTAL INTERACTIONS IN BLOCK COPOLYMERS OF POLY(ISOPRENE : STYRENE) IN SOLUTION

By J. R. URWIN*

[Manuscript received January 17, 1969]

## *Summary*

Binary cluster integrals or excluded volumes for chemically different segment pairs in block copolymers of poly(isoprene : styrene) have been calculated from the equation derived by Froelich and Benoit for a two-sequence block copolymer. Expansion factors have been recalculated assuming a linear relation for $[\eta]_\theta$ with respect to composition employing published values for polystyrene and polyisoprene. The results are discussed in relation to possible conformations of block copolymers.

## INTRODUCTION

The phenomenon of phase separation in a three-component system containing two polymer species in a common solvent has been known for many years.[1] The thermodynamics of such systems is also well understood[2] and has been studied in a number of systems. It is argued that the two polymers in the ternary system avoid overlap partly by shrinkage of the individual molecular coil and partly by a tendency to segregation. The state of minimum free energy results from the interplay between the loss of entropy due to both the shrinkage and segregation and the lower energy thus made possible.[3] It has been proposed that an analogous situation occurs in block copolymers in solution giving rise to *intramolecular* phase separation.[4] However, the experimental evidence for this phenomenon is difficult to adduce in an unambiguous manner.[5] The reason seems to be, in part, due to the necessity to employ theories and concepts developed for homopolymers which on extrapolation to copolymers are no longer completely valid. One may quote, as example, the weight average molecular weight which, when obtained in the usual manner from light-scattering data, yields only an apparent value in the case of copolymers. The radius of gyration determined by the same technique also yields an apparent value, but the molecular weight may be evaluated, at least in principle, from determinations in

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[1] Dobry, A., and Boyer-Kawenoki, F., *J. Polym. Sci.*, 1947, **2**, 90.

[2] Flory, P. J., "Principles of Polymer Chemistry." (Cornell University Press: Ithaca, N.Y., 1953.)

[3] Allen, G., Gee, G., and Nicholson, J. P., *Polymer*, 1960, **1**, 56.

[4] Burnett, G. M., Meares, P., and Paton, C., *Trans. Faraday Soc.*, 1962, **58**, 737.

[5] Dondos, A., Rempp, P., and Benoit, H., *Eur. Polym. J.*, 1967, **3**, 657.

*Aust. J. Chem.*, 1969, **22**, 1649–54

three solvents with different refractive indices, whereas for the radius of gyration to be determined unambiguously requires measurements in solvents in which the volume effect is the same.[6] This is very difficult, if not impossible, to achieve.

Such concepts as the unperturbed configuration of a molecule are inapplicable to block or graft copolymers except for a particular solvent where the $\theta$ point of each block coincides. One can, in general, only determine a particular temperature at which the second virial coefficient, which is a function of the interactions of both blocks in the copolymer, is reduced to zero. At this point, in the case of a two-sequence block copolymer, one sequence is slightly more expanded than unperturbed and the other less expanded, the contributions to the virial coefficient cancelling.

In recent years, interest has increased in the extent to which hetero-contacts, that is contacts between different kinds of segments occurring in the copolymer molecule, contribute towards the overall dimensions. These studies are of particular importance, since it is from such information that one may reasonably expect to deduce the molecular conformation.

## THEORY

The effect of repulsive long-range interactions in terms of the excluded volume was employed by Inagaki[7] to explain the increased dimensions of block copolymers which were observed to occur in the middle of the composition scale. The binary cluster integral, which may be interpreted as the excluded volume for a pair of segments, must contain contributions from contacts between like segments and also between different segments. The probability of contact may be evaluated, in the simple picture, according to the number of each kind of segments present. For a polymer comprised of two sequences the resulting formula is just:

$$\bar{\beta} = x^2\beta_{11}+(1-x)^2\beta_{22}+2x(1-x)\beta_{12} \tag{1}$$

where $x$ is the mole fraction and $\beta_{11}$, $\beta_{22}$, and $\beta_{12}$ are the cluster integrals for pure polymer 1 and 2 and the hetero-contacts between different segments respectively.

Froelich and Benoit[8] have examined this problem in greater detail and have shown that equation (1) only applies to random copolymers where the probability of contact is directly proportional to the numbers of segments. In the case of block copolymers, the theory must take account of the relative position of segments on each chain in the calculation. The expansion factor $\alpha$, defined by the ratio of the radius of gyration in the solvent to the unperturbed value $\alpha = (\bar{s}^2/\bar{s}_0^{\,2})^{\frac{1}{2}}$, was calculated assuming a Gaussian distribution of segments about the centre of gravity and assuming that the value of $\alpha$ is approaching unity. For a homopolymer with the above restrictions the expansion factor is given by

$$\alpha^2 = 1+(134/105)z \tag{2}$$

or

$$\alpha^2 = 1+(134/105)[(3/2)\pi]^{3/2}\beta a^{-3}n^{\frac{1}{2}} \tag{3}$$

where $a$ is the unperturbed effective segmental length, $n$ the number of segments, and $\beta$ the cluster integral assuming that only binary contacts are significant. The

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[6] Benoit, H., *Ber. Bunsenges. phys. Chem.*, 1966, **70**, 286.

[7] Inagaki, H., *Makromolek. Chem.*, 1965, **86**, 289.

[8] Froelich, D., and Benoit, H., *Makromolek. Chem.*, 1966, **92**, 224.

method of calculation employed by these authors is that due to Fixman.[9] The mean square distance between two links in the chain is given by

$$\langle L_{ij}{}^2\rangle = \langle L_{ij}{}^2\rangle_0 + [(3/2)\pi]^{3/2} a^{-3} n^{\frac{1}{2}} \sum_k \sum_l C_2{}^2/C_1{}^{5/2}\beta_{kl} + \dots \tag{4}$$

where $\langle L_{ij}{}^2\rangle_0$ is the mean square distance in the absence of any volume effect. The derivation of this equation involves, firstly, calculation of the probability that the links $i$ and $j$ are at a distance $L_{ij}$, secondly the probability that segments $k$ and $l$ are in the same volume element, and finally the probability that these events occur simultaneously. The excluded volume for a pair of segments becomes, in the case of a two-sequence block copolymer, three separate parameters $\beta_{11}$, $\beta_{22}$, and $\beta_{12}$ representing interactions between similar and different segments respectively. The quantities $C_1$ and $C_2$ are just the number of links which comprise the sequence between $k$ and $l$ and the number of segments common to the sequences comprised between $k$ and $l$ of one part and $i$ and $j$ of the other part. It is necessary to consider three cases: ($a$) when $i$ and $j$ are on the first sequence of the block, ($b$) when $i$ is found on one sequence and $j$ on the other, and ($c$) when $i$ and $j$ are both on the second sequence. Replacing summations with integrals and using the usual relation for the radius of gyration

$$\langle s^2\rangle = (1/2)n^2 \sum_i \sum_j \langle L_{ij}{}^2\rangle \tag{5}$$

the final expression becomes:

$$\alpha^2 = \frac{\langle \bar{s}_0{}^2\rangle}{\langle \bar{s}^2\rangle} = 1 + [(3/2)\pi]^{3/2} a^{-3} n^{\frac{1}{2}} \left[\beta_{11}\frac{x^{5/2}}{105}(392-258x) + \beta_{22}\frac{(1-x)^{5/2}}{105}(258x+134) \right.$$
$$\left. + \beta_{12}\left\{\frac{134}{105} - \frac{x^{5/2}}{105}(392-258x) - \frac{(1-x)^{5/2}}{105}(258x+134)\right\}\right] \tag{6}$$

Thus, if values for $\beta_{11}$ and $\beta_{22}$ are known the value of $\beta_{12}$ for hetero-contacts may be determined directly from the expansion factors.

Cramond and Urwin[10] have recently examined a series of four block copolymers of poly(isoprene : styrene) and determined values for the expansion factor calculated by employing the equation of Orofino and Flory[11] for the second virial coefficient. In this expression values of $A_2$, $[\eta]$, $\overline{M}_{\mathrm{w}}$ are substituted into the equation to yield values of $\alpha$. This is somewhat cumbersome and includes rather large errors in the three individual parameters. Some simplification is achieved by adopting the procedure whereby $\alpha$ is calculated from

$$\alpha^3 = [\eta]/[\eta]_\theta \tag{7}$$

provided $[\eta]_\theta$ is known or can be calculated from reliable published data. The limiting viscosity number at the theta point may be computed by assuming the relation

$$[\eta]_\theta = [x[\eta]_\theta{}^1 + (1-x)[\eta]_\theta{}^2] \tag{8}$$

a relation which implies that the magnitude of interactions in a solvent in which $A_2 = 0$ is negligible or that the interactions from each sequence, although still

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[9] Fixman, M., *J. chem. Phys.*, 1955, **23**, 1656.

[10] Cramond, D. N., and Urwin, J. R., *Eur. Polym. J.*, in press.

[11] Orofino, T. A., and Flory, P. J., *J. chem. Phys.*, 1957, **26**, 1067.

significant, are equal and opposite in sign. Values for $[\eta]_\theta$ may be obtained for polystyrene in cyclohexane at 34° and natural rubber in n-propyl ketone at 14·5°[12] which on substitution into the simple relation

$$[\eta]_\theta = KM^{\frac{1}{2}} \tag{9}$$

yields values for $[\eta]_\theta$ for homopolymers 1 and 2. It has been shown experimentally[10] that equation (8) is obeyed, at least to a reasonable approximation, for this system. Thus this method of arriving at $\alpha$ eliminates one parameter with its concomitant error from the calculation. Unfortunately, lack of polymer prevented any actual measurements in theta solvents for this system making it necessary to resort to this kind of calculation.

## RESULTS

In Table 1 are listed values for $[\eta]_\theta$ calculated from equation (8), $[\eta]$ at 30° in three solvents, toluene, cyclohexane, and isobutyl methyl ketone, and the values of $\alpha$ computed from equation (7) for the four polymers. The first three copolymers listed are block copolymers which were prepared, as previously described, in all-glass, all-break-seal apparatus to ensure narrow distributions of composition and molecular weight.[13] The fourth polymer, IS4, was prepared by polymerizing a mixture of monomers with butyllithium in benzene. This polymer appears to be essentially a block copolymer with some shorter sequences in the middle of the chain.

TABLE 1

DATA FOR THE POLYMERS IS1–4

The expansion factors $\alpha$, limiting viscosity number $[\eta]$ in the solvents toluene, cyclohexane, and isobutyl methyl ketone (IMK) at 30°, and $[\eta]_\theta$ calculated from equation (8)

| Polymer | $10^{-5}\bar{M}_W$ | $\alpha$* | | | $[\eta]_\theta$ | $[\eta]$ | | |
|---|---|---|---|---|---|---|---|---|
| | | Tol. | Cyc. | IMK | | Tol. | Cyc. | IMK |
| IS1 | 2·56 | 1·42 (1·42) | 1·36 (1·39) | 1·08 (1·15) | 55·7 | 161·1 | 141·0 | 69·5 |
| IS2 | 2·21 | 1·43 (1·42) | 1·32 (1·32) | 1·08 (1·13) | 47·6 | 140·3 | 112·5 | 59·9 |
| IS3 | 2·59 | 1·39 (1·44) | 1·22 (1·31) | 1·08 (1·20) | 47·4 | 126·8 | 86·3 | 60·2 |
| IS4 | 3·70 | 1·43 (1·46) | 1·33 (1·36) | 1·16 (1·20) | 62·3 | 183·0 | 145·7 | 97·0 |

* Values in brackets were calculated from the relation of Orofino and Flory.[11]

Only minor differences were found between the values of $\alpha$ calculated from the Orofino–Flory equation and those determined according to equation (7). For all solvents the greatest difference occurred with IS3, that is the block containing the highest percentage of polystyrene. It should be noted that $\alpha$ remains constant in toluene, a good solvent for both polymers, and in isobutyl methyl ketone, a poor solvent for both, but decreases in cyclohexane with increasing styrene content. Cyclohexane is a $\theta$ solvent for polystyrene at 34° but is a good solvent for polyisoprene.

The excluded volume for chemically different pairs of segments has been calculated from equation (6) by substituting the values of $\alpha$ and the appropriate

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[12] Polymer Handbook. (Eds. J. Brandrup and E. A. Immergut.) (Interscience: New York 1966.)

[13] Cramond, D. N., and Urwin, J. R., *Aust. J. Chem.*, 1968, **21**, 1835.

mole fractions for the several block copolymers. The results are shown in Table 2 along with the values of the cluster integrals for the homopolymers calculated from data on samples of polystyrene and polyisoprene.[14]

TABLE 2

BINARY CLUSTER INTEGRALS (Å$^3$) DUE TO HETERO-CONTACTS FOR THE BLOCK COPOLYMERS IN TOLUENE, CYCLOHEXANE, AND ISOBUTYL METHYL KETONE

| Polymer | Toluene | | Cyclohexane | | Isobutyl Methyl Ketone | |
|---|---|---|---|---|---|---|
| | $\beta$ | $\beta_{12}$ | $\beta$ | $\beta_{12}$ | $\beta$ | $\beta_{12}$ |
| PS | 1·41 | | 1·68 | | 0·034 | |
| IS1 | | 2·65 | | 2·81 | | 0·44 |
| IS2 | | 4·84 | | 9·54 | | 1·76 |
| IS3 | | 2·21 | | 8·10 | | 1·62 |
| IS4 | | 1·00 | | 6·32 | | 3·03 |
| PI | 4·20 | | 0 | | 0·29 | |

## DISCUSSION

Expansion factors calculated by the two methods are in good agreement in toluene and agreement is also satisfactory for all except IS3 in cyclohexane and isobutyl methyl ketone. In view of the rather large errors involved in the calculation, even the latter values might be considered reasonable. Nevertheless, the method using the ratio $\alpha^3 = [\eta]/[\eta]_\theta$ is probably the more reliable. The binary cluster integrals calculated from this data show a general trend in that there is a maximum value at about the middle of the composition scale rather than a constant value which might have been expected. Curiously, the greatest value occurs in cyclohexane in which at 30° polystyrene shrinks below unperturbed dimensions. It is of interest to compare the values of $\beta$ for the homopolymers with those for hetero-contacts. In the case of toluene all values are of the same order but for the other solvents values for hetero-contacts are larger; in isobutyl methyl ketone by a factor of 10.

Before attempting an explanation of these results it might be appropriate to examine the extreme conformations that can be imagined for these copolymers. In Figure 1 two-dimensional diagrams [(*A*)–(*D*)] have been drawn to represent the several possible conformations based on intramolecular phase separation on the one hand and a random coil on the other. Diagram (*A*) represents two separate coils joined by an umbilical cord at the point where the two sequences meet. Diagram (*B*) represents a model in which phase separation is complete, but where some interpenetration can occur in the boundary region. Diagrams (*C*) and (*D*) represent random coils in a good solvent and poor solvent respectively. Insets show the situation enlarged in (*C*) and (*D*). Diagram (*A*) seems an unlikely possibility in that the average dimensions of the molecules measured experimentally would then be smaller than those of either parent homopolymer of similar molecular weight. This was not found to be the case from data already published on molecular dimensions of these

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[14] Cramond, D. N., Ph.D. Thesis, Adelaide, 1968.

polymers. Diagram ($C$) may be representative of the situation in a solvent such as toluene if the random coil structure prevails. Diagram ($D$) is possibly representative of the situation in the other two solvents, again assuming the random structure. It seems then that the choice lies within the two extreme models depicted in ($B$) and ($C$) or ($D$).

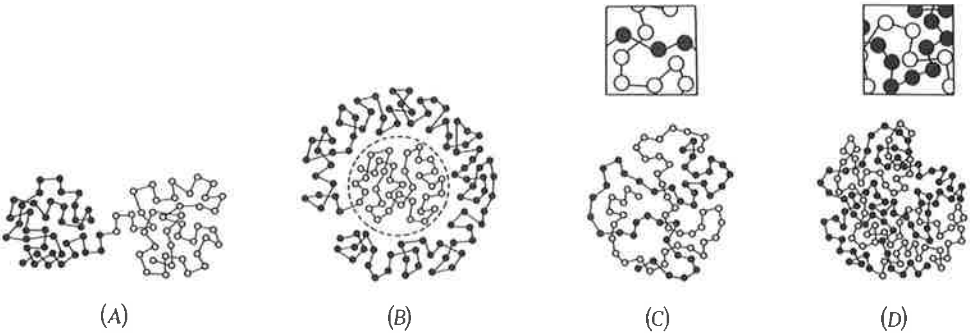

Fig. 1

One should proceed with caution in attempting to interpret these results in relation to possible conformations, since in the first place, the theory given above is applicable only when $\alpha$ is approaching unity, a condition only satisfied by isobutyl methyl ketone. Secondly, if intramolecular phase separation takes place, even to some degree, the condition of Gaussian distribution demanded by the theory is not satisfied. Nevertheless, one is tempted to speculate to the extent that the larger values of $\beta_{12}$ in cyclohexane and isobutyl methyl ketone may be due, at least in part, to clusters of higher order, which have been ignored in the derivation of equation (6). This would be expected if the random coil structure as shown in ($D$) prevails giving rise to an increase in the excluded volume due to the greater repulsions. The effect of polymer segments replacing solvent due to theta or near theta conditions in these solvents, for polyisoprene in one case and polystyrene in the other, may also affect the magnitude of the cluster integral which is known to depend intimately on the medium surrounding the cluster. It is all too tempting to argue on this basis that the model of diagram ($B$) is ruled out since the number of contacts between chemically different segments is reduced to negligible proportions by the complete separation. However, even some interpenetration at the boundary between the two phases may give rise to increased excluded volume if the magnitude of the repulsions between hetero-contacts is large. Obviously, a different approach is required to determine the magnitude of these repulsions.

It is to be hoped that a more detailed study using a wider range of polymer compositions and in a wider range of solvents will supplement this meagre information to give further insight into the problem. Studies to this effect are already under way in this laboratory. It is important to realize that it is only by this kind of enquiry that one will ultimately be able to assign structures to these molecules in solution. Obviously, the extent of intramolecular phase separation, if it occurs in this particular system, cannot be stated unequivocally at this stage.

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# THE SPECIFIC REFRACTIVE INDEX INCREMENTS OF POLYISOPRENES IN VARIOUS SOLVENTS

By P. J. Reed* and J. R. Urwin*

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*Abstract*

Specific refractive index increments of polyisoprenes with high *cis*-1,4 content have been determined in six solvents at 20° and $\lambda$ 546 nm. A linear relationship was found between the refractive index increment $dn/dc = \tilde{n}$ and the refractive index of the solvent $n_1$:

$$\tilde{n}_{546}{}^{20} = 1\cdot687-1\cdot105n_1$$

The results are compared with the best values reported for natural rubber which are usually employed for polyisoprene in light scattering measurements.

## Introduction

The specific refractive index increments of natural rubber have been determined in a number of solvents[1,2] but those of synthetic polyisoprenes appear not to have been studied. Since the refractive index increment $\tilde{n}$ appears as a squared term in the light scattering equation, accurate values of $\tilde{n}$ for synthetic polyisoprenes are an essential prerequisite to the determination of the weight average moleculear weight ($\overline{M}_{\mathrm{w}}$).

To obtain accurate values of $\tilde{n}$ requires the use of an accurate differential refractometer. The high cost of such an instrument, together with the fact that the determination of $\tilde{n}$ in different solvents is time-consuming, has possibly deterred differential refractometry studies in many laboratories. However, since $\tilde{n}$ depends directly upon the refractive index of the solvent $n_1$, an accurate determination of the relationship means that $\tilde{n}$ may then be calculated from it provided the value of $n_1$ is known.

The specific refractive index increment $\tilde{n}$ is obtained as the slope of the plot of the refractive index difference between solution $n$ and solvent, i.e. $(n-n_1)$ against $c$ at concentrations below $0\cdot03$ g/ml. At higher concentrations however, the relation is no longer linear and assumes a parabolic form.

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[1] Huglin, M. B., *J. appl. Polym. Sci.*, 1965, **9**, 3963.

[2] Brandrup, J., and Immergut, E. H., (Eds.) "Polymer Handbook." (Interscience: New York 1966.)

*Aust. J. Chem.*, 1970, **23**, 1743–7

It can readily be shown that $\tilde{n}$ depends on $n_1$ and $n_2$, the refractive indices of solvent and polymer respectively, and $d_2$ the density of the polymer, according to

$$\tilde{n} = n_2/d_2 - (1/d_2)n_1 \tag{1}$$

A plot of $\tilde{n}$ against $n_1$ is therefore linear with a negative slope. Once the relationship is established $\tilde{n}$ may be read off for any particular $n_1$. From the same plot, the refractive index of the polymer ($n_2$) may be obtained from the intercept ($n_2/d_2$); however, this requires a rather extended extrapolation with its attendant inaccuracy and it is therefore preferable to determine the intercept at $\tilde{n} = 0$ where $n_1 = n_2$.

Evidence for the dependence of $\tilde{n}$ on molecular weight has been adduced for certain polymers[3] and the possible dependence of $\tilde{n}$ on molecular weight must therefore be investigated as a routine measure. This was done in this study with four of the samples.

Huglin[1] finds that the Gladstone–Dale rule applies rigorously to pure and mixed solvents, but that the Lorenz–Lorentz expression is preferred for calculation of $n_2$; even so, there is still some loss of accuracy when the calculated value is compared with the experimental determination of $\tilde{n}$. This author reports that the Gladstone–Dale rule, which has the form

$$\tilde{n} = \bar{v}_2(n_2 - n_1) \tag{2}$$

for the binary mixture and where $\bar{v}_2$ is the partial specific volume of the polymer, may be employed to calculate $n_2$, values of which are found to vary in the second decimal place. The more soundly based Lorenz–Lorentz equation[1]

$$(n^2-1)/(n^2+2) = (c/d_2)(n_2^2-1)/(\bar{n}_2^2+2)+(1-c/d_2)(n_1^2-1)/(n_1^2+2) \tag{3}$$

has been shown to yield values which vary in the third decimal place. Part of the error in the Gladstone–Dale method stems from the common use of the reciprocal density in place of the partial specific volume which depends, to some extent, on the nature of the solvent. Both calculations of $n_2$ used to compute $\tilde{n}$ give results which sacrifice accuracy to some extent when compared with the experimental determination of $\tilde{n}$.

## EXPERIMENTAL

### *The Polymers*

Polyisoprenes were prepared anionically, initiated by butyllithium in the solvent benzene. The polymers were synthesized using high-vacuum techniques including all-glass reaction vessels as has been previously described in some detail.[4] G.p.c. measurements demonstrated that they were all of narrow molecular-weight distribution and the polyisoprenes showed high *cis*-1,4 content (73–80%) as determined by n.m.r. Actually, polymers made by using butyllithium prepared from laboratory-grade lithium (purity 98%) were found to have a *cis*-1,4 content of 73–74% but with the use of 99·8% lithium as supplied by Koch–Light the synthesis gave a much improved yield of the *cis*-isomer (79–80%). $\overline{M}_N$ was evaluated by osmometry with a Hewlett–Packard high speed membrane type osmometer.

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[3] Barrall, E. M., Cantow, M. J. R., and Johnson, J. F., *J. appl. Sci.*, 1968, **12**, 1373.

[4] Cramond, D. N., and Urwin, J. R., *Aust. J. Chem.*, 1968, **21**, 1835.

### *Solvents*

AnalaR-grade solvents were employed throughout. After drying over $CaH_2$ for 24 hr all solvents were fractionated immediately prior to use. Refractive index measurements agreed with literature values.

### *Differential Refractometer*

The refractometer was a Brice–Phoenix laboratory type differential refractometer suitable for values of $n$ up to 1·62. A limiting sensitivity of 3 units in the sixth decimal place is claimed for this instrument by the manufacturers, and confirmed by us experimentally. Measurements were all made in an air-conditioned room maintained at a steady 20°.

### *Calibration*

The cell constant $k = \Delta n/\Delta d$, i.e. variation in $n$ per mm deflection, was evaluated from five solutions of potassium chloride made up in doubly distilled water and using the least squares plot of the highly accurate results of Kruis[5] at $\lambda$ 546 nm. All calibration solutions were prepared from carefully dried A.R. KCl by weighings. The concentrations ranged from 0·9 g/100 g $H_2O$ to 2·8 g/100 g $H_2O$. A series of 10 consecutive readings were taken separately by each of two experimenters and the results averaged. The average in $\Delta d$ between the two experimenters always agreed within 0·1–0·2%.

### *Measurements on Polymer Solutions*

Concentrations of 1% to 2% were used depending on the value of $\Delta d$. Generally, the solutions were allowed to stand for 1–2 weeks to ensure complete solution and the solutions then made up to the mark in A-grade volumetric flasks in the air-conditioned room at 20°. Readings were always made in duplicate solutions to check the homogeneity. Concentrations were then expressed in g/ml at 20°.

## RESULTS

A series of four polyisoprenes with number average molecular weights $\overline{M}_N$ of 28000, 52000, 116000, and 220000 were examined in six solvents with a range of refractive indices from 1·375–1·557. The two lower molecular weight samples were synthesized using butyllithium prepared from ordinary laboratory-grade lithium (98%) whereas the higher molecular weight samples were synthesized with butyllithium from the high purity lithium (99·8%). There was no discernible difference in $\tilde{n}$ between the two species in any of the solvents. All four polymers were examined in n-hexane, methyl isobutyl ketone, cyclohexane, and toluene for evidence of molecular weight dependence of $\tilde{n}$ but, again, no significant difference was observed.

TABLE 1

SPECIFIC REFRACTIVE INDEX INCREMENT FOR POLYISOPRENES IN VARIOUS SOLVENTS, $\tilde{n}_{546}{}^{20}$ AT 20° AND 546 nm

| Solvent | $n_D{}^{20}$ | $\tilde{n}_{546}{}^{20}$ (av.) | Solvent | $n_D{}^{20}$ | $\tilde{n}_{546}{}^{20}$ (av.) |
|---|---|---|---|---|---|
| *n*-Hexane | 1·372 | 0·168±0·001 | toluene | 1·494 | 0·028±0·002 |
| Methyl isobutyl ketone | 1·394 | 0·139±0·002 | *o*-chlorotoluene | 1·524 | −0·003 |
| Cyclohexane | 1·424 | 0·104±0·001 | bromobenzene | 1·557 | −0·041 |

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[5] Kruis, A., *Z. phys. Chem.* (*B*), 1936, **34**, 13.

Values of the specific refractive index increment at 20° and 546 nm ($\tilde{n}_{546}{}^{20}$) obtained in the six solvents are shown in Table 1. The first four results are averaged values of the four polymers and the deviations are given in the last column. The value of $\tilde{n}_{546}{}^{20}$ in *o*-chlorotoluene is included although its magnitude is very small and must therefore contain a fairly large error. The refractive index is almost the same as $n_2$ for polyisoprene. One single value for the solvent bromobenzene was obtained with the polymer $\overline{M}_{\mathrm{N}} = 28000$.

A plot of $\tilde{n}_{546}{}^{20}$ against the refractive index of the solvent $n_1$ is shown in Figure 1 along with a similar plot of the most reliable data for natural rubber taken from values reported in refs.[1,2] A linear plot with a common point at $\tilde{n}_{546}{}^{20} = 0$ was obtained for both the natural rubber and synthetic polyisoprene but different slopes were obtained in each case.

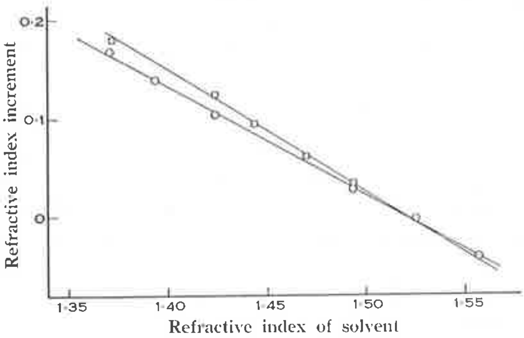

Fig. 1.—Specific refractive index increments at 20° (λ 546 nm) against the refractive index of the solvent for the polyisoprenes in various solvents (see text).
○ Polyisoprenes;
☐ natural rubber.[1,2]
The solid lines represent equation (1).

## Discussion

The difference in the specific refractive index increment for natural rubber and polyisoprene becomes particularly obvious with increasing $\tilde{n}_{546}{}^{20}$. In the solvent n-hexane the difference is about 0·02 refractive index units, that is almost 12% larger than in the case of natural rubber. The error in molecular weight due to assuming that published values of $\tilde{n}_{546}{}^{20}$ for rubber are equivalent to polyisoprene is therefore about 24%.

From the intercept at $\tilde{n} = 0$ we find $n_2 = 1{\cdot}520$ for the polyisoprene; the same value is found for natural rubber. The density may then be found from the slope of the lines through the experimental points; $d_2$ for polyisoprene is 0·91 and equation (1) becomes

$$\tilde{n}_{546}{}^{20} = 1{\cdot}687 - 1{\cdot}105 n_1$$

Thus the value of $\tilde{n}$ in any solvent is readily computed if $n_1$ is known, or can be measured. The density determined by equation (1) agreed well with the value for natural rubber quoted in the Polymer Handbook,[2] $d_2 = 0{\cdot}913$ g/ml. (Values range from 0·906 to 0·916.) This is in contrast to $d_2 = 0{\cdot}80$ calculated for natural rubber from the slope of the line through the reported values. An error in $\tilde{n}$ of about 1% may be expected due to the use of partial specific volumes in equation (1) but the reason for the large deviation between the experimental and calculated $d_2$ is obscure.

The *maximum* error in $\tilde{n}_{546}{}^{20}$ is certainly not greater than 1% in the present work with the error in determining the deflection $\Delta d$ making the maximum contribution to the total error (the maximum deviation from linearity in equation (1) was 0·6%). Use of somewhat higher concentrations, so as to achieve a greater deflection in the instrument, would improve the accuracy but the value of $\tilde{n}_{546}{}^{20}$ calculated from equation (1) is probably satisfactory for the molecular weight determinations of homopolymers such as polyisoprenes etc.

Values of $\tilde{n}_{546}{}^{20}$ for several block copolymers of polyisoprene+polystyrene of varying composition were measured and the linear dependence on composition in terms of the $\tilde{n}$ for the homopolymers was demonstrated. However, the error in the calculated and the experimental value of the refractive index increment was far too large for use with the light scattering relation used for copolymers.[6,7] More accurate determinations of $\tilde{n}$ have been achieved for certain polymers (within 0·1%) by using more refined techniques.[8] The conventional methods, using common laboratory equipment, such as that used in this study, cannot hope to achieve $\tilde{n}$ to better than 0·5% even with the greatest attention to detail, and then only in the range of $\tilde{n} > 0{\cdot}1$. For molecular weight determinations of binary copolymers such as random, graft, and block copolymers, an accuracy in $\tilde{n}$ of 0·1% *at least* is essential in order to obtain values of $\overline{M}_{\mathrm{w}}$ with an accuracy comparable to that achieved for homopolymers.

## ACKNOWLEDGMENTS

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[6] Bushuk, W., and Benoit, H., *Can. J. Chem.*, 1958, **36**, 1616.

[7] Krause, S., *J. phys. Chem.*, 1961, **65**, 1618.

[8] Norberg, P. N., and Sundelöf, L. O., *Makromolek. Chem.*, 1964, **77**, 77.

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# Light Scattering Parameters of Block Copolymers by Application of Computer Programming

by

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# Light Scattering Parameters of Block Copolymers by Application of Computer Programming

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(Eingegangen am 3. August 1970)

SUMMARY:

A computer program has been adapted for use with the Sofica Light Scattering Photometer and extended for application to block copolymer studies. In the first part of the program, which is equally suitable for homopolymers and copolymers alike, the apparent molecular weight, $M_{app}$, radius of gyration $\langle S^2\rangle^{1/2}$, and the virial coefficients $A_2$, $A_3$ are obtained in individual solvents. In the second part, $\overline{M}_w$ and the parameters characterizing the heterogeneity in composition of the copolymer are calculated. This is achieved by solving three simultaneous equations from all combinations of experiments in six or more solvents with different refractive index increments. The first stage has been tested using data from a sample of polystyrene. The complete program has been applied to data originally treated by the usual graphical methods. Finally, the parameters derived by the two techniques are compared and discussed.

ZUSAMMENFASSUNG:

Für den Gebrauch des Sofica-Streulichtphotometers wurde ein Computer-Programm aufgestellt und zum Studium der Blockcpolymeren eingesetzt. Im ersten Teil des Programms, das gleichermaßen für Homopolymere und ähnliche Copolymere geeignet ist, werden das scheinbare Molekulargewicht $M_{app}$, der Trägheitsradius $\langle S^2\rangle^{1/2}$ und die Virialkoeffizienten $A_2$ und $A_3$ im jeweiligen Lösungsmittel erhalten. Im zweiten Teil werden $M_w$ und die Parameter berechnet, die die Heterogenität der Zusammensetzung des Copolymeren charakterisieren. Dieses wird durch die Lösung von drei Simultangleichungen erreicht, und zwar auf der Grundlage aller Kombinationen von Experimenten in sechs oder mehr Lösungsmitteln mit verschiedenen Brechungsindex-Inkrementen. Die erste Stufe wurde an Hand der Daten für eine Polystyrolprobe überprüft. Das vollständige Rechenprogramm wurde auf die Daten angewendet, die ursprünglich nach den üblichen graphischen Methoden behandelt wurden. Am Schluß werden dann die Parameter, die sich aus den beiden Bearbeitungsmethoden herleiten, verglichen und diskutiert.

## *Introduction*

Computer techniques are beginning to play a more important role in polymer studies, particularly in those areas amenable to treatment by statistical methods[1]. Recently, a program for the manipulation of light scattering data was published[2] for use with the instrument manufactured by BRICE-PHOENIX. We have adapted and extended the program for use with the Sofica Light Scattering Photometer, a commercial instrument which is widely used. The program was written in ALGOL, originally for use with the English Electric KDF9 computer, but has been adapted for operation with the CDC 6400 computer at the University of Adelaide with the aid of the ALGOL compiler. The program has been extended by writing a second part in FORTRAN IV to allow it to be applied to copolymers. In the second stage $\overline{M}_W$ is calculated by solving three simultaneous equations 3), although it is recommended that results should be averaged from all combinations of data obtained in up to six solvents 4). The heterogeneity parameters P and Q, which characterize the heterogeneity in composition, are also calculated.

Unfortunately light scattering is still not a routine operation. Considerable care is required in setting up the instrument, the calibration procedure and in the general operation. In this respect, the programmed technique offers a valuable additional check on the progress of the experiments in that the differences between experimental values and values derived by the method of least squares at individual angles and concentrations are printed out for inspection. Isolated values which show large deviations may be discarded and the same solutions remeasured. The rapidity of processing the data makes this entirely feasible. The improvement in the overall accuracy, which should result, is very encouraging and particularly so in the case of block copolymers where the weight-average molecular weight can be obtained only from measurements in a series of solvents. This procedure normally makes the cumulative error for copolymers much larger than is the case with homopolymers which require measurements in a single solvent only. The most important factor in the statistical method of treating the data is that it eliminates the personal bias involved in fitting experimental points graphically. With good experimental data the accuracy of the method should depend almost entirely on the independent determination of the refractive index increment.

In this study we recalibrated the apparatus and checked the first stage of the program by processing data obtained on a sample of polystyrene in toluene. Particular attention was paid to reproducibility of galvanometer readings at individual angles and concentrations. The complete program was then used to recalculate the light scattering parameters from data treated originally by the more usual graphical methods with the object of improving the accuracy of the parameters and to check the amount of scatter in the results. This data, which was from a recent study of block copolymers 5) of poly(isoprene/styrene), was considered to be of acceptable accuracy except for two experiments in a single solvent where the deviations were as high as 20 % in some values. One set of data had to be discarded and the original determination of $\overline{M}_w$ for this particular polymer may be considered questionable. The parameters derived by both techniques for the remaining polymers are compared and discussed.

## *The Light Scattering Equation*

The Rayleigh ratio $R_\Theta$ is determined for eleven preselected angles from 30–150° and at five concentrations from measurements of the galvanometer deflections for solution ($G_{\Theta\ \mathrm{soln.}}$) and solvent ($G_{\Theta\ \mathrm{solv.}}$). The slit width on the Sofica is set for some arbitrary value of the galvanometer deflection for pure benzene at 90° ($G_{90\ \mathrm{benz}}$) or, alternatively, using a glass scatterer, where the ratio between glass and benzene has been previously determined, the slit width is set at an arbitrary setting of the glass[6]. The Rayleigh ratio is then given by

$$R_\Theta = WYZR_{\Theta\ \mathrm{benz}}$$

where

$$W = 1/G_{q0\ \mathrm{benz}}$$

$$Y = \sin\Theta/(1 + \cos^2\Theta)$$

$$Z = (G_{\Theta\ \mathrm{soln.}} - G_{\Theta\ \mathrm{solv.}})$$

in which $\sin\Theta$ corrects for the volume change on viewing the solution at different angles and $(1 + \cos^2\Theta)$ corrects for the state of polarization of the scattered light. We obtain then a series of values of $K'c/R_\Theta$ where

$$K' = \nu^2 2\pi^2/\lambda^4 N_A R_{90\ \mathrm{benz}}$$

$\nu^2$ is the specific refractive index increment and $R_{q0\ \mathrm{benz}}$ is obtained from published values at the same wave length as used experimentally; c is the concentration in g/ml. It should be noted that $n_0^2$, the refractive index of the solvent which usually appears in this equation, is eliminated by the refraction correction[6].

The dependence of $K'c/R_\Theta$ on concentration and angle is given by

$$\lim_{\Theta=0} (K'c/R_\Theta) = \overline{M}_w^{-1} + 2A_2c + 3A_3c^2$$

and

$$\lim_{c=0} (K'c/R_\Theta) = \overline{M}_w^{-1}P(\Theta)^{-1}$$

in which the particle scattering factor $P(\Theta)$ is given by[7]

$$P(\Theta)^{-1} = 1 + u/3$$

and

$$u = 16\pi^2 n_1^2 \lambda^{-2}\langle S^2\rangle \sin^2\Theta/2$$

Combining these relations yields the equation

$$c/R_\Theta = (W/K')\,\overline{M}_w^{-1}\,[1 + (16/3)\pi^2 n_1^2\,\lambda^{-2}\langle S^2\rangle \sin^2\Theta/2] + (W/K')\,2A_2c + (W/K')\,3A_3c^2$$

## *The Program*

The treatment employed in the program is to write $X_{ij}$ for $c/R_\Theta$ at $\Theta_i$ and $c_j$. The function X which fits the values of $X_{ij}$ in the form

$$X = l + mx_i + nc_j + bc_j^2$$

where

$$x_i = \sin^2\Theta/2$$

is then found by the method of least squares.

Once the values for $l$, m, n, and b have been evaluated, the differences between the experimental values of c/R and the corresponding values calculated employing the least squares equations are printed out for the concentrations and angles of the experiment. The coefficients $l$, m, n, and b may then be converted to the parameters of the system as follows

$$l = (W/K')\,\overline{M}_w^{-1}$$

$$m/l = (16/3)\,\pi^2 n_1^2\,\lambda^{-2}\langle S^2\rangle$$

$$n = (W/K')\,2A_2$$

$$b = (W/K')\,3A_3$$

The published program of EVANS *et al.*[2)] does not include the conversion to $\overline{M}_w$, $\langle S^2\rangle^{1/2}$, $A_2$, and $A_3$. We had therefore to make the necessary additions in order to have these parameters printed out in this form. Minor omissions in the published program were found and corrected.

The final stage of the treatment of the data is to evaluate the weight average molecular weight and the heterogeneity parameters P and Q for the relation

$$M_{app} = \overline{M}_w + 2P[(\nu_A - \nu_B)/\nu_0] + Q[(\nu_A - \nu_B)/\nu_0]^2$$

which may be solved for $\overline{M}_w$, P, and Q by solving three simultaneous equations for results of experiments in three different solvents during different refractive index increments. In practice, it is recommended that all combinations taken three at a time from up to six solvents be averaged to arrive at $\overline{M}_w$. One of us, M. GIROLAMO, has written a separate program in FORTRAN IV for this final step.

## *Experimental*

The Sofica instrument was operated at 30 °C using unpolarized light of $\lambda = 5460\cdot10^{-8}$ cm. A check on the volume correction was made with aqueous fluorescein solutions with a red filter placed in the photomultiplier compartment to remove scattered light. Application of the sin $\Theta$ correction gave satisfactory results over the whole range of angles for 30 to 150°. No dissymmetry correction was required. A range of concns. was prepared by diluting a conc. solution to 80, 60, 40, and 20 % of the original. Concns. were adjusted so that the smallest scattering was not less than twice the value of the solvents. A standard benzene was prepared from A.R. grade benzene, distd. from over three fresh batches of calcium hydride and finally treated with unterminated polystyryl-lithium purge. The sample of benzene was flash distd. into a cell sealed on to the *vac.* line. It was sealed off from the line and cemented into a specially prepared stainless steel holder.

The Rayleigh ratio of benzene was taken from the results of Coumou[8] $R_{90} = 15.8\cdot10^{-6}$ at $\lambda = 5460\cdot10^{-8}$ cm. The volume correction was found to be satisfactory, after allowing for depolarization as discussed in Coumou's paper. The dedusting procedure adopted was centrifugation in a Spinco model L centrifuge using a swinging bucket rotor and stainless steel inserts. Solutions were centrifuged at 30,000 G for three hrs, removed to a specially constructed transfer apparatus which allows the transfer of all solutions mechanically within 15 min of stopping the rotor. In this apparatus disturbance of dust is avoided by the very slow rate of withdrawal of the solution from the stainless steel inserts of the rotor buckets.

All solvents were A.R. grade, dried as described above and fractionated in a 3 ft. (= 91.44 cm) column before use. The first and last fraction were discarded, and the refractive index measured and checked against best literature values.

## *Results*

A preliminary test was made with a sample of narrow distribution polystyrene ($\overline{M}_w/\overline{M}_n = 1.07$; $\overline{M}_w = 2.67\cdot10^5$ obtained by Zimm plot) in the solvent toluene. Inspection of the differences between experimental and least squares results, printed out in the program, showed that the three higher concentrations were all less than 1 % of the least square values. However, the two lower concentrations had differences of up to 10 % scattered throughout the range of angles, probably due to inadequate dedusting. These results were discarded and two new solutions prepared and measured. This time the differences were all less than 1 % as with the higher concentrations. The program was then completed and the results obtained are shown in Table 1 along with the values obtained by Evans *et al.*[2].

Table 1. Light scattering parameters from the study of polystyrene in toluene at 30 °C

| | This study | Evans *et al.*[2] | | This study | Evans *et al.*[2] |
|---|---|---|---|---|---|
| $\overline{M}_w$ | $2.57\cdot10^5$ | $2.54\cdot10^5$ | $\langle S^2\rangle^{1/2}_w$ | $242\cdot10^{-8}$ cm | $226\cdot10^{-8}$ cm |
| $\overline{M}_w/\overline{M}_n$ | 1.07 | 2.1 | $A_2$ | $3.82\cdot10^{-4}$ | $3.86\cdot10^{-4}$ |
| $\langle S^2\rangle^{1/2}_{L.S.}$ | $252\cdot10^{-8}$ cm | $288\cdot10^{-8}$ cm | $A_3$ | $3.56\cdot10^{-2}$ | $1.31\cdot10^{-2}$ |

The value of the refractive index increment for polystyrene in benzene determined by Norberg and Sundelöf[9], $\partial n/\partial c = 0.109$, was adopted by this work. The raw data from the earlier study were reexamined with the modified program of Evans *et al.*[2]. Values of $\partial n/\partial c$ for the parent polymers in the various solvents were taken from the collected values of Huglin[10] and the Polymer Handbook[11]. To be consistent the same values were employed in the computer technique as those used for the manual calculations.

Once again the printed differences between experimental and least squares results were examined. The polymers labelled BCP1, BCP2, BCP3, which are model block copolymers[12] synthesised under strict conditions as described elsewhere were found to be mainly within the acceptable ± 1 % deviation in the solvent MBK (methyl isobutyl ketone); a few values exceeded this in cyclohexane but no deviation exceeded 2 %. In toluene values were within 2 % for BCP1, within 2–3 % for BCP3 but there was a lot of scatter for BCP2, more than half the values being in excess of 5 % and at one particular angle (135°) differences of 20 % were shown right throughout the concentration range. The copolymer RCP1 which has some random character as well as containing long sequences showed a similar pattern in two solvents but wide scatter of up to 20 % was observed throughout in toluene. These results were therefore rejected. This meant that the second stage of the computer program whereby $\overline{M}_w$, P, and Q may be obtained by solving the three simultaneous equations could not be applied to RCP1. The other copolymers were processed to obtain these parameters and the results are set out in Tables 2 and 3. Values obtained by manual computation are given for comparison. The third virial coefficient $A_3$ was not calculated using the manual technique.

## *Discussion*

The parameters obtained from the study of the polystyrene sample may be compared with similar results in the same solvent reported by Evans, Huglin, and Lindley[2] (Table 1). The molecular weight of the polystyrene sample used was very close to that of our sample (*i.e.* $2.54\cdot10^5$). These authors found $\langle S^2\rangle^{1/2} = 288\cdot10^{-8}$ cm and the value of $g = 0.34$ calculated from the relationship $A_3 = gA_2^2M$, in which g is expected to range between the limits 1/4 and 5/8.

The root-mean-square radius of gyration as measured by light scattering was converted to the weight average value $\langle S^2\rangle_w^{1/2}$ by application of the correlation factor of Van Leemput and Stein[13], *viz.*,

$$\langle S^2\rangle_w^{1/2} = \langle S^2\rangle_{L.S.}^{1/2}\,[(\gamma - 1)/(\gamma + 2 + \beta)]^{1/2}$$

Table 2. Light scattering results obtained by computer program and graphical methods. Values in parentheses by graphical methods

| | BCP 1 | | | BCP 2 | | | BCP 3 | | | RCP 1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tol | $C_6H_{12}$ | MBK | Tol | $C_6H_{12}$ | MBK | Tol | $C_6H_{12}$ | MBK | Tol | $C_6H_{12}$ | MBK |
| $M_{app}\cdot10^{-5}$ | 2.83<br>(2.93) | 2.79<br>(2.68) | 2.72<br>(2.63) | 2.28<br>(2.89) | 2.71<br>(2.64) | 2.58<br>(2.50) | 2.53<br>(3.19) | 2.85<br>(2.69) | 2.73<br>(2.63) | –<br>(5.20) | 3.44<br>(3.42) | 3.56<br>(3.44) |
| $\langle S^2\rangle^{1/2}\cdot10^8$ cm | 205<br>(245) | 303<br>(235) | 198<br>(186) | 319<br>(223) | 255<br>(207) | 179<br>(168) | 144<br>(227) | 218<br>(200) | 190<br>(177) | –<br>(289) | 312<br>(234) | 252<br>(234) |
| $A_2\cdot10^4$ | 8.35<br>(8.10) | 7.84<br>(7.66) | 1.31<br>(1.38) | 6.23<br>(9.04) | 5.31<br>(5.51) | 1.06<br>(1.25) | 5.60<br>(8.78) | 4.89<br>(3.48) | 1.55<br>(1.60) | –<br>(10.2) | 4.27<br>(4.40) | 1.64<br>(1.74) |
| $A_3\cdot10^2$ | −0.55 | −1.42 | 0.04 | 1.51 | −0.77 | 0.72 | 2.32 | −8.9 | 0.03 | | 3.87 | 0.14 |

Tol = toluene; $C_6H_{12}$ = cyclohexane; MBK = methyl isobutyl ketone.

Table 3. The weight average molecular weight and heterogeneity parameters. Values calculated manually are shown in brackets

| | BCP 1 | | BCP 2 | | BCP 3 | | RCP 1 | |
|---|---|---|---|---|---|---|---|---|
| $\overline{M}_w\cdot10^{-5}$ | 2.56 | (2.56) | 2.21 | (2.21) | 2.33 | (2.59) | – | (3.70) |
| $P/\overline{M}_w$ | 0.16 | (0.07) | 0.50 | (0.36) | 0.54 | (0.15) | – | (−0.26) |
| $Q/\overline{M}_w$ | −0.17 | (−0.01) | −0.95 | (−0.40) | −1.1 | (0.34) | – | (0.86) |

where $\beta \cong (2\nu - 1)/2.43$, $\nu$ is the KUHN-MARK-HOUWINK exponent for this system, and $\gamma$ characterizes the width of the distribution, thus

$$\overline{M}_w/\overline{M}_n = (\gamma + 1)/\gamma$$

Substituting $\overline{M}_w/\overline{M}_n = 1.07$ and the value of $\nu$, we find for our sample of polystyrene $\langle S^2\rangle^{1/2}_w = 242\cdot10^{-8}$ cm which compares favourably with the value $226\cdot10^{-8}$ cm calculated by EVANS *et al.*[2)]. The argument is particularly satisfactory when one considers the much broader distribution of the sample used by these authors.

Comparing the values for the virial coefficients shown in Table 1 one observes that the second virial coefficient coincides, which is very encouraging. The third virial coefficient, however, agrees only in the order. The values obtained by us seem to be too large. There is no obvious explanation that we can offer at this moment but it is clear that the program is not at fault. We had insufficient quantities of this polymer to repeat the measurements and therefore clarification of this point will have to wait for the synthesis of new samples.

Inspection of Table 2 shows good agreement between computed and manual calculations for $M_{app}$ except for values in toluene although even in this solvent the values for BCP1 are quite satisfactory. The programmed values should be more representative of the experimental data than those estimated by manual curve fitting. The values of the radius of gyration show wide deviations in toluene and cyclohexane. Even in methyl isobutyl ketone, which is a poor solvent, the computed values are 5 to 7 % greater than the graphical values although the deviations are consistent. This is all the more fortunate since the calculations of molecular dimensions of these polymers were based on values in MBK.

Examination of the printed differences indicates that the results are good in the solvent MBK. All differences are within 1 % and many better than 0.1 %. These differences increase in cyclohexane but remain within the 2 % range. Results in toluene, however, are not so satisfactory.

BCP1 values remain within 2 % and BCP3 did not exceed 3 %. However, scrutiny of the results for BCP2 in toluene showed that differences were greatest for the angle 135° reaching 20 % throughout.

Omitting these from the calculation and using only a 10× 5 matrix instead of the usual 11× 5 produced the result,

$$\overline{M}_{app} = 2.3 \cdot 10^5$$

$$\langle S^2 \rangle^{1/2} = 143 \cdot 10^{-8}\ \text{cm}$$

$$A_2 = 7.0 \cdot 10^{-4}$$

$$A_3 = 1.0 \cdot 10^{-2}$$

with an improvement in the differences to the extent that there was a reduction to within 2 % for all except the lowest concentration which still displayed differences as high as 7 %. This was eliminated from the calculation and a 10× 4 matrix calculated which yielded the values for the same parameters as follows,

$$M_{app} = 2.1 \cdot 10^5$$

$$\langle S^2 \rangle^{1/2} = 89 \cdot 10^{-8}\ \text{cm}$$

$$A_2 = 6.6 \cdot 10^{-4}$$

$$A_3 = 1.3 \cdot 10^{-2}$$

The printed differences were then all within 2 %.

The effect of these manipulations was to produce (a) minor changes in $M_{app}$, (b) significant changes in the radius of gyration, (c) little change in the virial coefficients. When seeking an explanation of these effects two factors must be kept in mind. Firstly, manipulation of the data by the graphical method allows for the sacrifice of a few points for the sake of the majority whereas the program considers all points. This may be remedied by elimination from the matrix of one set of measurements that might appear faulty, but is impracticable when the scatter is too random. The program is more demanding of the experimenter but has the advantage of removing the tedium of calculation. Secondly, the program takes into consideration the curvature in the $\Theta = 0$ extrapolation which is ignored in the graphical method, a procedure which is not justified if the curvature is significant.

The calculation of the weight-average molecular weight can be made in this instance only from the three values of $M_{app}$. The values for BCP 1 and BCP 2 are identical with the manual calculation but for BCP 3 the value is too small since it is smaller than the number average $\overline{M}_n$ obtained by osmometry. The reason for this curious result is probably to be found in the choice of solvent. The value for $\partial n/\partial c$ in toluene is only half that in the other two solvents and since this quantity appears as the square of the value in the light scattering equation the error in the determination of $\overline{M}_w$ is very dependent on the accuracy with which $\partial n/\partial c$ may be determined. The low value requires the use of greater concentrations of polymer in obtaining light scattering data and in the determination of the $\partial n/\partial c$ itself. It would seem therefore that optimum accuracy is not attained only by increasing the number of solvents, but it is also necessary to ensure that these solvents have high values of $\partial n/\partial c$. This seems to be borne out by the excellent results in MBK. It would appear therefore that solvents with $\partial n/\partial c$ below that of cyclohexane should not be employed in this system.

Similar problems arise in the determination of the radius of gyration, once again only an apparent value can be obtained in a particular solvent. The decline in the apparent values for BCP 2 in toluene, after discarding values for $\Theta = 135\,°$, seems inexplicable, since these values are lower even than the value in MBK. The variation shown on discarding the greatest deviations probably underlines the need for better experimental points, the program tends to exaggerate the errors since all points are considered and a 2 % variation in the differences may be unacceptable for this method.

The problems raised by the wide spread of the experimental points are carried over into the determination of the heterogeneity parameters P and Q. The sign of P is the same as found graphically but now all values of Q are negative. This effect seems to be due to the large cumulative error as stated previously. Clearly the program method of obtaining the light scattering parameters demands a higher degree of precision in the determination of experimental points than may be acceptable for manual manipulation. However, once this is achieved the program method offers the advantages of removing the tedium of calculation, eliminating the personal bias of curve fitting and takes account of the curvature in the $\Theta = 0$ extrapolation. Furthermore, the printed differences allow a readily available critical analysis of the experimental points to be made. For the data examined here, the program achieves nothing over the more usual graphical method and in fact the graphical results are to be preferred.

1) L. H. Tung, J. appl. Polymer Sci. **10** (1966) 375, 1271.

2) J. M. Evans, M. B. Huglin, and J. Lindley, J. appl. Polymer Sci. **11** (1967) 2159.

3) W. Bushuk and H. Benoit, Canad. J. Chem. **36** (1958) 1616.

4) S. Krause, J. physic. Chem. **65** (1961) 1618.

5) D. N. Cramond and J. R. Urwin, European Polymer J. **5** (1969) 35.

6) SOFICA Operation Manual.

7) F. W. Peaker, in Techniques of Polymer Characterization, Ed. by P. W. Allen, Butterworths, London 1959.

8) D. J. Coumou, J. Colloid Sci. **15** (1960) 408.

9) A. N. Norberg and L. O. Sundelöf, Makromolekulare Chem. **77** (1964) 77.

10) M. B. Huglin, J. appl. Polymer Sci. **9** (1965) 3963.

11) Polymer Handbook, Ed. by J. Brandrup and E. H. Immergut, Interscience Publ., New York 1966.

12) D. N. Cramond and J. R. Urwin, Austral. J. Chem. **21** (1968) 1835.

13) R. Van Leemput and R. Stein, J. Polymer Sci. A **1** (1963) 985.

European Polymer Journal, 1971, Vol. 7, pp. 693–698. Pergamon Press. Printed in England

# ANOMALOUS VISCOSITY BEHAVIOUR OF BLOCK COPOLYMERS AS A FUNCTION OF THE TEMPERATURE FOR TWO SEQUENCE OR AB TYPE POLY(ISOPRENE: STYRENE)

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**Abstract**—The intrinsic viscosities of two sequence block copolymers of poly(isoprene: styrene), plotted as a function of the temperature in the solvent cyclohexane, have been found to exhibit anomalous behaviour. However, this type of behaviour is not confined to this particular solvent. A transition temperature, which is represented by a peak in the $[\eta]$ vs. $T$ curve and which is well defined and reproducible, has been shown to vary with both the composition and the molecular weight. The general shape of the $[\eta]$ vs. $T$ plot, which is common to these polymers, is discussed, a qualitative explanation of the curve and the transition point has been proposed.

## INTRODUCTION

Studies of the solution properties of block copolymers of poly(isoprene: styrene) of the two sequence or AB type, in several solvents, were reported from this laboratory recently.(1,2) The present work was intended to reinforce the rather sparce data obtained previously in the same solvents, so as to define more clearly the general trends observed in that study.

In the report of the previous study, it was shown that plots of $\eta$ sp/$c$ vs. $c$, and the complementary plot of ln $\eta$ rel/$c$ vs. $c$, had the usual positive and negative slopes respectively, with the usual common intercept. In other words, the block copolymers behaved normally in toluene (a good solvent for both sequences) and in methyl isobutyl ketone (a poor solvent for both polymer sequences). Minor anomalies which were observed in cyclohexane were noted but not considered significant and therefore neglected. However, in this work, plots of $\eta$ sp/$c$ vs. $c$ were observed to have negative slopes for the particular polymer examined and the results were therefore repeated several times. Since the effect was clearly reproducible, it was decided to examine other polymers in detail and investigate the anomaly further.

In view of this behaviour, it was decided to study the effect of temperature to see whether the slope of the $\eta$ sp/$c$ plot may not change to a positive slope with increasing temperature. As a result of this study, values of $[\eta]$ plotted as a function of temperature produced well defined, sharp transition points in the form of a peak in the curve. A series of polymers, with a range of compositions from 12 to 50 per cent polystyrene by weight and a further two polymers, with molecular weight twice those in the first group but with the same compositions, were all carefully examined. The transition temperature was found to be a function of both composition and the molecular weight. Although the overall shape was obviously the same for all polymers, the magnitude of the peak in the curve was very dependent on composition.

## EXPERIMENTAL

### *The polymers*

The synthesis and analysis followed the methods described previously,(3) except that the monomers were purged over a mixture of BuLi and styryllithium. The concentration of initiator used for the synthesis was dispensed and determined spectrophotometrically according to the technique described by Urwin and Reed(4) which allowed an accurate choice of the molecular weights and composition to better than 2 per cent between batches. The dispensing of volumes of monomer was probably the largest source of error. Composition was determined by u.v. analysis, the *cis* 1,4 isomer content by N.M.R. analysis, the molecular weight distribution by gel permeation chromatography and molecular weight ($\overline{M}_N$) by osmometry using the high speed equipment described in the earlier publication.(3) All polymers used were therefore well characterized samples.

### *Viscometry*

The viscometer was of the highly accurate automatic timing type constructed after the design of Steel.(5) Flared capillaries(6) were always employed to eliminate the need for the usual kinetic energy corrections. Three such viscometers, with flow times ranging up to twice the flow time normally used, were employed to test non-Newtonian behaviour but the viscosity measurements showed that the measurements were all independent of shear rate, at least over the concentration range measured.

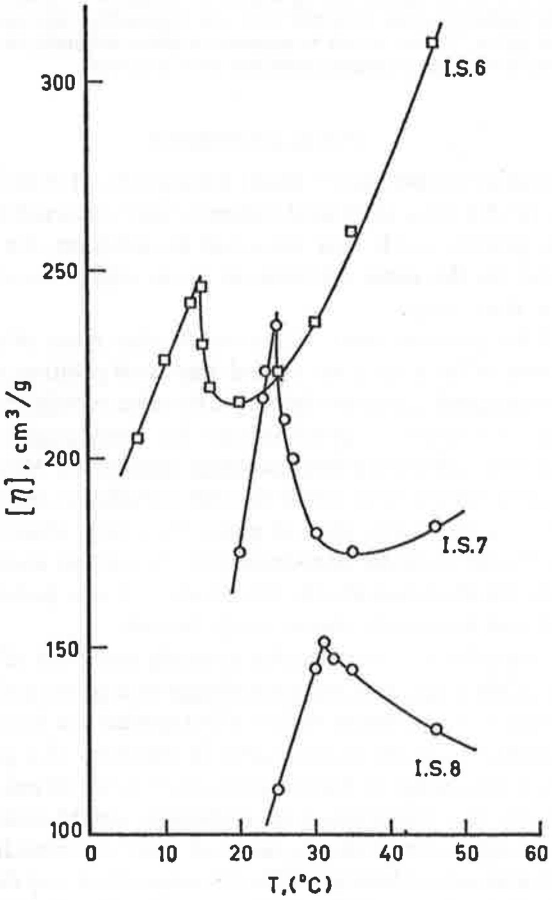

FIG. 1. Intrinsic viscosities as a function of temperature for block copolymers I.S.6, I.S.7 and I.S.8.

## RESULTS

Graphs of the intinsic viscosity [$\eta$] versus temperature for three block copolymers of constant molecular weight ($\bar{M}_N = 250{,}000$) and with compositions approx. 12, 25 and 50 per cent by weight of polystyrene are shown in Fig. 1. Plots of $\eta$ sp/$c$ vs. $c$ and ln $\eta$ rel/$c$ vs. $c$ were linear for all polymers and had a common intercept. The general features of the shape of the graphs shown in the figure are common to all. They show a rising value of [$\eta$] with temperature and a discontinuity in [$\eta$] at a particular temperature $T_p$, which we have called the transition point. This is followed by a sharp fall in viscosity to a minimum value and then by a further rise after passing through the minimum. The difference in temperature between $T_p$ and the point at which the minimum occurs depends on composition. It increases with increasing polystyrene content, e.g. for I.S.6, a 5° difference is observed, I.S.7, 10° and with I.S.8 the minimum had not appeared even at 15° above $T_p$.

Two other blocks with molecular weights double that of the first group and with compositions the same as in the first group, i.e. 25 and 50 per cent respectively are displayed in Fig. 2. The values of the transition point temperatures $T_p$ for all five block copolymers are given in Table 1. along with their respective compositions and number average molecular weight $\bar{M}_N$. Inspection of $T_p$ values in the table show that they are a function of the composition of the copolymer as well as its molecular weight;

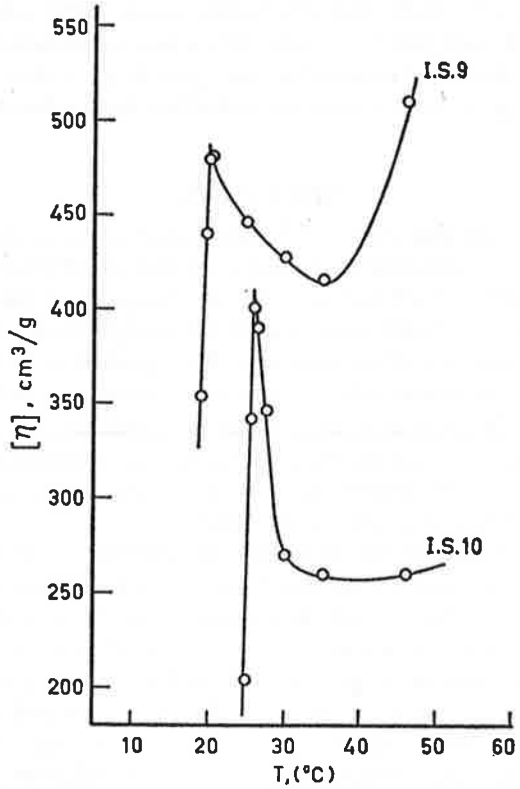

FIG. 2. Intrinsic viscosities as a function of temperature for block copolymers I.S.9 and I.S.10.

it is seen that $T_p$ increases with increasing polystyrene content and that the values for the higher molecular weight polymers are both about 5° lower than those for the polymers with the corresponding composition in the lower molecular weight range. The same polymers in the solvent methyl cyclohexane exhibited the same phenomenon thus indicating that the anomalous behaviour is not confined to a particular solvent.

TABLE 1. THE TRANSITION TEMPERATURE $T_p$ FOR BLOCK COPOLYMERS WITH VARIOUS COMPOSITIONS AND MOLECULAR WEIGHT IN CYCLOHEXANE

| Polymer | $\overline{M}_N \times 10^{-3}$ | Composition % polystyrene | $T_p$ (°C) |
|---|---|---|---|
| I.S.6 | 2·54 | 11·8 | 15 |
| I.S.7 | 2·49 | 25·5 | 24·5 |
| I.S.8 | 2·48 | 48·5 | 31 |
| I.S.9 | 4·97 | 25·1 | 20 |
| I.S.10 | 4·97 | 49·7 | 26 |

All these polymers at very high concentration show an iridescence which occurs when the polymer is being dissolved and which must be due to the scattering of light from aggregations in a solution in which the refractive indices of polymer and solvent are significantly different. This effect disappears on complete solution and, since the concentrations used in viscometry (1–2 g/l) are low by comparison with that used in the osmotic measurements (where concentrations up to 20 g/l were used and where there was no evidence of aggregation), then no such effect can be involved here.

## DISCUSSION

In the earlier work on this system,(1,2) there was evidence, particularly concerning molecular dimensions, indicating that AB type block copolymers of poly(isoprene: styrene) exist in a random conformation at least in a good solvent for both sequences such as toluene. With a solvent such as methyl isobutyl ketone which was relatively poor for both sequences, the phase separated form seemed to be the more likely. On the other hand, in cyclohexane, which is good as a solvent for polyisoprene but poor for polystyrene ($\theta = 34°$), the situation was far less conclusive.(7) We have assumed in this work that the peak in the $[\eta]$ vs. $T$ curve, which is characteristic of the curve, corresponds to a transition temperature which actually marks the change from the phase separated form to the random conformation.

If this explanation is correct then at the transition temperature $T_p$ the free energy of mixing must be zero; it must be positive below $T_p$ and negative above it. The large entropy change due to mixing, which would accompany the change, favours the transition from the one form to the other. The enthalpies of mixing, at temperatures well below the transition, must be large and positive for the two polymers, negative for polyisoprene and solvent and must have a positive value for polystyrene and solvent. With increasing temperature, the latter will become smaller and the polystyrene domain swells rapidly; the increased dimensions are reflected in a corresponding increase in viscosity.

At the transition point, contributions to the free energy from the enthalpy and entropy terms must cancel, so that mixing takes place. On mixing, the environment of the polyisoprene, which up to this point has consisted almost entirely of cyclohexane molecules and isoprene segments except for a small region of interpenetration at the junction of the two domains, now becomes a mixture of all segments, including polystyrene. This environment is a poorer solvent for polyisoprene than the previous one and consequently the whole molecule shrinks. The rapid decline in solvent power becomes more obvious with increasing concentration of polystyrene. This is made evident by the larger difference between the value of $[\eta]$ at $T_p$ and at the minimum, expressed as a percentage of the viscosity. For I.S.6 the difference between the value at $T_p$ and at the minimum, relative to the minimum value, is about 20 per cent; for I.S.7 this ratio is doubled. That is the minimum occurs at a lower $[\eta]$ and higher $T$ with increasing concentration of polystyrene. A similar effect was found with the solvent methyl cyclohexane, which has a theta temperature for polystyrene of 71° compared with 34° for cyclohexane. The only effect observed was a shift in $T_p$ to higher temperatures with the poorer solvent. The same phenomenon was observed by using a mixture of *n*-heptane and cyclohexane which produced a poorer solvent and resulted in the shift of $T_p$ to higher temperatures.

We believe that discussion is qualitatively correct, and at least a working hypothesis. Experiments designed to establish the true nature of the transition are under way with a wider range of polymers and solvents. With different techniques and complementary data from other studies, it is hoped ultimately to be more explicit as to the mechanism involved.

*Acknowledgements*—Our thanks are due to Mrs. J. Walsh for assisting with the viscosity study in the later stages and to the A.R.G.C. for financial assistance and use of the high speed osmometer.

## REFERENCES

(1) D. N. Cramond and J. R. Urwin, *Europ. Polym. J.* **5**, 35 (1969).
(2) D. N. Cramond and J. R. Urwin, *Europ. Polym. J.* **5**, 45 (1969).
(3) D. N. Cramond and J. R. Urwin, *Aust. J. Chem.* **21**, 1835 (1968).
(4) J. R. Urwin and P. J. Reed, *J. organometal Chem.* **15**, 1 (1968).
(5) B. J. Steel, *J. scient. Instr.* **42**, 751 (1965).
(6) W. A. Caw and R. G. Wylie, *Br. J. appl. Phys.* **12**, 94 (1961).
(7) J. R. Urwin, *Aust. J. Chem.* **22**, 1649 (1969).

**Résumé**—Les viscosités intrinsèques de copolymères blocks à double séquence de poly(isoprènc: styrène) représentés graphiquement en fonction de la température dans le cyclohexane comme solvant, montrent des anomalies dans le comportement. Ce genre de comportement cependant n'est pas restreint à ce seul solvant. Une température de transition qui est représentée par une crête dans la courbe de $[\eta]$ en fonction de $T$ et qui est bien définie et reproduisible, indique une variation selon la composition et le poids moléculaire. La forme générale de la courbe de $[\eta]$ en fonction de $T$ commune à ces polymères est discutée, et l'on propose une explication qualitative de la courbe et du point de transition.

**Sommario**—Si è scoperto che la viscosità intrinseca di copolimeri in blocco di tipo a due sequenze di poli(isoprene : stirene), messa in funzione della temperatura nel solvente cicloesano, presenta un comportamento anomalo, che però non è limitato a tale particolare solvente. Si mostra che la temperatura di trasformazione, che à rappresentata da una cuspide nella curva $[\eta]$ in funzione di $T$ e che è ben definita e riproducibile, varia sia con la composizione che con il peso molecolare. Si discute la forma generale della curva $[\eta]$ in funzione di $T$, la quale è comune a tali polimeri, e si suggerisce una spiegazione qualitativa della curva e del punto di trasformazione.

**Züsämmenfässüng**—Es wurde festgestellt, daß die Grenzviskositäten von zwei Sequenz-Blockcopolymeren aus Poly(isopren:styrol) in Cyclohexan als Lösungsmittel anomales Verhalten zeigen, wenn man sie als Funktion der Temperatur aufträgt. Diese Art des Verhaltens ist jedoch nicht auf dieses spezielle Lösungsmittel beschränkt. Es zeigte sich, daß eine Ubergangstemperatur, die durch einen peak in der $(\eta)$ gegen $T$ Kurve gekennzeichnet ist und die gut definiert sowie reproduzierbar ist, sich sowohl mit der Zusammensetzung wie auch mit dem Molekulargewicht verändert. Der generelle Verlauf der $(\eta)$ gegen T Auftragung, der allen diesen Polymeren gemeinsam ist, wird diskutiert; eine qualitative Erklärung der Kurve und des Übergangspunktes wird vorgeschlagen.

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# CONFORMATIONAL TRANSITIONS IN BLOCK COPOLYMERS IN SOLUTION FROM LIGHT SCATTERING DATA

By M. Girolamo* and J. R. Urwin*

[Manuscript received October 26, 1970]

*Abstract*

Data obtained from light scattering studies on block copolymers of styrene and isoprene, in the solvent cyclohexane, show a change in apparent radius of gyration as a function of temperature at the same temperature, $T_p$, as was observed in studies of $[\eta]$ against $T$ in this solvent. The phenomenon observed in these independent experimental methods is believed to be due to a change in the hydrodynamic volume of the polymer, brought about by an intramolecular rearrangement of the molecule, from a phase-separated to a phase-mixed conformation, as the temperature increases through $T_p$.

## Introduction

Although considerable interest has been shown in phase transitions in block copolymers in recent years, particularly since the discovery of the commercial value of thermoplastic elastomers,[1,2] these investigations have been mainly concerned with rheological studies.[3] However, it has long been realized that much information on the molecular behaviour of these materials may be obtained from the study of the properties in dilute solutions.[4] Various studies of films cast from different solvents have demonstrated the existence of a wealth of structures from spherical domains to laminated layers,[5–7] some of which result from different methods of casting, but a full explanation is still forthcoming.

In recent studies of two-sequence or AB type block copolymers of polystyrene and polyisoprene in solution we have reported that a discontinuity is exhibited in the $[\eta]$ against $T$ plots of these materials in several solvents, including cyclohexane[8] and mixtures of cyclohexane and n-heptane.[9] The temperature, at which this discontinuity occurs ($T_p$), has been shown to be a function of several parameters and appears to correspond to the point of zero free energy of mixing of the two block sequences and the solvent in the immediate vicinity.

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[1] Holden, G., and Milkovich, R., Belg. Pat. 627,652, 1963 (*Chem. Abstr.*, 1964, **60**, 14714*f*).

[2] Bailey, J. T., Biship, E. T., Hendricks, W. R., Holden, G., and Legge, N. R., *Rubb. Age*, 1966, **98**(10), 69.

[3] Estes, G. M., Cooper, S. L., and Tobolsky, A. V., *J. macromol. Chem.* (*Rev.*) (*C*), in press.

[4] Utracki, L. A., Simha, R., and Fetters, L. J., *J. Polym. Sci.* (*A*-2), 1968, **6**, 2051.

[5] Inoue, T., Sone, T., Kawai, H., Fakatsu, M., and Kurata, M., *Polym. Lett.*, 1968, **6**, 75.

[6] Holden, G., Bishop, T., and Legge, N. R., *J. Polym. Sci.* (*C*), 1969, **26**, 37.

[7] Bradford, E. B., and Vanzo, E., *J. Polym. Sci.* (*C*), 1969, **26**, 161.

[8] Girolamo, M., and Urwin, J. R., *Eur. Polym. J.*, in press.

[9] Urwin, J. R., and Girolamo, M., *Eur. Polym. J.*, in press.

*Aust. J. Chem.*, 1971, **24**, 729–34

It has been postulated[8] that the intrinsic viscosity against temperature plots reflect the change in hydrodynamic volume or, at least qualitatively, the change in the representative parameter of the end-to-end distance of the polymer chain, with respect to temperature. These studies have demonstrated that $T_p$ is a function of molecular weight, composition, and the nature of the solvent present in the solution. Mixed solvents of cyclohexane and a non-solvent n-heptane exhibit the same phenomenon which may be observed when the intrinsic viscosity is plotted as a function of the solvent+non-solvent composition $\gamma$, at constant temperature. This has been interpreted[9] to mean that the temperature of the experiment is equivalent to $T_p$, for that particular composition.

As a further attempt to provide evidence that the phenomenon being observed is, in reality, a change in hydrodynamic volume with temperature, we have measured the "apparent" radius of gyration, as a function of temperature, in cyclohexane for several of the polymers previously investigated. The results of this study, their interpretation, and their relation to the previous work is discussed.

## EXPERIMENTAL

The synthesis of these polymers has been described elsewhere.[10] The only modifications made have been in the more accurate dispensing of initiator which has led to better predictability of molecular weight and composition. The purging solution used has been changed to a mixture of n-butyllithium and low molecular weight polystyryllithium. The polymers were well characterized in that they were all of narrow molecular weight, contained no homopolymer (demonstrated by gel permeation chromatography), and contained a high *cis*-1,4 content in the polyisoprene sequence. The results of n.m.r. studies using the method of Chen[11] have been employed to determine the microstructure, with the modification that an empirical correction has been made to allow for the broad styrene band which occurs in the spectrum beneath the peaks used to determine the *cis*-1,4 content.

Light scattering data were obtained on a Sofica 4200 photogoniometer. Solutions were dedusted in a Beckman L centrifuge for 3–4 hr at 25000 r.p.m. using swinging bucket rotors and stainless steel insert tubes. Calibration of the instrument was based on the Rayleigh ratio of benzene, $R_{90} = 15\cdot 8\times 10^{-6}$ at $\lambda$ 546 nm. After due allowance for depolarization it was found that the volume correction, sin $\theta$, was obeyed over the range of angles 30–150°.

Refractive index increments were determined using a Brice–Phoenix differential refractometer.[12] Experimental values agreed with calculated values assuming the relationship

$$(\mathrm{d}n/\mathrm{d}c)_0 = x(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}}+(1-x)(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PI}}$$

where $x$ is the weight fraction of polystyrene and $(\mathrm{d}n/\mathrm{d}c)_0$, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}}$, and $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PI}}$ are the refractive index increments of copolymer, polystyrene, and polyisoprene respectively.

The determination of an absolute radius of gyration has been discussed exhaustively and has been shown to lead to an apparent value only,[13] but the deviation from the correct value for these block copolymers is relatively small in cyclohexane.[14] An absolute value for the radius of gyration is very difficult, if not impossible, to obtain under normal circumstances. However, a useful measure of the change in hydrodynamic volume may be obtained, despite the difficulties of determining the absolute radius of gyration.

Values of the radius of gyration were calculated with the aid of a computer program[15] on the University C.D.C. 6400 computer. The same program is used to obtain $\bar{M}_w$, $A_2$, and $A_3$ as well.

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[10] Cramond, D. N., and Urwin, J. R., *Aust. J. Chem.*, 1968, **21**, 1835.

[11] Chen, H. Y., *Analyt. Chem.*, 1962, **34**, 1134, 1793.

[12] Reed, P. J., and Urwin, J. R., *Aust. J. Chem.*, 1970, **23**, 1743.

[13] Benoit, H., *Ber. Bunsenges. phys. Chem.*, 1966, **70**, 286.

[14] Cramond, D. N., and Urwin, J. R., *Eur. Polym. J.*, 1969, **5**, 35.

[15] Evans, J. M., Huglin, M. B., and Lindley, J., *J. appl. Polym. Sci.*, 1967, **11**, 2159.

## RESULTS

Four block copolymers were examined in the light of the previous results obtained from a study of $[\eta]$ against $T$ in various solvents. The temperature was lowered to a point below $T_{\mathrm{p}}$, determined from the $[\eta]$ against $T$ plots, and then raised in small increments. The graphs of radius of gyration against temperature for polymers IS8, IS9, and IS10 are shown in Figure 1. The peak temperature at the discontinuity coincides with the temperature found in the viscosity studies. A discontinuity peak was also found at the corresponding value of $T_{\mathrm{p}}$ for IS7 (not shown in Fig. 1). Values of $T_{\mathrm{p}}$ for all four polymers are given in Table 1.

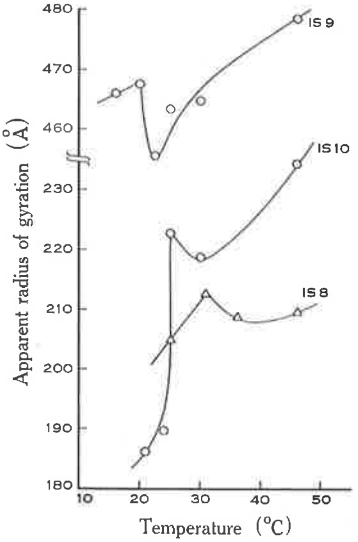

Fig. 1.—Plots of apparent radius of gyration against temperature for the block copolymers IS8, IS9, and IS10.

TABLE 1

THE TRANSITION TEMPERATURE $T_{\mathrm{p}}$ IN CYCLOHEXANE FOR BLOCK COPOLYMERS OF POLYSTYRENE AND POLYISOPRENE

| Polymer | $10^{-5}\overline{M}_{\mathrm{w}}$ | Composition (% P.S.) | $T_{\mathrm{p}}$ (°C) |
|---|---|---|---|
| IS7 | 2·5 | 25·5 | 24·5 |
| IS8 | 2·5 | 48·5 | 31·0 |
| IS9 | 5·0 | 25·1 | 20·0 |
| IS10 | 5·0 | 49·7 | 26·0 |

In Table 2 the apparent radii of gyration determined by light scattering for the three polymers IS8, IS9, IS10 are given for several temperatures. For the purpose of comparison, the values designated $(\langle\bar{s}^2\rangle_\eta)^{1/2}$ have been calculated from intrinsic viscosity measurements at the same temperatures, assuming the relation

$$[\eta] = \Phi\langle\bar{r}^2\rangle^{3/2}M^{-1} \tag{1}$$

where $\langle\bar{r}^2\rangle$ is the square of the end-to-end distance and $\Phi$ has the value $2\cdot0\times10^{23}$.

The values for $(\langle \bar{s}^2\rangle_\eta)^{1/2}$ have been calculated assuming

$$\langle \bar{r}^2\rangle^{1/2} = (6\langle \bar{s}^2\rangle)^{1/2} \tag{2}$$

to hold for each polymer and at each temperature. The validity of these assumptions will be discussed later.

Table 2

RADIUS OF GYRATION AS A FUNCTION OF TEMPERATURE FOR BLOCK COPOLYMERS DETERMINED BY LIGHT SCATTERING AND BY VISCOSITY USING EQN. (2)

| Polymer | $T$ (°C) | $10^6(\langle \bar{s}^2\rangle_\eta)^{1/2}$ (cm) | $10^6(\langle \bar{s}^2\rangle_{\mathrm{LS}})^{1/2}$ (cm) |
|---|---|---|---|
| IS8 | 25 | 2·12 | 2·05 |
| | 31 | 2·34 | 2·13 |
| | 36 | 2·30 | 2·09 |
| | 46 | 2·22 | 2·09 |
| IS9 | 20 | 4·32 | 4·67 |
| | 30 | 4·18 | 4·65 |
| | 46 | 4·43 | 4·78 |
| IS10 | 25 | 3·26 | 2·06 |
| | 30 | 3·58 | 2·18 |
| | 46 | 3·54 | 2·34 |

## Discussion

The dimensions of linear flexible molecules may be obtained from either viscosity or light scattering data. The former measures the end-to-end distance or the hydrodynamic volume whereas the latter measures the radius of gyration. For molecules where the radial distribution of segments about the centre of gravity is Gaussian, or not too far from Gaussian, the two quantities are related according to equation (2).[16] However, determination of the true radius of gyration is difficult in the case of block copolymers. The radius of gyration obtained by the usual method applied to homopolymers, that is from the limiting slope of $Kc/R_\theta$ as $c \to 0$, yields an apparent value only.[13] For a block copolymer of weight fraction in $A$ equal to $x$ with two types of segments having refractive index increments $\nu_{\mathrm{A}}$, $\nu_{\mathrm{B}}$, and $\nu_{\mathrm{cop}}$ for the copolymer, the expression for the radius of gyration is

$$\langle \bar{s}^2\rangle_{\mathrm{app}} = \alpha^2\langle \bar{s}^2\rangle_{\mathrm{A}} + \beta\langle \bar{s}^2\rangle_{\mathrm{B}} + 2\alpha\beta\langle \bar{s}^2\rangle_{\mathrm{AB}}$$

where $\alpha = \mathrm{x}\nu_{\mathrm{A}}/\nu$, $\beta = (1-\mathrm{x})\nu_{\mathrm{B}}/\nu$, and $\langle \bar{s}^2\rangle_{\mathrm{AB}}$ is defined by

$$\langle \bar{s}^2\rangle_{\mathrm{AB}} = \tfrac{1}{2}\{\langle \bar{s}^2\rangle_{\mathrm{A}} + \langle \bar{s}^2\rangle_{\mathrm{B}} + (G_{\mathrm{A}}G_{\mathrm{B}})^2\}$$

$(G_{\mathrm{A}}G_{\mathrm{B}})^2$ is the mean square distance of the centre of gravity of blocks A and B. In principle, at least, we should be able to measure $\langle \bar{s}^2\rangle_{\mathrm{A}}$, $\langle \bar{s}^2\rangle_{\mathrm{B}}$, and $(G_{\mathrm{A}}G_{\mathrm{B}})^2$ by determinations in three different solvents with sufficiently different values of $\mathrm{d}n/\mathrm{d}c$. However, the volume effect should be negligible and the sample uniform in composition. The former is difficult to achieve, practically, due to the limitation on the volume effect in

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[16] Florey, P. J., "Principles of Polymer Chemistry." Ch. 10. (Cornell University Press: Ithaca, N.Y., 1953.)

each solvent. Nevertheless, the change in apparent radius of gyration should be useful as a measure of the change in the effective hydrodynamic volume.

The test usually applied as to whether the intrinsic viscosity is related to the change in the hydrodynamic volume according to equation (1) is whether the Mark–Houwink equation is obeyed.

Plots of $\log[\eta]$ against $\log M$, for these polymers with a range of molecular weights of 100000, 250000, 500000 at constant composition, showed that a linear relationship held for all samples, at each temperature. Consequently, we might reasonably expect some sort of correlation between viscosity and light scattering and in fact, comparison of $\langle \bar{s}^2 \rangle^{1/2}$ calculated directly from light scattering and indirectly from viscosity, assuming equation (2), is very encouraging. The correlation is within about 5% in IS8 and 7–8% in IS9. The values are much greater for IS10 (up to 30% variation). The reason for this is obscure at present.

The values of $K$ in the Mark–Houwink equation, obtained from the logarithmic plots of $[\eta]$ against $M$, reflected the volume change fairly well. The exponent was approximately $0 \cdot 8$ for all plots, except at 20° when the exponent rose to $1 \cdot 0$. However, the error is relatively large with only three points and therefore a critical analysis seems inappropriate without a more detailed exploration.

The graphs of $\langle \bar{s}^2 \rangle^{1/2}$ against $T$ show a remarkable similarity to the viscosity curves and considering the larger errors in light scattering due to the small change in $\langle \bar{s}^2 \rangle^{1/2}$ the correlation is good. The viscosity results probably reflect the changes in the hydrodynamic volume much more accurately but the light scattering data add weight to the argument. It has been shown[17,18] that, for homopolymers, the hydrodynamic radius from viscometry is less sensitive to solvent power than is the radius of gyration and the situation here is much more complex. It seems most likely however that the discontinuity observed is due to a change in hydrodynamic volume and this infers that there has been a conformational change. The correlation between the data obtained by these two independent methods encourages us to believe that this substantiates the previously postulated intramolecular phase transition, from a phase-separated to a phase-mixed form, as the temperature is raised through $T_p$ and that the spherical particle model[19] represents the overall conformation fairly well at infinite dilution.

It is interesting to speculate on the radial distribution of segments for this model. In the phase-separated region the inner sphere of polystyrene would have a high segment density and the outer region containing isoprene a rather low segment density. In view of the incompatibility there would be a node at the interface region almost corresponding to a void. On phase mixing, we could expect a pseudo-Gaussian distribution as the polystyrene segments move out into the polyisoprene domain and vice versa.

The theory of viscosity for various models of homopolymers predicts that the semi-permeable coil should have an exponent in the Mark–Houwink equation from $0 \cdot 5$ to $0 \cdot 8$ and for a free-draining coil an exponent of $1 \cdot 0$ or greater. It seems plausible, therefore, that the rise in the exponent from about $0 \cdot 8$ to $1 \cdot 0$ at 20° may be real and perhaps due to the conformational change from a semi-permeable coil, which would be

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[17] Kurata, M., and Yamakawa, H., *J. chem. Phys.*, 1958, **29**, 311.

[18] Ptitsyn, O. B. and Eisner, Y. Y., *J. tech. Phys. USSR*, 1959, **29**, 1117.

[19] Urwin, J. R., *Aust. J. Chem.*, 1969, **22**, 1649.

expected for the pseudo-Gaussian segmental distribution at temperatures above $T_p$, to the separated conformation which may approach the free-draining structure at temperatures below $T_p$. This is of course a purely speculative and qualitative approach.

## ACKNOWLEDGMENT

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# CONFORMATIONAL TRANSITIONS IN SOLUTIONS OF BLOCK COPOLYMERS IN MIXED SOLVENTS

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**Abstract**—Intrinsic viscosity vs. composition curves of block copolymers of polyisoprene and polystyrene in a mixed solvent (cyclohexane + *n*-heptane) show a transition at a critical composition ($\gamma_c$) provided the temperature of the system is above a conformational transition temperature ($T_p$) found previously in [$\eta$] vs. $T$ plots in the single solvent cyclohexane. The plots of [$\eta$] vs. $\gamma$ at temperature below $T_p$ show no such discontinuity. It is proposed that $\gamma_c$ represents the composition of the mixed solvent for which $T_p$ is the same as the experimental temperature or a solvent of composition $\gamma_c$ would show a conformational transition $T_p = T$ where $T$ is the temperature of the system.

## INTRODUCTION

IN ATTEMPTING to extend the study of the solution properties of the block copolymers, we have shown in a previous publication that a conformational transition exists in the intrinsic viscosity vs. temperature curve for block copolymers of polystyrene + isoprene in cyclohexane as a single solvent. It was attributed to an intramolecular phase transition from a phase-separated to a phase-mixed conformation. Preliminary results with methyl cyclohexane and decalin as solvents show the same phenomenon. The transition temperature $T_p$ seems therefore to represent the temperature at which the free energy of mixing for this particular system is zero. Above $T_p$, a mixed phase is considered to exist whereas below $T_p$ a phase separated conformation must occur.

In this study we have employed a mixed solvent containing cyclohexane, a good solvent for polyisoprene but a theta solvent for polystyrene at 34°, and *n*-heptane which is also a good solvent for polyisoprene but a non-solvent for the polystyrene moiety. With this system, the solvent may be made progressively poorer for the polystyrene sequence in the block copolymer and therefore provide a wide range of solvents with variable theta temperatures for polystyrene. A plot of [$\eta$] vs. composition of the solvent ($\gamma$) at temperatures above $T_p$ produces a transition similar in character to the [$\eta$] vs. $T$ plot in a single solvent. In both cases the plot is really [$\eta$] vs. a parameter defining a progressively better solvent with rise in temperature or increasing cyclohexane content, therefore the general behaviour is expected to be similar. On the other hand, at temperatures below $T_p$, the intramolecular phase transition would not be expected since the phase-separated conformation must always exist.

## EXPERIMENTAL

The block copolymers were synthesized anionically with butyl lithium initiator in benzene, following the general method described in detail elsewhere.(4) All glass, greaseless apparatus was employed using generally accepted high vacuum techniques. Vessels were flamed out and evacuated to $10^{-5}$ torr. Prepurging of apparatus, monomers and solvents was carried out with a mixture of low molecular weight polystyrllithium and butyl lithium. The monomers were allowed to stand over the mixture for 0·5–1 hr at 0° for styrene and at room temperatures for isoprene. The polymers were isolated by precipitation from benzene solution with dry methanol, then dried and stored in vacuum. Antioxidant was added during the precipitation. The polymers were analysed by gel permeation chromatography for distribution of molecular weight.[5] A single curve was obtained for the polymers which indicated the complete absence of extraneous homopolymer. $\overline{M}_w$ and $\overline{M}_n$ were determined by light scattering and osmometry respectively. The heterogeneity ratio $\overline{M}_w/\overline{M}_n$ was 1·05–1·10 for the whole range of polymers.

The composition was obtained from the optical density of chloroform solutions at 262 nm by u.v. spectrophotometry. The method yields the percentage polystyrene in the copolymer. N.M.R. analysis[6] of copolymer with the lowest polystyrene content showed a high *cis* 1,4 content in the block copolymers similar to that found in samples of pure polyisoprene prepared using the same initiator and solvent.

The viscometer was the Ubbelohde suspended level type with flared capillaries[7] to eliminate end corrections. Flow times for the solvents exceeded 200 sec in each case. An automatic timing device was used, constructed according to the design of Steel.[8] Two photocells are placed above and below the top bulb of the viscometer, the optical system is then arranged so that a beam of light is scattered from the walls of the capillary when empty but which allows the beam to pass through the capillary when filled with solvent or solution. The photocells form two arms of a Wheatstone bridge so that a current large enough to trigger an electronic timer flows when the bridge is unbalanced. When the viscometer is filled with solution, the timing circuit does not operate but is triggered by the solution passing the top photocell and cancelled by the solution flowing past the lower photocell. The time of flow is reproducible to 0·05 sec. Evidence for non-Newtonian behaviour was sought using several capillaries with different flow times; none could be found and it was concluded that the viscosities were independent of the shear rate.

## RESULTS

A plot of $[\eta]$ vs. the solvent composition ($\gamma$), expressed as a percentage of cyclohexane by volume, is shown in Fig. 1 for the block copolymer I.S. 10 containing 50% by weight of polystyrene. The curves are typical of the plots observed at a temperature above and below $T_p$. In this case, where $T_p = 26°$, the upper curve which shows the expected peak due to the conformational transition was determined at 35°. The lower

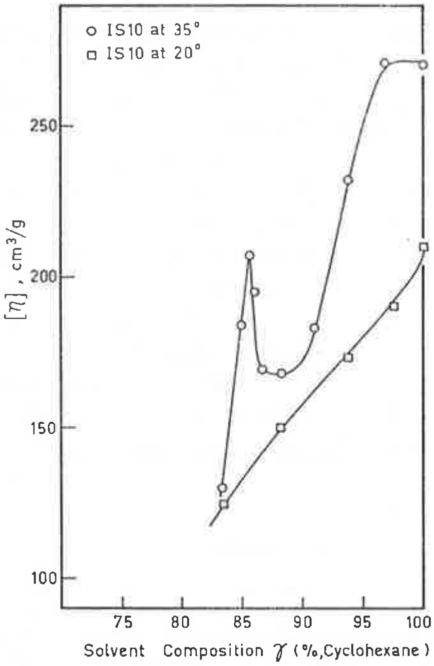

FIG. 1. Intrinsic viscosities as a function of the composition ($\gamma$) of the solvent, expressed as % cyclohexane in its mixture with *n*-heptane.

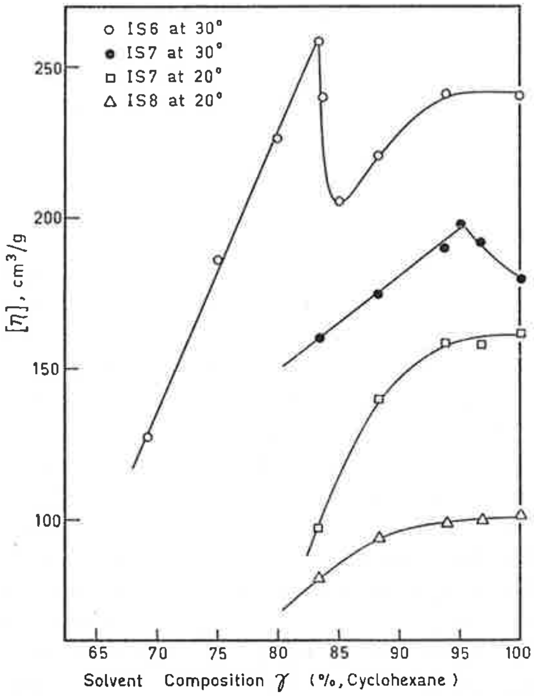

FIG. 2. Intrinsic viscosities as a function of the composition ($\gamma$) of the solvent, expressed as % cyclohexane in its mixture with $n$-heptane.

curve which was measured at 20° shows the absence of any peak in the region of interest, i.e. the region between 86% cyclohexane and pure cyclohexane. This is based on the simple argument that the poorer the solvent the earlier should be the appearance of the transition and, since lowering of the temperature produces a poorer solvent, the peak should occur at a composition with more than 86% cyclohexane. Three other block copolymers, with molecular weight only half that for I.S. 10, were also examined in the same way (see Fig. 2). However, on practical grounds only I.S. 7 was explored at temperatures above and below $T_p$. I.S. 6 was examined above $T_p$, but not below, because of the low value of $T_p$ (15°). Similarly I.S. 8 was run at a temperature below $T_p$ (31°),

TABLE 1. CRITICAL COMPOSITION OF THE MIXED SOLVENT ($\gamma_c$) FOR THE PARTICULAR COPOLYMER AT THE STATED TEMPERATURE

| Polymer | $T$ (°C) | $\overline{M}_n \times 10^{-5}$ | Block copolymer composition (% polystyrene) | $\gamma_c$ % Cyclohexane | $T_p$ (°C) |
|---|---|---|---|---|---|
| I.S. 6 | 30 | 2·54 | 11·8 | 83 | 15 |
| I.S. 7 | 30 | 2·49 | 25·5 | 95 | 24·5 |
| | 20 | — | — | No peak | — |
| I.S. 8 | 20 | 2·48 | 48·5 | No peak | 31 |
| I.S. 10 | 35 | 4·97 | 49·7 | 86 | 26 |
| | 20 | — | — | No peak | — |

but not above, because of the rather high value. All the plots of $[\eta]$ vs. the composition of the solvent show the expected behaviour, depending upon whether they are above or below $T_p$. The values of $\gamma_c$, the critical composition of the solvent at which the peak in the curve appears for the given temperature $T$ ($T = T_p$ for the particular composition) are given in Table 1. Values of $T_p$ in pure cyclohexane are listed for easy reference in the Discussion.

## DISCUSSION

A qualitative explanation of the transition in the $[\eta]$ vs. solvent composition, at constant $T$, curve could resemble that given in the earlier description of the $[\eta]$ vs. $T$ plot in cyclohexane.(3) There is, of course the additional factor, that the solvent may be better or worse for polyisoprene than cyclohexane as the concentration of *n*-heptane is increased. The evidence for this, based on the values of the cohesive energy density for *n*-heptane ($\delta = 7{\cdot}4$) and polyisoprene is conflicting. Values of $\delta$ are the same if the calculated value for polyisoprene is accepted as the true value.(9) However, the values derived from swelling studies appear to average at 8·05 suggesting that *n*-heptane is a poorer solvent than cyclohexane. ($\delta$ for natural rubber ranges from 7·9 to 8·35.) Considering the pure cyclohexane end of the composition scale, the addition of *n*-heptane results in the solvent becoming progressively poorer in a similar manner to that produced by the lowering of the temperature in pure cyclohexane. The collapse of the molecule which follows the addition of *n*-heptane is therefore to be expected and is reflected in the decrease in $[\eta]$. Two factors may be operating at this point, firstly there is the overall collapse of the whole molecule due to a process of desolvation at least of the polystyrene sequence and possibly the polyisoprene also; this is a segment–solvent effect. The second factor which may be considered likely to influence $[\eta]$ would be the expansion due to repulsions between unlike segments of the polymer chain. This is probably ineffective in its influence on $[\eta]$ until the molecule approaches the critical composition $\gamma_c$. The value at the peak ($\gamma_c$) represents the composition of the mixed solvent for which $T_p$ is the same as $T$ in the experiment. In other words a solvent of composition $\gamma_c$ would show conformational transition at $T_p = T$. However, as the point $\gamma_c$ is approached, the repulsions between heterocontacts become important and the fall in $[\eta]$ is halted. Further addition of *n*-heptane would result in $[\eta]$ increasing up to the value at $\gamma_c$.

At the transition point, we assume that a change in conformation from phase-mixed to phase-separated form occurs and is followed by continued collapse of the molecule with further desolvation. An alternative explanation, based on the change in environment, was given in the paper on $[\eta]$ vs. $T$ in cyclohexane.(3) The plots at the lower temperature show no discontinuity as was expected from the previous study in cyclohexane. We conclude that this indicates a phase-separated conformation below $T_p$.

It is of interest to note the relative positions of the peak in the $[\eta]$ vs. $\gamma$ curve with respect to composition of the polymer. As the styrene content increases the peak falls below the final value of $[\eta]$ in cyclohexane. This is shown in the curves above $T_p$ for I.S. 6 and I.S. 10 where there is a pronounced drop with increase in polystyrene content from 12 to 50 per cent. However, this trend is not observed when comparing I.S. 6 and I.S. 7. Of course, the influence of molecular weight would have to be considered also in explaining this effect. The reasons for this behaviour and the absence of a minimum in the I.S. 7 curve are ambiguous.

Inspection of the results listed in Table 1 shows that $\gamma_c$ increases with increasing polystyrene content. This is quite evident from comparison of the values for I.S. 6 and I.S. 7. The trend is consistent with the similar behaviour in the values of $T_p$ found in cyclohexane. By analogy therefore, we can expect that $\gamma_c$ will decrease with increasing molecular weight. As was observed in the study in pure cyclohexane and also in this study, the difference between $[\eta]$ at the minimum and at the peak is large. For I.S.10 and I.S. 6 it is more than 25 per cent of the absolute value. This is in contrast to the much smaller (5–10 per cent) change observed on graft copolymers of poly di phenyl-3-3-propene + polystyrene.$^{(10)}$

It would be quite feasible, once a few points have been established, to select a range of solvents for other studies and thereby extend the rather limited range of solvents available for solution studies, for this system in this region. The present work reinforces the explanation given previously that the discontinuity in the $[\eta]$ vs. $T$ plot represents a conformational transition from a phase-mixed to phase-separated form. The phenomena is essentially the same whether the method of decreasing the solvent power is by lowering of the temperature or by addition of a non-solvent for the polystyrene sequence.

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## REFERENCES

(1) D. N. Crammond and J. R. Urwin, *Europ. Polym. J.* **5,** 35, 45 (1968).
(2) J. R. Urwin, *Aust. J. Chem.* **22,** 1649 (1969).
(3) M. Girolamo and J. R. Urwin, *Europ. Polym. J.* **7,** 693 (1971).
(4) D. N. Cramond and J. R. Urwin, *Aust. J. Chem.* **21,** 1835 (1968).
(5) D. N. Cramond, J. M. Hammond and J. R. Urwin, *Europ. Polym. J.* **4,** 451 (1968).
(6) H. Y. Chen, *Analyt. Chem.* **34,** 1793 (1962).
(7) W. A. Caw and R. C. Wylie, *Brit. J. appl. Phys.* **12,** 94 (1961).
(8) B. J. Steel, *J. scient. Instrum.* **42,** 751 (1965).
(9) J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook.* Interscience, New York (1966).
(10) A. Dondos, *Makromol. Chem.* **99,** 275 (1966).

**Résumé**—Les courbes représentant la variation de la viscosité intrinsèque en fonction de la composition de copolymères séquencés de polyisoprène et de polystyrène dans un solvant mixte (cyclohexane + *n*-heptane) présentent une transition pour une composition critique ($\gamma_c$) à condition que la température du système soit supérieure à une température de transition de conformation ($T_p$) déterminée précédemment au moyen des courbes de $[\eta]$ en fonction de $T$ dans un solvant unique: le cyclohexane. Les courbes de $[\eta]$ en fonction de $\gamma$ obtenues pour des températures inférieures à $T_p$ ne présentent pas une telle discontinuité. On propose que $\gamma_c$ représenterait la composition du solvant mixte pour laquelle $T_p$ est identique à la température de l'expérience ou qu'un solvant de composition $\gamma_c$ présenterait une température de transition conformationnelle $T_p = T$, $T$ étant la température du système.

**Sommario**—La viscosità intrinsica vs. curve di composizione di blocchi copolimeri di polisoprene e polistirene in un solvente misto (cicloexane + *n*-eptane) dimostrano una transizione ad una composizione critica ($\gamma_c$) a condizione che la temperatura del sistema sia al disopra di una temperatura transitoria di conformazione ($T_p$) trovatasi prima in $[\eta]$ vs. $T$ gruppi nel solvente singolo cicloexane. Il gruppo $[\eta]$ vs. $\gamma$ a temperature al disotto di $T_p$ non fanno vedere tale discontinuità. Si propone che $\gamma_c$ ripresenti la composizione del solvente misto per il quale $T_p$ è lo stesso che la temperatura sperimentale o un solvente di composizione $\gamma_c$ o un solvente di composizione $\gamma_c$ dimostrerebbe una transizione conformazionale $T_p = T$ dove $T$ è la temperatura del sistema.

**Zusammenfassung**—Die Kurven der Grenzviskosität gegen die Zusammensetzung von Block-Copolymeren aus Polyisopren und Polystyrol in einem gemischten Lösungsmittel (Cyclonexan + *n*-Heptan) zeigen bei einer kritischen Zusammensetzung ($\gamma_c$) einem Übergang, wenn die Temperatur

des Systems über der Konformations umwandlungstemperatur ($T_p$) liegt, die kürzlich für das einfache Lösungsmittel Cyclonexan aus Auftragungen von $[\eta]$ gegen $T$ gefunden wurde. Eine klarunge Diskontinuität zeigen, auftragungen von $[\eta]$ gegan $\gamma$ bei Temperaturen unter $T_p$ nicht. Es wird vorschlagen daß $\gamma_c$ die Zusammensetzung des gemischten Lösungsmittels vorstellt für die $T_p$ gleich ist methoden experimentellen Temperatur oder ein Lösungsmittel der Zusammensetzung $\gamma_c$ würde eine Konformations umwandlungtemperatur $T_p = T$ wobei $T$ die Temperatur des System ist.

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# Intramolecular Phase Transitions of Block Copolymers in Solution from Viscosity – Temperature Studies

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# Intramolecular Phase Transitions of Block Copolymers in Solution from Viscosity – Temperature Studies

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(Eingegangen am 15. Februar 1971)

## SUMMARY:

Intrinsic viscosity against temperature plots for two sequence block copolymers of isoprene and styrene in decalin and methyl cyclohexane confirm the general behaviour of these polymers in preferential solvents. The operative parameters are the mol. wt., composition and Θ temperature of the less soluble polymer in the particular solvent. The Stockmayer-Fixman relation $[\eta]\overline{M}_n^{-1/2} = \Phi_0(A_\eta^3 + 0.51\, B_\eta \overline{M}_n^{1/2})$ is obeyed, for a particular composition, at all temperatures, but the unperturbed dimensions in the block appear to drop significantly at temperatures below the transition temperature. Since the constant $\Phi_0$ is influenced by the segmental distribution, the drop in unperturbed dimensions may be considered to reflect the conformation change from the phase-mixed to phase-separated form. The characteristic ratio, $C_\infty = \langle r^2 \rangle_0 / nl^2$, which is calcd. from K in the Kuhn-Mark-Houwink Eq. determined directly from $[\eta]_0$ ($\Theta = 44\,°C$ in methyl ethyl ketone) is identical with that obtained by extrapolation using the Stockmayer-Fixman relation at 46 °C. Moreover, $C_\infty$ may be calcd. directly from $C_{\infty\text{Block}} = xC_{\infty\text{PS}} + (1-x)C_{\infty\text{PI}}$ after taking account of the isomeric composition of the polyisoprene.

## ZUSAMMENFASSUNG:

Die Auftragung der Grenzviskositäten der aus einem Isopren- und einem Styrol-Block bestehenden, in Decalin bzw. Methylcyclohexan gelösten Blockcopolymeren als Funktionen der Temperatur bestätigen das allgemeine Verhalten dieser Polymeren in bevorzugten Lösungsmitteln. Die eingehenden Parameter sind das Mol.-Gew., die Zusammensetzung und die Θ-Temperatur des in diesem speziellen Lösungsmittel weniger löslichen Polymeren. Die Stockmayer-Fixman-Beziehung $[\eta]\overline{M}_n^{-1/2} = \Phi_0(A_\eta^3 + 0{,}51\, B_\eta \overline{M}_n^{1/2})$ ist bei einer speziellen Zusammensetzung für alle Temperaturen erfüllt, die ungestörten Dimensionen in dem Block scheinen jedoch bei Temperaturen unterhalb der Übergangstemperatur bemerkenswert abzunehmen. Da die Konstante $\Phi_0$ von der Segmentverteilung beeinflußt wird, kann die Abnahme der ungestörten Dimensionen auf einer Konformationsänderung beim Übergang vom Ein- zum Zweiphasensystem beruhen. Das charakteristische Verhältnis, $C_\infty = \langle r^2 \rangle_0 / nl^2$, berechnet aus dem Wert für K der Kuhn-Mark-Houwink-Gleichung, welcher direkt aus $[\eta]_0$ bestimmt wurde ($\Theta = 44\,°C$ in Methyläthylketon), ist mit dem Verhältnis, das durch Extrapolation unter Verwendung der Stockmayer-Fixman-Beziehung (Versuchstemperatur 46 °C) erhalten wurde, identisch. Außerdem kann $C_\infty$ unter Berücksichtigung der isomeren Zusammensetzung des Polyisoprens direkt aus $C_{\infty\text{Block}} = xC_{\infty\text{PS}} + (1-x)C_{\infty\text{PI}}$ berechnet werden.

## *Introduction*

The plots of intrinsic viscosity against temperature for AB type block copolymers of polyisoprene and polystyrene exhibit an intramolecular phase transition at a specific temperature in cyclohexane, methyl cyclohexane, decalin, and mixtures of cyclohexane and *n*-heptane. The viscosity of the mixtures is best studied as a function of the composition of the mixture. The critical temperature, $T_p$, or the critical composition, $\gamma_c$, corresponding to a particular value of $T_p$, appears to mark the point of zero free energy of mixing for the copolymer and the solvent. Intramolecular phase separation must occur below $T_p$ and a phase mixed conformation above it.

Viscosity-temperature studies in cyclohexane and in the mixed solvent have been reported previously[1,2]. In the present paper the results in two other solvents, methylcyclohexane and decalin, are presented and the situation is summarized as briefly as is consistent with clarity. Discontinuities in the plot of $[\eta]$ against T were observed in the solvents examined similar to that observed in cyclohexane, thereby demonstrating the general nature of the transition in preferential solvents, that is, those solvents which are good solvents for one sequence of the block copolymer but which are poor solvents for the other sequence. The number of solvents suitable for use in these studies is, unfortunately, limited and the temperature range over which the phenomenon may be observed is restricted by volatility at higher temperatures and thermostating problems at the lowest temperatures.

Results in a solvent with a $\Theta$ temperature for polystyrene above cyclohexane together with another just below that for cyclohexane are reported here. The applicability of viscosity theory to these solutions is examined in some detail.

## *Experimental*

The synthesis of "model" block copolymers suitable for solution studies has been discussed earlier[3]. The polymers used in this work were synthesized by this technique. They were all well characterized two sequence blocks containing polystyrene and polyisoprene (80% *cis*-1.4 isomer) without either homopolymer being present. All polymers were checked regularly, for signs of degradation, by gel permeation chromatography[4].

The chromatograms showed the polymers to be of narrow mol. wt. distribution with a width of distribution expressed as $\overline{M}_w/\overline{M}_n \leqslant 1.14$. Light scattering studies using a Sofica 4200 photogoniometer to measure $\overline{M}_w$ and osmometry using a Hewlett-Packard Mechrolab 501 osmometer to obtain $\overline{M}_n$ (Table 1) confirmed this result. Compositions in terms of polystyrene content were obtained by UV spectrophotometry at 262 and 269 nm using the method described by BURNETT *et al.*[5] ($E_{max} = 2.21$ was employed).

The microstructure was determined by PMR spectroscopy on a Varian H.A. 60 spectrometer. Unfortunately, for this system the PMR peaks normally used to determine the various isomers (peaks No. 5, 5 a, according to CHEN's[6] assignment) also contain a contribution from the polystyrene in the block. Assuming the same composition as that found in pure polyisoprene synthesised with the same initiator and observing the same conditions of synthesis, it was found that the amount to be substracted, when calculating the *cis*-1.4 content, was a linear function of the polystyrene content. A suitable correction can be applied according to the Eq. % *cis*-1.4 = $A_{5a}/A_5(1 - 0.6w)$ where $A_{5a}$ and $A_5$ are the areas under peak 5a, the total under peak 5 and w is the weight fraction of polystyrene.

Viscosities were measured with suspended level viscometers fitted with an automatic timing device which gave reproducible flow times to 0.05 sec with all times in excess of 200 sec. Experiments showed that there was no evidence of non-NEWTONian behaviour in any of these solutions.

## *Results and Discussion*

The block copolymers investigated in decalin and methyl cyclohexane had a constant molecular weight 250000 but variable compositions, namely 11.8, 25.5, and 48.5% polystyrene by weight. The two solvents differed

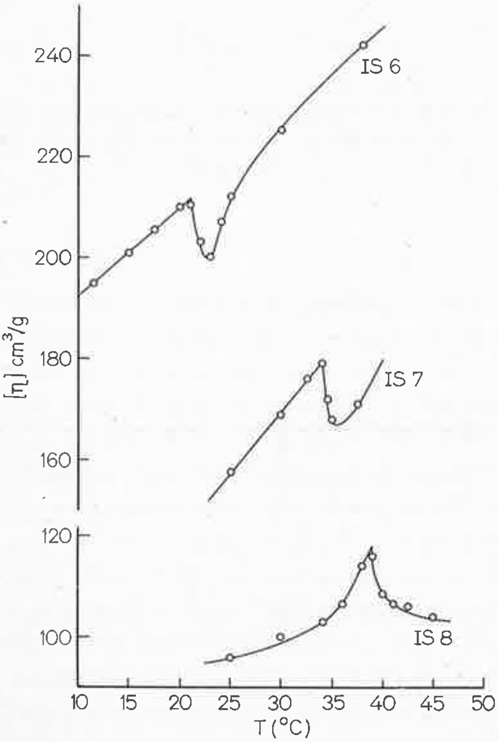

Fig. 1. Intrinsic viscosity *vs.* temperature for block copolymers of isoprene and styrene in methyl cyclohexane

in that the Θ temperature for polystyrene in these solvents is 71 °C in methyl cyclohexane and 31 °C in decalin, that is on either side of the value in cyclohexane (34 °C). Methyl cyclohexane is thus the poorer solvent for polystyrene. Curves of intrinsic viscosity *vs.* temperature are shown for methyl cyclohexane in Fig. 1 and for decalin in Fig. 2. The typical discontinuity observed in cyclohexane, resulting in a peak in the curve, can be seen for each polymer. The depth from peak to trough is somewhat smaller than that observed for cyclohexane but the drop in $[\eta]$ after reaching the peak is still quite marked. It is also interesting to note that the minimum has not yet appeared in IS8 in methyl cyclohexane as was also observed with the solvent cyclohexane, however it is clearly observed with the same polymer in decalin. The temperature corresponding to the peak has been tabulated for these polymers in both solvents in Table 1. Values in cyclohexane include the results from two polymers with compositions similar to IS7 and IS8 but with molecular weights double that of IS6–IS8. The results on one other polymer in this solvent (IS4), not previously reported, have been included for the purposes of discussion. The last column gives the temperature at which peaks occur in a mixed

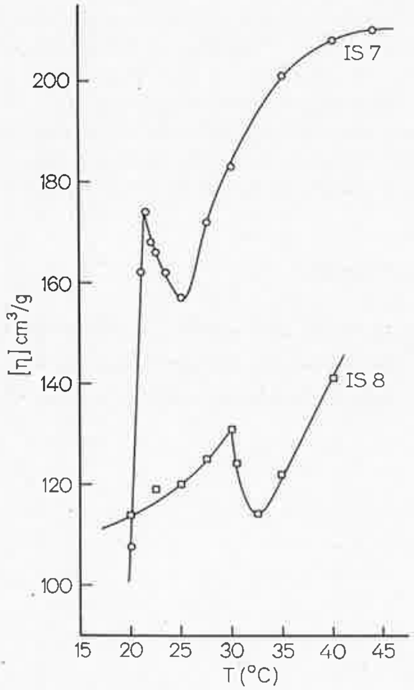

Fig. 2. Intrinsic viscosity *vs.* temperature for block copolymers of isoprene and styrene in decalin

Table 1. Conformational transition temperature $T_p$ for block copolymers of polystyrene and polyisoprene

| Polymer | $\overline{M}_n \cdot 10^{-5}$ | Composition % polystyrene | $T_p$ (°C) cyclo-hexane | methyl cyclohexane | decalin | mixed solvent |
|---|---|---|---|---|---|---|
| IS4 | 1.04 | 52.2 | 32 | | | |
| IS6 | 2.54 | 11.8 | 15 | 21 | | 30(83) |
| IS7 | 2.49 | 25.5 | 24.5 | 34 | 21.5 | 30(95) |
| IS8 | 2.48 | 48.5 | 31 | 39 | 30 | |
| IS9 | 4.97 | 25.1 | 20 | | | |
| IS10 | 4.97 | 49.7 | 26 | | | 35(86) |

Figures in brackets are percentage cyclohexane in the mixed solvent.

solvent of cyclohexane and *n*-heptane and have been included since they correspond to $T_p$ for the polymers in these specific mixtures.

Inspection of Table 1 shows that $T_p$ is similar in solvents with similar $\Theta$ temperatures for polystyrene in those solvents. The value of $\Theta$ for polystyrene seems therefore to be one controlling factor. The values of $T_p$ are obviously highest in the poorest solvent for polystyrene; *e.g.* compare the values for cyclohexane and methyl cyclohexane. The same effect can be observed by comparing $T_p$'s for IS6 and IS7 in pure cyclohexane and the values in the mixtures of cyclohexane and *n*-heptane, *i.e.* 83 and 95 % cyclohexane respectively. IS10 shows a significant increase in 86 % cyclohexane when compared with the pure solvent. It is also clear that $T_p$ is a function of the composition; $T_p$ is greater with increasing styrene content. Finally, $T_p$ is also a function of the molecular weight, this is seen by comparing the values for IS7 with IS9 and IS8 with IS10. $T_p$ actually decreases with increasing molecular weight. To sum up, $T_p$ has been shown to be a function of molecular weight, composition and the $\Theta$ temperature of the least soluble polymer in the particular solvent.

The temperature at which the peak in the $[\eta]$ against T plot occurs may be taken to represent the temperature where the free energy of mixing of the copolymer and the solvent becomes zero. Above this temperature ($T_p$) a mixed phase is possible but below it, phase separation must occur. In an attempt to demonstrate that this explanation was viable, we prepared films from solutions of the blocks and determined the glass transition temperature when the films were cast at temperatures (i) well above $T_p$ and (ii) well below $T_p$. The films cast from temperatures below $T_p$ showed two $T_g$'s representing pure polystyrene and pure polyisoprene. On the other hand, thermograms of casts from temperatures above $T_p$

showed the same $T_g$ for polyisoprene, but a new $T_g$ appeared, which was found to be a simple function of the polystyrene content. We concluded that this new $T_g$ corresponded to a mixed phase and that the continued existence of $T_g$ for isoprene was due to the large excess of that polymer in the block and also was related to the casting process[7]. This evidence is based on materials cast from solutions which are progressively concentrated during the casting. Nevertheless, we consider it to be a strong support for the interpretation given to the viscosity behaviour of the dilute solutions.

More recently light scattering data have been shown to reinforce the viscosity studies[8], in that the apparent radius of gyration showed the same behaviour with respect to temperature as viscosity. Further confirmatory evidence comes from the absence of any peak in the $[\eta]$ *vs.* solvent composition plots in mixed solvents at temperatures below $T_p$ where intramolecular phase separation has already taken place.

In view of the observation that the light scattering data indicated a close correlation between the change in radius of gyration and the variation in intrinsic viscosity, it can be accepted that we are observing a change in hydrodynamic volume. It is of interest therefore to discover just how far the MARK-HOUWINK Eq. is obeyed. Only the results in cyclohexane are extensive enough, in view of the practical temperature range restriction, to be useful for this purpose. Firstly the HUGGINS and KRAEMER constants in the well known Eqs.

$$\eta_{sp}/c = [\eta] + k'[\eta]c \qquad (1)$$

$$\ln \eta_{rel}/c = [\eta] - k''[\eta]c \qquad (2)$$

were found to obey the relation $k' + k'' = 0.5 \pm 0.03$ in good agreement with homopolymers[9]. The exponent "a" in the viscosity-molecular weight Eq.

$$[\eta] = KM^a \qquad (3)$$

obtained from logarithmic plots of $[\eta]$ *vs.* $\overline{M}_n$ remained constant at 0.8 for all temperatures except 20 °C when it rose to 1.0. This suggests a change in conformation of some sort at this lower temperature.

To investigate the matter further, we must attempt to estimate the unperturbed dimensions and, if possible, the effect and extent of long range interactions, particularly with regard to hetero-contacts between different segments. Unperturbed dimensions have been obtained from intrinsic viscosity-molecular weight data, irrespective of the solvent, provided the hydrodynamic draining effect is negligible, by application of the relation[9]

$$[\eta] = KM^{1/2}\alpha_\eta^3 \qquad (4)$$

where $\alpha_\eta$ is the viscosity expansion factor and

$$K = \Phi_0(\langle r^2\rangle_0/M)^{3/2} \tag{5}$$

in which $\Phi_0 = 2.68 \cdot 10^{23}$ is the universal viscosity constant in theta solvents[10], $\langle r^2\rangle_0$ is the average, unperturbed square of the end-to-end distance.

STOCKMAYER and FIXMAN[11] have shown that by substituting

$$\alpha_\eta^3 = 1 + 1.55z \tag{6}$$

where

$$z = (3/2\pi)^{3/2}B(\langle r^2\rangle_0/M)^{-3/2}M^{1/2} \tag{7}$$

into Eq. (4) and combining Eq. (5) leads to the simple Eq.

$$[\eta] = KM^{1/2} + 0.51\,\Phi_0 BM \tag{8}$$

which gives a clean separation of the short and long range interactions. Graphically, $[\eta]M^{-1/2}$ is plotted against $M^{1/2}$. The ordinate intercept yields K, and the slope, the long range parameter B. Alternatively the binary cluster integral $\beta$ may be directly calculated from B with the aid of the relation

$$B = \beta/M_0^2 \tag{9}$$

where $M_0$ is the molecular weight of the statistical segment, which in the case of the block copolymer is given by

$$M_{0B} = \sum_i M_{0i}x_i \tag{10}$$

thus Eq. (9) for the block copolymer becomes

$$B_B = \beta_B/M_{0B}^2 \tag{11}$$

and, of course, $\beta_B$ contains contributions from similar as well as different segments[12,13].

Table 2. Values for K and B of the STOCKMAYER-FIXMAN relation at various temperatures and the limiting characteristic ratio $C_\infty$ for block copolymers in cyclohexane

| Temp. (°C) | $K \cdot 10^2$ (ml/g) | $(\langle r^2\rangle_0/M)^{1/2} \cdot 10^{11}$ | $C_\infty$ meas. | $B \cdot 10^{28}$ |
|---|---|---|---|---|
| 20 | 1.0 | 334 | 1.3 | 28 |
| 25 | 6.1 | 611 | 4.3 | 23 |
| 30 | 5.0 | 572 | 3.8 | 34 |
| 35 | 8.5 | 683 | 5.3 | 29 |
| 46 | 11.6 | 756 | 6.6 | 25 |
| Θ[a] | 11.63 | 757 | 6.57 | |

[a] Direct measurements in Θ-solvent, *i.e.* MEK at 44°C.

Data for the block copolymers which have been studied are only sufficient in cyclohexane. In this solvent $[\eta]$ has been examined at constant composition (50 wt.-%) for molecular weights $10 \cdot 10^4$ (IS4); $25 \cdot 10^4$ (IS8); $50 \cdot 10^4$ (IS10), over the temperature range 20 to 46 °C. Plots of $[\eta]M^{-1/2}$ against $M^{1/2}$ were linear at all temperatures. The intercept K and parameter B obtained from the slope are given in Table 2 for each temperature. The intercept at 20 °C is seen to be noticeably smaller than at the other temperatures.

Values for $(\langle r^2\rangle_0/M)^{1/2}$ have been calculated from the intercepts using $\Phi_0 = 2.68 \cdot 10^{23}$. The limiting characteristic ratio $C_\infty$ is defined by[14)]

$$C_\infty = \langle r^2\rangle_0/nl^2 \tag{12}$$

where $nl^2$ is derived from the freely jointed chain, which is preferred for comparison purposes to the ratio $\langle r^2\rangle_0/M$, but may, nevertheless, be calculated from it by virtue of the relationship in the limit for long chains

$$C_\infty = (\langle r^2\rangle_0/M)_\infty(M_b/l^2) \tag{13}$$

in which $M_b$ is the mean molecular weight per skeletal bond. In the case of a block copolymer, the appropriate value may be calculated from

$$l^2/M_b = \sum_i w_i(nl^2)_i/M_i \tag{14}$$

where $M_i$ is the molecular weight of individual segments.

The characteristic ratio may be obtained directly in a $\Theta$ solvent from

$$K_0 = [\eta]_0/\Phi_0$$

with the aid of Eqs. (4) and (13), the value of $K_0$ and therefore the unperturbed dimension is the value at the temperature $\Theta$ °K. Actually, $\langle r^2\rangle_0$ is not very temperature dependent. Determinations of $d \ln \langle r^2\rangle_0/dT$ for polystyrene and *cis*-1.4 polyisoprene (natural rubber) indicate that both have a value of about $0.4 \cdot 10^{-3}$ deg$^{-1}$. The trans isomer has a similar but negative value ($-0.3 \cdot 10^{-3}$deg$^{-1}$). We can assume therefore that the value for the block is probably somewhat smaller than for *cis*-1.4 polyisoprene.

The determination of $\Theta$ point for the block in methyl ethyl ketone by both cloud point method and by extrapolation of second virial coefficients from osmotic data to $A_{2\pi} = 0$ for the 50 % composition polymers yielded a value of $\Theta = 44$ °C. Thus the experimental K from $[\eta]_0$ was found to be $K_{(44°)} = 11.63$, which is identical with the extrapolated value in cyclohexane measured at 46 °C. This suggests that $\Theta$ temperatures for these block copolymers must represent a temperature at which the deviations from the unperturbed conformation in individual blocks are fairly small. In this connection we could expect that the characteristic ratio for the block copolymers might therefore be calculated according to the simple formula

$$C_\infty = xC_{\infty PS} + (1-x)C_{\infty PI} \tag{15}$$

where x is the mole fraction and $C_\infty$ for polystyrene and *cis*-polyisoprene are 9.9 and 4.7 respectively. We calculate $C_{\infty B} = 6.7$, *i.e.* within 2 % of the experimental value.

These results seem to indicate that at 46 °, which is well above $T_p$ for these polymers, the behaviour is that of a random distribution of segments. The drop in $C_\infty$ with temperature decrease may well indicate a change in distribution which should influence $\Phi_0$. The sudden drop in $C_\infty$ at 20 °C would therefore indicate an even greater change in distribution. Such a change is consistent with the proposed conformational change from phase mixed to phase separated conformations. $\Phi_0$ is a function of bond lengths, angles and rotational potentials which would not be expected to change greatly over a small temperature range; however $\Phi_0$ is also dependent on the actual distribution of segments which in the phase separated structure would be quite different from the approximately GAUSSian distribution expected for the mixed phase conformation – it could conceivably even be bi-modal. In these circumstances the calculated values of B may be expected to change with change in $\Phi_0$. The value at 46 °C is probably the most reliable estimate of the binary cluster integral, values at other temperatures are less reliable and at 20 °C the result is ambiguous; contributions from hetero-contacts should be reduced to negligible proportions anyway.

It is nevertheless of interest to note that the viscosity relations derived for homopolymers are obeyed by the copolymers throughout, even the conformational change does not invalidate them. The dimensions of the block copolymer may be calculated, with reasonable accuracy, from viscosity data at temperatures well above $T_p$ in these preferential solvents, but data at temperatures near or below $T_p$ are not so readily interpreted.

All the evidence obtained so far points to a conformational change; the most likely is an intramolecular phase transition. A thermodynamic explanation, which seems to fit the facts and which is based on models used to discuss intramolecular interactions15), can be given. At $T_p$, $\Delta G_{mix}$ for the block copolymer and the surrounding solvent is zero. Increasing the temperature means that $\Delta G_{mix}$ becomes negative. The entropy of mixing favours the transition, that is, an intramolecular phase transition from phase separated to phase mixed form. Enthalpies of mixing, well below $T_p$, should be large and positive for the copolymers, but negative for polyisoprene and solvent and must be positive for polystyrene and solvent. Increasing the temperature decreases the latter, causing swelling of the polystyrene domain, which is reflected in the viscosity increase. Once the temperature $T_p$ is reached the contributions from the enthalpy and entropy terms cancel and further increase in temperature results in mixing of the domains.

At the transition point, the polystyrene domain environment consists of cyclohexane molecules and styrene segments, except for the small region at the interface between the domains of the two blocks. On raising the temperature above $T_p$, cyclohexane molecules are partly replaced by polyisoprene which may be regarded as a poorer solvent and which causes shrinking until the whole molecule has expanded enough to overcome the effect. Above this point, the volume begins to increase again as shown by the plots of $[\eta]$ against T.

The explanation offered is, of course, speculative. The implication is that $T_p$ is a point similar in many respects to $\Theta$ measured for homopolymers. Certainly, the $\Theta$ temperature of block copolymers as determined by the usual extrapolation to $A_2 = 0$ from osmotic measurements is a more ambiguous quantity, since one cannot have an unperturbed situation for both polymers at this point. Perhaps $T_p$ may prove to be a more meaningful quantity in the interpretation of the solution properties of block copolymers in these solvents. A report on a detailed general study of the solution properties of the polymers is being prepared.

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1) M. GIROLAMO and J. R. URWIN, European Polymer J. **7** (1971) 693.
2) J. R. URWIN and M. GIROLAMO, European Polymer J. **7** (1971) 785.
3) D. N. CRAMOND and J. R. URWIN, Australian J. Chem. **21** (1968) 1835.
4) D. N. CRAMOND, J. M. HAMMOND, and J. R. URWIN, European Polymer J. **4** (1968) 451.
5) G. M. BURNETT, P. EVANS, and H. W. MELVILLE, Trans. Faraday Soc. **49** (1953) 1096.
6) H. Y. CHEN, Anal. Chem. **34** (1962) 1793.
7) M. GIROLAMO and J. R. URWIN, European Polymer J. **7** (1971) 225.
8) M. GIROLAMO and J. R. URWIN, Australian J. Chem. **24** (1971) 729.
9) P. J. FLORY, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N. Y., 1953, p. 310.
10) G. W. PYUN and M. FIXMAN, J. Chem. Phys. **44** (1966) 2107.
11) W. H. STOCKMAYER and M. FIXMAN, J. Polymer Sci. C **1** (1963) 137.
12) L. A. UTRACHI, R. SIMHA, and L. J. FETTERS, J. Polymer Sci. Part A-2, **6** (1968) 2051.
13) J. R. URWIN, Australian J. Chem. **22** (1969) 1649.
14) P. J. FLORY, Statistical Mechanics of Chain Molecules, Wiley, Interscience Publ., New York 1969, p. 11.
15) D. FROELICH and H. BENOÎT, Makromol. Chem. **92** (1966) 224.

European Polymer Journal, 1971, Vol. 7, pp. 225–230. Pergamon Press. Printed in England.

# MULTIPLE GLASS TRANSITIONS IN BLOCK COPOLYMER FILMS CAST FROM CYCLOHEXANE SOLUTIONS AT TWO TEMPERATURES

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**Abstract**—Films of block copolymers of polystyrene + *iso*prene, cast from cyclohexane at temperatures above and below a conformational transition temperature ($T_p$) derived from the plot of $[\eta]$ vs. $T$, have been examined for glass transition temperatures. In every case, two glass transitions were found, $T_{g_1}$ (poly*iso*prene) and $T_{g_2}$ (polystyrene) or $T_{g_1}$ and $T_g$ (an intermediate species). $T_g$ is assumed to be characteristic of a mixed phase thus providing further evidence that $T_p$ marks a conformational transition from a phase-separated to a phase-mixed form.

## INTRODUCTION

The graph of $[\eta]$ vs. temperature of block copolymers of polystyrene and poly*iso*prene in the solvent cyclohexane, which is a poor solvent for polystyrene but a good solvent for poly*iso*prene, exhibited a discontinuity at a particular temperature ($T_p$) reported earlier and assumed to be due to a change in conformation.(1) In this study, films of the polymer were cast from solutions in the same solvent at two different temperatures, one above and the other below the range over which this transition temperature $T_p$ is observed. The films were examined by differential scanning calorimetry; the thermal behaviour was found to differ according to the casting temperature. Multiple glass transitions occur in each case, but a new species was observed in the films cast from the higher temperature. The glass transition temperature for the intermediate species was shown to be a function of the composition of the copolymer. These observations are considered to reinforce the conclusion, arrived at from the study of $[\eta]$ vs. $T$, that $T_p$ represents a conformational transition in which there is a change from a phase-separated to phase-mixed form in solution. The present work is an extension of the study of the solution properties of these polymers to studies in the solid state, with the secondary aim of relating the two.

## EXPERIMENTAL

### *The polymers*

The methods adopted in the synthesis and analysis of the block copolymers have been described previously.(2) They were all materials of narrow molecular weight distribution. Composition was determined spectrophotometrically and homogeneity from Gel Permeation Chromatography.(3) The polymers investigated were all two sequence block copolymers of polystyrene and poly*iso*prene, with high *cis* 1,4 content (80 per cent) determined by NMR.

### *Instrumental*

The instrument was a Perkin–Elmer differential scanning calorimeter, Type DSC.1B. The theory and operating principles have been discussed elsewhere.(4–6) Calibration of the temperature scale was effected in the higher temperature range with sealed samples of indium, lead and tin. In the low temperature range the melting points of several pure organic solvents were used for the calibration. Samples of about 20 mg weight were cut from the films and encapsulated in aluminium pans. The temperature was lowered to the operating limit (−80°) by cooling with liquid nitrogen in a dewar flask. The rate of heating was selected from programmed rates over the range 64°/min to 0·5°/min. Glass temperatures reported in Table 1 were determined from the extrapolation of log $T_g$ vs. heating rate (from three different heating rates) to zero rate.

TABLE 1. GLASS TRANSITION TEMPERATURES OF BLOCK COPOLYMERS OF POLYSTYRENE + POLY*iso*PRENE CAST FROM CYCLOHEXANE AT 8° AND 50°

| Polymer | Composition (Wt.% P.S.) | $\bar{M}_n$ $\times 10^{-3}$ | Casting temperature (°C) | $T_{g1}$ (°C) | $T_g$ (°C) | $T_{g2}$ (°C) |
|---|---|---|---|---|---|---|
| IS. 5 | 78·2 | 102 | 8 | −65 | | 89 |
| | | | 50 | −64 | −1 | |
| IS. 6 | 11·8 | 254 | 8 | −62 | | 75 |
| | | | 50 | −61 | −36 | |
| IS. 7 | 25·5 | 249 | 8 | −63 | | 76 |
| | | | 50 | −64 | −29 | |
| IS. 8 | 48·5 | 248 | 8 | −64 | | 47 |
| | | | 50 | −61 | −25 | |
| IS. 9 | 25·1 | 497 | 8 | −64 | | 78 |
| | | | 50 | −64 | −30 | |
| IS. 10 | 49·7 | 497 | 8 | −64 | | 94 |
| | | | 50 | −64 | −22 | |
| IS. 8* | 48·5 | 248 | 0 | −64 | 21 | |
| | | | 50 | −64 | 8 | |
| IS. 10† | 49·7 | 497 | 0 | −64 | | 78 |
| | | | 60 | −64 | | 84 |

* Cast from toluene.
† Cast from a mixture of cyclohexane + *n*-heptane 84:16 by volumes.

### *Preparation of films*

Polymer films were formed by casting them from 0·5 per cent solutions in cyclohexane. One polymer IS.8 was also cast from toluene and another IS.10 from a mixture of cyclohexane and *n*-heptane Specially constructed glass pans were employed so as to produce thin films of even thickness. Films prepared at the higher temperature (50°) were formed by placing the glass pans in a vacuum oven, thermostatted at 50°, and then allowing slow evaporation of the solvent. After the films had formed, they were kept under high vacuum for a further 48 hr at 50°. The films prepared at the low temperature (8°) were formed by the slow removal of the solvent in a vacuum desiccator placed in a thermostat bath at the correct temperature. Again, the films which formed were then kept at 8° under high vacuum ($10^{-5}$ Torr) for a further 24 hr.

## RESULTS

Thermograms showing the rate of heat flow d*q*/d*t* (mcal $\sec^{-1}$) vs. temperature (°C) for block copolymer IS.9 in cyclohexane are given in Fig. 1, which is generally representative of all the thermograms. The value of $T_g$ was the temperature taken at the

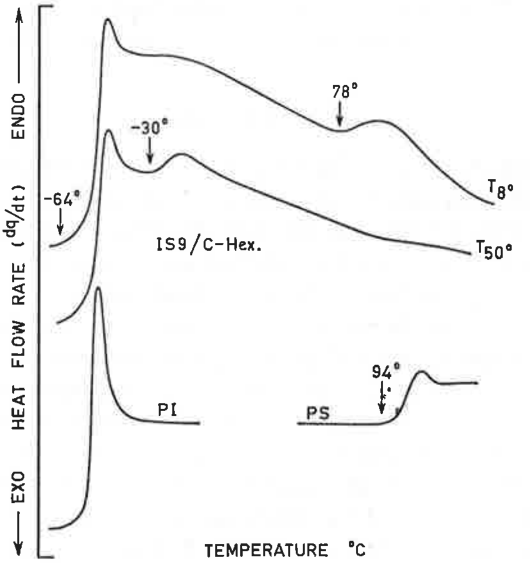

FIG. 1. Thermograms for block copolymer, poly*iso*prene and polystyrene.

beginning of the change in slope for each transition. Two samples of each homopolymer, poly*iso*prene and polystyrene were measured to check the operation of the instrument. $T_g$'s for these polymers fall within the acceptable range of published values.(7–9) $T_g$ for poly*iso*prene was —64°, see Fig. 1. $T_g$ for polystyrene 94° was measured separately and is plotted on the same graph. The value for poly*iso*prene is the generally accepted value for rubber or poly*iso*prene. The reported $T_g$'s for polystyrene range from 70° to 100° depending, to some extent, on the method of synthesis and the molecular weight. The generally accepted relationship between $T_g$ and molecular weight takes the form(9)

$$T_g = T_g(\infty) - K/\mathrm{M} \tag{1}$$

where $T_g(\infty)$ is the value at infinite molecular weight and $K$ is a constant for the specific polymer. For polystyrene, the relation becomes

$$T_g = 100° - \frac{(2 \times 10^5)}{\mathrm{M}} \tag{2}$$

but the method of measurement may also influence this result. The experimental value 94° therefore seems a reasonable value for the polymer measured.

Table 1 lists the glass transition temperatures determined by extrapolation to zero scan rate. $T_{g_1}$ is the value for poly*iso*prene, $T_{g_2}$ for polystyrene and $T_g$ the glass transition temperature of the third or intermediate species which appears at temperatures between the other two. The polymer IS.8 was cast from toluene and IS.10 from a mixed solvent (84:16 by volumes of cycohexane + *n*-heptane) as well as in pure cyclohexane. In each case, the film cast at the higher temperature shows $T_{g_1}$ and $T_g$ only; the films cast from the lower temperature exhibit $T_{g_1}$ and $T_{g_2}$ only, except for the toluene cast film in which the result is the same as the higher temperature casts at both temperatures. Similarly, the film cast from the mixed solvent shows the same thermal behaviour at both temperatures but this time only $T_{g_1}$ and $T_{g_2}$ are observed.

## DISCUSSION

The most significant point emerging from these results is the appearance of a new species characterized by $T_g$ and the absence of $T_{g_2}$ in all films cast from the higher temperatures in cyclohexane; this contrasts with the films cast at the lower temperature in which only $T_{g_1}$ and $T_{g_2}$ appear. The simplest conclusion we can draw is that, at temperatures of casting well below the conformational transition temperature $T_p$ derived from $[\eta]$ vs. $T$ plots in the same solvent, there exists phase separation in which polystyrene and poly*iso*prene are confined to separate domains. On the other hand, the polystyrene domain has disappeared in films cast at temperatures well above $T_p$ and instead, a mixed phase has formed in its place. The continued existence of poly*iso*prene means that not all of the poly*iso*prene continuum is involved in the mixing process. This observation is confirmed by the relationship found when the mixed-phase glass transition temperatures are plotted as a function of composition.

Glass transitions in mixtures of two compatible homopolymers or a random copolymer which forms one single phase have been discussed by others.(10) It was found that a relation having the form:

$$T_g = K\,(T_{g_2} - T_g)\,\frac{w_2}{1 - w_2} + T_{g_1} \tag{3}$$

is generally obeyed, where $Tg_1$ and $Tg_2$ are the glass transition temperatures of the two homopolymers and $T_g$ the glass temperature of the mixed phase. Here, $w_2$ is the weight fraction of polymer 2. A plot of $(T_{g_2} - T_g)\,w_2/(1 - w_2)$ vs. $T_g$ should be linear with the intercept at $w_2 = 0$ equal to the glass transition temperature of polymer 1. If we assume that the intermediate species which appears in the films cast at the higher temperatures to be a mixed phase of poly*iso*prene ($T_{g_1}$) and polystyrene ($T_{g_2}$) then the

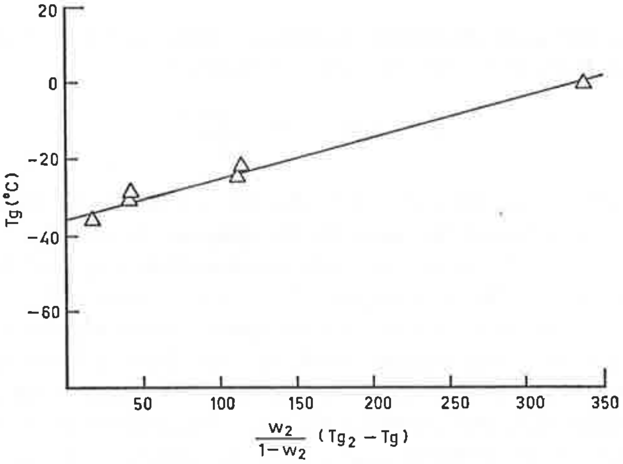

FIG. 2. Dependence of glass transition temperature upon composition.

relation is obeyed to the extent that the plot is linear (Fig. 2) but in this case, extrapolation to $w_2 = 0$ does not yield the expected glass transition temperature of poly*iso*prene. However, as has already been observed, the poly*iso*prene is still present in sufficient quantity to show a glass temperature $T_{g_1}$ in the presence of the mixed phase. This means that the weight fraction $w_2$, calculated on the basis of the original polymer, underestimates the polystyrene composition of the mixed phase. The composition of this mixed phase would nevertheless appear to be proportional to the original composition but to deviate sufficiently to shift the value of $T_{g_1}$ calculated by application of equation (3). In plotting Fig. 2, the value of $T_{g_2}$ used to calculate $(T_{g_2} - T_g)$ was assumed to be that found experimentally for the homopolymer, i.e. 94°.

It seems clear that, at temperatures above $T_p$ in cyclohexane, the two sequences in the block copolymer are mixed forming a single phase. In the process of casting the film, some poly*iso*prene, which is present in excess in all except IS.5, remains in the very concentrated solution which is associated with the gelled mixed phase. In IS.5 the typical sharp endotherm observed with thermograms of poly*iso*prene, which is due to the lag in the equilibrium free volume with scanning rate,$^{(11)}$ is no longer present even though the scanning rate remains the same. However, long enough sequences remain for it to retain its intrinsic identity. It was noted that the poly*iso*prene transitions were always sharper than the polystyrene. If we can speculate that the sharpness is in some way related to the purity of the phase then we may assume that mixing of the poly*iso*prene occurs only at its boundaries, that is interfacial mixing. Polystyrene domains on the other hand seem to be much more intimately mixed, giving rise to a broader peak. If this is assumed, then the degree of mixing depends on the composition, so that at 50 per cent by weight or equimolar composition, there must surely be the greatest inter-mixing, which would account for the unusually low value for $T_{g_2}$ found for IS.8. On the basis of this argument and evidence presented earlier,$^{(12)}$ we would expect that films cast from good solvents such as toluene, whatever the casting temperature, should show the same pattern of behaviour as the higher temperature casts of the block copolymers in cyclohexane. The $T_g$'s for this particular solvent shown in Table 1 confirm this assumption. The behaviour in the mixed solvent (84:16 volume % of cyclohexane + *n*-heptane) appear to conflict with the other evidence at first sight, since $T_p$ for this mixture is 30°. Closer scrutiny of the probable composition of the solution existing during evaporation of the solvent reveals that, on removing the solvent, the cyclohexane evaporates more rapidly than *n*-heptane and the solution becomes more concentrated with respect to the latter, a non-solvent for polystyrene. The results is that films are cast from almost pure *n*-heptane at both temperatures and phase separation is therefore complete in the films formed at both casting temperatures. In films produced from cyclohexane at temperatures below $T_p$, only the two transitions $T_{g_1}$ and $T_{g_2}$ are observed and it therefore seems reasonable to assume that phase separation occurs in this case, into domains of polystyrene set in a matrix of poly*iso*prene.

The data presented provide substantial confirmatory evidence for the original contention that the transition temperature $T_p$ observed in plots of $[\eta]$ vs. $T$ in cyclohexane and similar liquids which are good solvents for one polymer sequence but poor for the other, marks a conformational transition from the phase-separated to phase-mixed forms. The phenomena which have been described also demonstrate that solution behaviour can be related directly to the morphology of solid state when the materials have been cast from solution. Although this work has dealt with double sequence or AB type polymers, it can be confidently expected that it is also applicable to triple sequence ABA or BAB type polymers as well.

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## REFERENCES

(1) M. Girolamo and J. R. Urwin, *Europ. Polym. J.* (in press).
(2) D. N. Cramond and J. R. Urwin, *Aust. J. Chem.* **21,** 1835 (1968).
(3) D. N. Cramond, J. M. Hammond and J. R. Urwin, *Europ. Polym. J.* **4,** 451 (1968).
(4) E. S. Watson, M. J. O'Neill, J. Justin and N. Brenner, *Anal. Chem.* **36,** 1233 (1964).
(5) M. J. O'Neil, *Anal. Chem.* **36,** 1238 (1964).
(6) S. Trella and P. F. Ewhardt, *J. appl. Polym. Sci.* **13,** 1373 (1969).
(7) *Polymer Handbook* (edited by J. Brandrup and E. H. Immergut). Interscience, New York (1966).
(8) J. F. Beecher, L. Marker, R. D. Bradford and S. L. Aggarwal, *J. Polym. Sci.* **C 26,** 117 (1969).
(9) F. Bueche, *Physical Properties of Polymers*, Chap. 5. Interscience, New York (1962).
(10) L. A. Wood, *J. Polym. Sci.* **28,** 319 (1958).
(11) B. Wunderlich, D. M. Bodily and M. H. Kaplan. *J. appl. Phys.* **35,** 95 (1964).
(12) J. R. Urwin. *Aust. J. Chem.* **22,** 1649 (1969).

**Résumé**—On a déterminé les températures de transition vitreuse de films de copolymères séquencés de polystyrène + isoprène dans le cyclohexane à des températures supérieures et inférieures à la température de transition de conformation ($T_p$) dérivée de la courbe représentant [$\eta$] en fonction de $T$. Dans tous les cas, deux transitions vitreuses ont été trouvées, $T_{g1}$ (poly*iso*prène) et $T_{g2}$ (polystyrène) ou $T_{g1}$ et $T_g$ (une espèce intermédiaire). On pense que $T_g$ est caractéristique d'une phase mixte ce qui donne une preuve supplémentaire de ce que $T_p$ repère une transition conformationnelle entre une forme à phases séparées et une forme à phase mixte.

**Sommario**—Si sono esaminate le temperature di trasformazione vetrosa di pellicole di copolimeri a blocchi di polistirene e poliisoprene, ricavate di fusione da cicloesano a temperature superiori e inferiori alla temperatura ($T_p$) di trasformazione strutturale derivata dal grafico di ($\eta$) in funzione di $T$. In ogni caso si trovarono due trasformazioni vetrose, $T_{g1}$ (poli*iso*prene) e $T_{g2}$ (polistirene) oppure $T_{g1}$ e Tg (una specie intermedia). Si presume che $T_g$ sia caratteristico di una fase mista, ciò che fornisce un'ulteriore prova che $T_p$ contrassegna una trasformazione strutturale da una forma a fasi separate ad una a fasi miscelate.

**Zusammenfassung**—Filme von Block-Copolymeren aus Polystyrol + Isopren, gegossen aus Cyclohexan bei Temperaturen über und unter der Konformations-Umwandlungstemperatur ($T_p$)—abgeleitet aus der Auftragung von [$\eta$] gegen $T$-wurden auf ihre Glasübergangstemperaturen hin untersucht. In jedem Fall wurden zwei Glasübergänge festgestellt, $T_{g1}$ (Poly*iso*pren) und $T_{g2}$ (Polystyrol) oder $T_{g1}$ und $T_g$ (eine intermediäre Spezies). Es wird angenommen, daß $T_g$ charakteristisch ist für eine gemischte Phase, und damit einen weiteren Hinweis dafür gibt, daß $T_p$ einen Konformationsübergang von einer Phasen-getrennten zu einer Phasengemischten Form anzeigt.

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# THERMODYNAMIC PARAMETERS FROM OSMOTIC STUDIES ON SOLUTIONS OF BLOCK COPOLYMERS OF POLYISOPRENE AND POLYSTYRENE

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**Abstract**—A series of ten block copolymers of poly(isoprene: styrene) have been examined by osmometry over a range of temperatures. Several solvents were used; one was a good solvent for both sequences (toluene), another was a bad solvent for both sequences (methyl *iso*-butyl ketone) and another was a preferential solvent (cyclohexane) which is a good solvent for the polyisoprene sequence but a poor solvent for polystyrene. Flory (or theta) temperatures have been determined for all polymers in the three solvents; a comparison is made with values of $\theta$ determined by cloud point methods using methyl ethyl ketone as solvent. The interaction parameter $\chi_1$ is separated into its enthalpic and entropic parts and examined in relation to composition and molecular weight. The molecular weight dependence of the second virial coefficient is also discussed. The inclusion of the composition parameter, in addition to those normally used for homopolymers in these systems, is not adequate for a complete description of solution properties of block copolymers, particularly in the case of preferential solvents where there is ample evidence for intramolecular phase separation.

## INTRODUCTION

THE MEASUREMENT of osmotic pressure of polymer solutions at low concentrations provides convenient access to the thermodynamic parameters which control solution behaviour. From conventional solution theory, the excess chemical potential of mixing of the solvent is directly related to the non-ideal terms in the virial expansion of the expression for the osmotic pressure.$^{(1)}$ The second virial coefficient $A_2$ is related to these parameters by the relations

$$A_2 = \frac{v_2^2}{V_1}(\tfrac{1}{2} - \chi_1)F(X) = \frac{v_2^2}{V_1}\psi(1 - \theta/T)F(X) \tag{1}$$

where $v_2$ = partial specific volume of polymer,

$V_1$ = molar volume of the solvent

and $F(X)$ is a function which reduces to unity at the theta or Flory temperature. The interaction parameter $\chi_1$ should be considered as empirical and to contain a temperature dependent enthalpic term $\chi_H$ which varies inversely as temperature and also a temperature independent entropic term $\chi_S$ such that $\chi_1$ is the sum of these terms.$^{(2,3)}$

$$\chi_1 = \chi_H + \chi_S. \tag{2}$$

The value of $\chi_1$ at the critical temperatue for a polymer of infinite molecular weights should approach $\tfrac{1}{2}$ and, introducing the entropy parameters, may be defined by the expression

$$\chi_1 = \tfrac{1}{2} - \psi(1 - \theta/T) \tag{3}$$

so that $\psi = \tfrac{1}{2} - \chi_S$.

At the theta temperature, $A_2 = 0$, therefore the plot of $A_2$ against $T$ or $1/T$ yields $\theta$. Such temperatures are not always practically attainable but may nevertheless be evaluated by extrapolation. The value for the entropy parameter $\psi$ is obtained from the slope at $T = \theta$ provided values of $v_2$ and $V_1$ are known or can be calculated. The two parameters $\psi$ and $\theta$ (or $\chi_S$ and $\chi_H$) are therefore of particular interest. In the case of block copolymers, we may anticipate that the composition of the polymers will also be an important variable in defining thermodynamic behaviour, as well as the molecular weight and size of the molecule in solution. It is important therefore to discover whether the theory, as it applies to homopolymers, can be extended to block copolymers with the simple addition of the composition parameter.

In an earlier paper from this laboratory,$^{(4)}$ several block copolymers were examined with the same aims in mind; it was found, however, that the limited number of polymers available for the study did not allow the specific contributions from molecular weight and composition to be separated. In the present work, the range of polymers has been wide enough to ensure examination of solution behaviour as a function of composition at constant molecular weight or as a function of molecular weight at constant composition. From gel permeation chromatography analyses, the polymers have been shown to be of narrow distribution, so that any effects due to polydispersity may be safely ignored.

## EXPERIMENTAL

A series of ten block copolymers of the two sequence, or *AB*, type where $A$ = polystyrene and $B$ = polyisoprene (coded I.S. 1 to I.S. 10) were synthesized by anionic initiation using *n*-butyl lithium in benzene as previously described.$^{(5)}$ The excellent predictability of the method is indicated by the agreement between $\bar{M}_{nk}$ and $\bar{M}_n$. The polymers were characterized by light scattering ($\bar{M}_w$), osmometry ($\bar{M}_n$), and the composition was determined by u.v. spectrophotometry. Gel permeation chromatograms of these polymers showed them to be free from homopolymer, and confirmed the narrow distribution indicated by the heterogeneity ratio $\bar{M}_w/\bar{M}_n$. The standard deviations obtained from GPC curves, expressed as the ratio $\bar{M}_w/\bar{M}_n$ according to a method described earlier,$^{(6)}$ were in good agreement with the heterogeneity ratio. A list of pertinent characteristics for all polymers is shown in Table 1.

Osmotic measurements were performed on a Hewlett–Packard, high speed, membrane osmometer (Model 501) with an electric heating attachment. This instrument has no provision for cooling, so setting the minimum operational temperature at room temperature. Membranes were of cellulose carefully conditioned to the appropriate solvents.

Cloud point determinations of theta points $^{(7,8)}$ were determined with a modified SOFICA photogoniometer. A 100-ml glass cell with ground glass lid was constructed so as to fit into the normal cell mounting. A stainless steel capillary attached to a microburette delivered the non-solvent at 0·5 ml/min through the domed lid; stirring was effected by an electric stirrer at 200 rev/min to avoid flocculation. The temperature was monitored by means of a glass thermistor probe. Change in transmission was readily observed as low as 0·001% weight of polymer by this method. Solutions of 1 to $10^{-3}$ weight per cent of polymer were titrated until the first appearance of turbidity. Plots of volume fraction of non-solvent against volume fraction of polymer fell on straight lines which could be easily extrapolated to pure polymer $\Phi_2 = 1$. Values of the volume fraction of non-solvent at $\Phi_2 = 1$ at three different temperatures plotted against $T$ were linear so that the solvent/non-solvent mixture corresponding to the $\theta$ composition could be read off for any given $T$ for any solvent/non-solvent system. This technique proved to be very useful and rapid.

## RESULTS

The reduced osmotic pressure ($\pi/c$) vs. concentration plots for all polymers displayed definite curvature in toluene and cyclohexane but was linear for methyl *iso*-butyl ketone (MIBK). However, plots of $(\pi/c)^{\frac{1}{2}}$ against concentration were all linear. Figure 1 shows $(\pi/c)^{\frac{1}{2}}$ vs. $c$ for one polymer in all three solvents.

TABLE 1. CHARACTERISTICS OF SERIES OF BLOCK COPOLYMERS OF ISOPRENE AND STYRENE USED IN THE STUDY

| Polymer code | $\bar{M}_{n_k}$§ × $10^{-5}$ | $\bar{M}_n$* × $10^{-5}$ | $\bar{M}_w$† × $10^{-5}$ | $\bar{M}_w/\bar{M}_n$ | Composition Wt. % P.S. calc. | Composition Wt. % P.S. found‖ | Standard deviation σ by G.P.C.‡ | |
|---|---|---|---|---|---|---|---|---|
| I.S. 1 | 1·00 | 1·02 | 1·08 | 1·06 | 11·8 | 13·5 | 0·287 | (1·08) |
| I.S. 2 | 1·00 | 1·00 | 1·09 | 1·07 | 25·0 | 24·7 | 0·312 | (1·10) |
| I.S. 3 | 1·00 | 1·01 | 1·12 | 1·10 | 28·6 | 28·2 | 0·230 | (1·05) |
| I.S. 4 | 1·00 | 1·05 | 1·11 | 1·07 | 50·0 | 52·2 | 0·277 | (1·08) |
| I.S. 5 | 1·00 | 1·04 | 1·12 | 1·09 | 77·8 | 78·2 | 0·285 | (1·08) |
| I.S. 6 | 2·50 | 2·54 | 2·69 | 1·06 | 11·8 | 11·8 | 0·317 | (1·10) |
| I.S. 7 | 2·50 | 2·49 | 2·71 | 1·07 | 25·0 | 25·5 | 0·287 | (1·08) |
| I.S. 8 | 2·50 | 2·48 | 2·67 | 1·05 | 50·0 | 48·5 | 0·272 | (1·07) |
| I.S. 9 | 5·00 | 4·97 | 5·42 | 1·09 | 25·0 | 25·1 | 0·327 | (1·11) |
| I.S. 10 | 5·00 | 4·97 | 5·53 | 1·10 | 50·0 | 49·7 | 0·352 | (1·13) |

* $\bar{M}_n$ by osmometry in MIBK. Values in toluene and cyclohexane were all within 2% of this value.

† $\bar{M}_w = \bar{M}_{app}$. determined by light scattering in methyl *iso*-butyl ketone.

‡ G.P.C. curves showed single peaks only with width of distribution similar to the heterogeneity ratio, $\bar{M}_w/\bar{M}_n$. The values in brackets are equivalent of $\bar{M}_w/\bar{M}_n$ ref. (6).

§ Calculated from $\bar{M}_{n_k} = \dfrac{\text{g monomer}}{\text{moles initiator.}}$

‖ Determined by u.v. spectrophotometry.

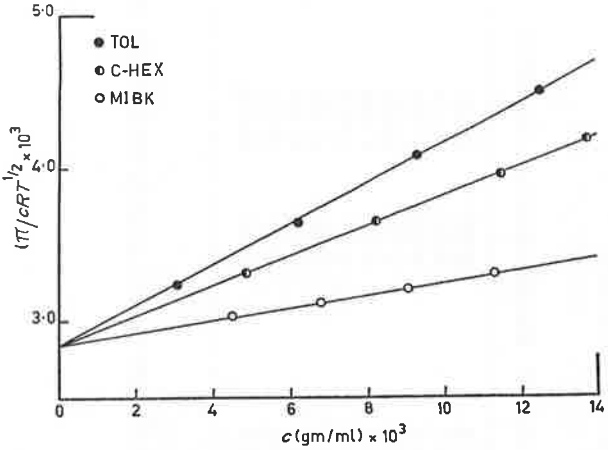

FIG. 1. Plots of $(\pi/cRT)^{\frac{1}{2}}$ against $c$ for I.S. 4 in toluene, cyclohexane and MIBK at 30°.

Results for both plots were identical for MIBK, thus all results reported here were obtained by means of the square root plot. Actually, this behaviour is to be expected, since the graph of $\pi/c$ vs. $c$ should be curved, unless the third virial coefficient is small or zero, when the cubic term in the osmotic virial expansion becomes negligible. The usual value for $g = 1/4$ connecting the second and third osmotic virial coefficients(1) was generally applicable to these systems. Values for $A_2$, obtained from all ten polymers in the three solvents at four temperatures, are set out in Table 2.

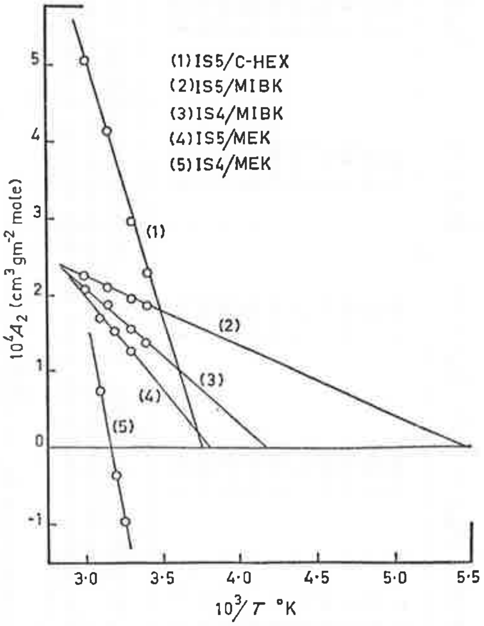

FIG. 2. Some plots of the second virial coefficients $A_2$ against $1/T$ for the block copolymers in cyclohexane, MEK and MIBK.

TABLE 2. SECOND VIRIAL COEFFICIENTS $A_2$ (cm$^3$ g$^{-2}$ mole × $10^4$) FOR THE BLOCK COPOLYMERS AT VARIOUS TEMPERATURES (°C) IN TOLUENE, CYCLOHEXANE AND METHYL *iso*-BUTYL KETONE

| Polymer | Toluene | | | | Cyclohexane | | | | Methyl *iso*-butyl ketone | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20° | 30° | 45° | 60° | 20° | 30° | 45° | 60° | 20° | 30° | 45° | 60° |
| I.S. 1 | 9·48 | 9·73 | 10·08 | 9·94 | 8·28 | 8·65 | 9·10 | 9·51 | 1·10 | 1·20 | 1·31 | 1·39 |
| I.S. 2 | 9·13 | 9·45 | 9·82 | 9·95 | 7·61 | 7·74 | 8·04 | 8·69 | 1·45 | 1·67 | 1·70 | 1·77 |
| I.S. 3 | 9·03 | 9·24 | 9·39 | 9·05 | 7·26 | 7·55 | 8·01 | 8·60 | 1·42 | 1·58 | 1·80 | 1·91 |
| I.S. 4 | 7·24 | 7·69 | 8·00 | 7·89 | 4·65 | 4·88 | 5·44 | 6·09 | 1·38 | 1·56 | 1·87 | 2·07 |
| I.S. 5 | 6·40 | 6·59 | 6·68 | 6·04 | 2·30 | 2·97 | 4·15 | 5·05 | 1·83 | 1·93 | 2·04 | 2·21 |
| | 22° | 30° | 40° | 50° | 22° | 30° | 40° | 50° | 22° | 30° | 40° | 50° |
| I.S. 6 | 7·24 | 7·57 | 7·67 | 7·72 | 6·34 | 6·68 | 6·84 | 7·25 | 1·05 | 1·13 | 1·21 | 1·31 |
| I.S. 7 | 6·46 | 6·68 | 6·82 | — | 5·30 | 5·63 | 5·71 | 6·02 | 1·18 | 1·21 | 1·30 | 1·37 |
| I.S. 8 | 5·78 | 6·10 | 6·29 | 6·43 | 3·66 | 4·29 | 4·55 | 4·90 | 1·30 | 1·48 | 1·68 | 1·86 |
| I.S. 9 | 5·03 | 5·24 | 5·37 | — | 4·39 | 4·40 | 4·52 | 4·84 | 1·13 | 1·18 | 1·25 | — |
| I.S. 10 | 4·71 | 4·86 | 5·08 | 5·24 | 3·13 | 3·52 | 3·50 | 3·98 | 1·42 | 1·60 | 1·84 | — |

TABLE 3. VALUES OF THE THERMODYNAMIC PARAMETERS $\theta$, $\chi_S$, $\chi_H$ (30°C) AND THE INTERACTION PARAMETER $\chi_1$ FOR THE BLOCK COPOLYMERS, DERIVED FROM OSMOTIC DATA IN SEVERAL SOLVENTS

| | Toluene | | | | Cyclohexane | | | | Methyl *iso*-butyl ketone | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Polymer | θ(°K) | $\chi_S$ | $\chi_H$ | $\chi_1$ | θ(°K) | $\chi_S$ | $\chi_H$ | $\chi_1$ | θ(°K) | $\chi_S$ | $\chi_H$ | $\chi_1$ |
| I.S. 1 | 133 | 0·339 | 0·071 | 0·409 | 159 | 0·329 | 0·090 | 0·419 | 201 | 0·462 | 0·025 | 0·487 |
| I.S. 2 | 148 | 0·321 | 0·087 | 0·407 | 177 | 0·318 | 0·106 | 0·424 | 190 | 0·454 | 0·029 | 0·483 |
| I.S. 3 | 146 | 0·324 | 0·085 | 0·409 | 182 | 0·312 | 0·113 | 0·425 | 215 | 0·437 | 0·045 | 0·482 |
| I.S. 4 | 185 | 0·291 | 0·127 | 0·419 | 221 | 0·304 | 0·143 | 0·447 | 240 | 0·405 | 0·075 | 0·480 |
| I.S. 6 | 175 | 0·311 | 0·110 | 0·420 | 267 | 0·188 | 0·275 | 0·463 | 183 | 0·431 | 0·041 | 0·473 |
| I.S. 6 | 134 | 0·378 | 0·054 | 0·432 | 165 | 0·361 | 0·076 | 0·437 | 214 | 0·458 | 0·030 | 0·488 |
| I.S. 7 | 158 | 0·365 | 0·071 | 0·435 | 172 | 0·374 | 0·072 | 0·445 | 190 | 0·462 | 0·024 | 0·486 |
| I.S. 8 | 181 | 0·341 | 0·095 | 0·436 | 224 | 0·327 | 0·128 | 0·455 | 244 | 0·405 | 0·076 | 0·481 |
| I.S. 9 | 153 | 0·398 | 0·051 | 0·450 | 174 | 0·278 | 0·059 | 0·456 | 188 | 0·465 | 0·022 | 0·486 |
| I.S. 10 | 179 | 0·373 | 0·075 | 9·448 | 221 | 0·364 | 0·099 | 0·463 | 243 | 0·398 | 0·082 | 0·480 |
| P.S.* | 160 | 0·389 | 0·058 | 0·448 | 307 | 0·119 | 0·384 | 0·504 | | | | |

* Ref. (9).

Plots of the second virial coefficients ($A_2$) against $1/T$ were all linear (Fig. 2). Extrapolation to $A_2 = 0$ then yields the theta or Flory temperature. The slope at $T = \theta$ is proportional to the entropy parameter $\psi$. To evaluate $\psi$, the values of $v_2$ must be known or calculated. For this work, volume additivity was assumed and the values were calculated from published densities of polystyrene and polyisoprene.(9) In Table 3, the values of $\theta$, $\chi_S = \frac{1}{2} - \psi$, $\chi_H$ and $\chi_1$ are collected together for all ten polymers in the three solvents. The appropriate data for polystyrene in toluene and cyclohexane are included to facilitate the discussion.

To provide a cross check on the theta temperatures found by osmometry and to provide practically useful theta conditions, cloud point determinations in a single solvent, methyl ethyl ketone (MEK), were undertaken on the first group of polymers, i.e. those with constant molecular weight $\bar{M} = 100{,}000$ but with a range of compositions. The results appear in Table 4. I.S.1 proved to be insoluble in MEK and therefore mixed solvents were necessary; MIBK with isopropyl alcohol was chosen. For I.S.5, for which $\theta$ has the inconvenient value of $-10°$, the solvent MEK was retained for the mixture. Values of $\theta$ obtained by the osmotic method are given for comparison. The polymers examined have constant molecular weight but cover the whole composition range studied.

TABLE 4. PRACTICALLY USEFUL THETA CONDITIONS FROM CLOUD POINT DATA IN METHYL ETHYL KETONE OR MIXED SOLVENTS FOR THE BLOCK COPOLYMERS
(Values in brackets from osmotic data)

| Polymer | $\theta$°C (MEK) | | Theta composition at 30° volume % I.P.A. |
|---|---|---|---|
| I.S. 1 | insoluble | | 5·6 (in MIBK) |
| I.S. 2 | — | (49) | |
| I.S. 3 | 46 | (48) | |
| I.S. 4 | 45 | (44) | |
| I.S. 5 | −10 | (−10) | 7·2 (in MEK) |

Second virial coefficients are known to vary with molecular weight both from theory(1) and from homopolymer studies.(10) In this work, two composition ranges were examined. These have been coded 25/75 (representing polymers containing 25% by weight polystyrene) and 50/50 (containing equal weights of each polymer). Analysed on a purely empirical basis, plots of log $A_2$ vs. log $\bar{M}$ were found to be linear (Fig. 3) at least over the molecular weight range studied. The slope gave the exponent of $\bar{M}$ in the empirical relation

$$A_2 = K\bar{M}^{-Y}. \tag{4}$$

Values of the exponent $Y$ are listed in Table 5 for the two ranges of composition and for the three solvents.

TABLE 5. THE MOLECULAR WEIGHT DEPENDENCE OF THE SECOND VIRIAL COEFFICIENT. VALUES OF THE EXPONENT $Y$ IN EQN. (4) IN THE THREE SOLVENTS

| Composition | Toluene | Cyclohexane | MIBK |
|---|---|---|---|
| 25/75 | 0·33 | 0·33 | 0·01 |
| 50/50 | 0·30 | 0·20 | 0·18 |

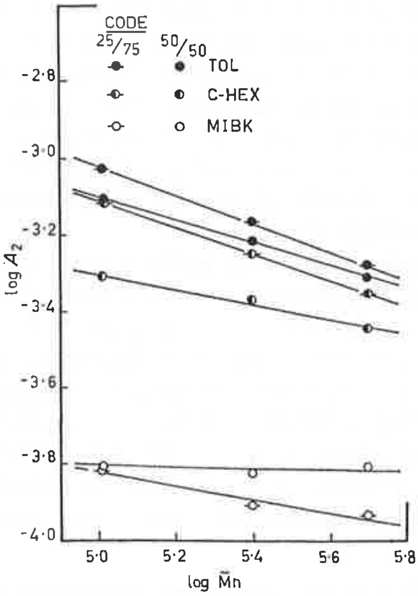

FIG. 3. Plots of log $A_2$ vs. log M̄ for two composition ranges in toluene, cyclohexane and MIBK.

## DISCUSSION

Second virial coefficients according to polymer theories(1,10) are molecular weight dependent. Practically, homopolymers and copolymers(11) obey the relation shown in Eqn. (4). Theory predicts that an upper limit for $Y$ should be about 0·15(10) but, experimentally in good solvents, values are higher generally and may even be as high as 0·3. It seems therefore, that values of $Y$ which exceed the expected value are general and not characteristic of block copolymers.

The results of the manipulation of the virial coefficients as a function of temperature to calculate $\theta$, $\chi_1$, $\chi_H$ and $\chi_S$ are collected in Table 3. In order to appreciate the general trends with composition and molecular weight, the results for the series I.S.1–I.S.5 are shown graphically in Figs. 4, 5 and 6. In this series, molecular weight is constant at 100,000 but composition varies. It can be seen that two other series can also be formed with constant composition viz. 25% (I.S.2, I.S.7, I.S.9) 50% (I.S.4, I.S.8, I.S.10), where the composition is expressed in weight per cent of polystyrene, which gives the series of molecular weights of 100,000–250,000–500,000. The plot of $\chi_1$ vs. composition demonstrates quite well the effectiveness of the interaction parameter as a measure of solubility. This is very clearly illustrated for all these solvents. In toluene and cyclohexane, $\chi_1$ increases linearly with increasing polystyrene content, as would be expected, since both are better solvents for polyisoprene than polystyrene. On the other hand, the opposite trend is observed for MIBK, again in keeping with the known solubility of the polymers in this solvent. $\chi_1$ shows a negligible dependence on molecular weight and the other values at higher molecular weight could be accommodated. However, a slight increase with increasing M̄ can be observed with toluene and cyclohexane, but this may be an artefact in view of the magnitude of the error in measurement. If it

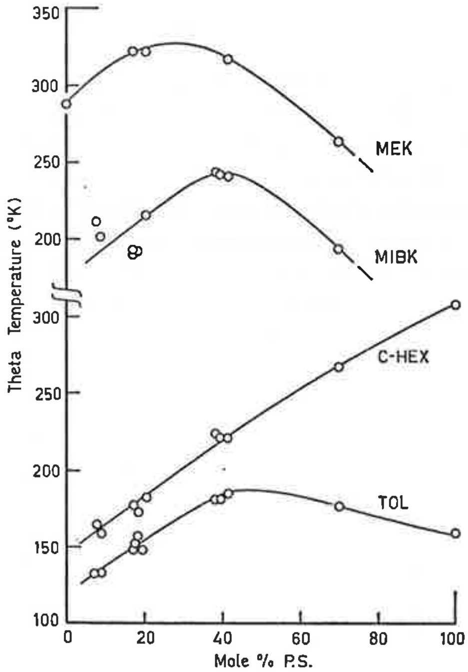

FIG. 4. Flory temperatures against composition for the block copolymers in toluene, cyclohexane, MIBK and MEK.

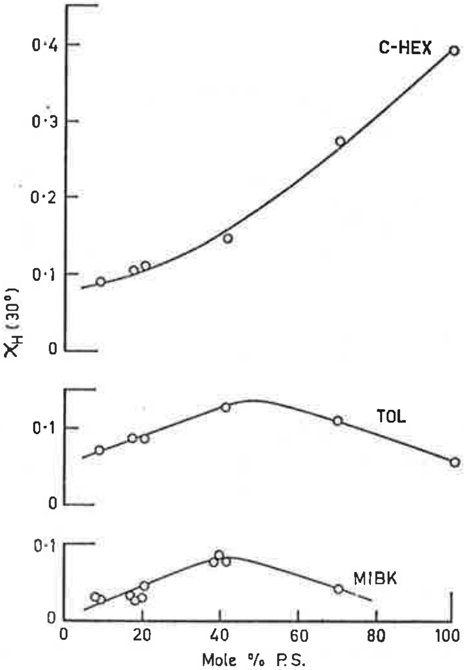

FIG. 5. The enthalpy parameter $\chi_H$ vs. composition for the block copolymers in toluene, cyclohexane and MIBK at 30°.

is authentic, at least it appears to be in the same direction as that observed in many homopolymers.

The theta point of flexible polymers is the temperature at which the average dimensions of the polymer are determined solely by the short-range interactions, which in a homopolymer defines the unperturbed configuration (in the sense used by Flory(12)). Practically, the theta temperature (at which $A_2 = 0$) is a convenient approach and is unambiguous. The values of a theta point for the block copolymers, determined at $A_2 = 0$, may therefore be expected to represent the temperature at which contributions to $A_2$ from both type of segments, and their cross interactions if the configuration is truly random, cancel each other except in the very special cases where both contributions attain a value of zero at the same temperature.

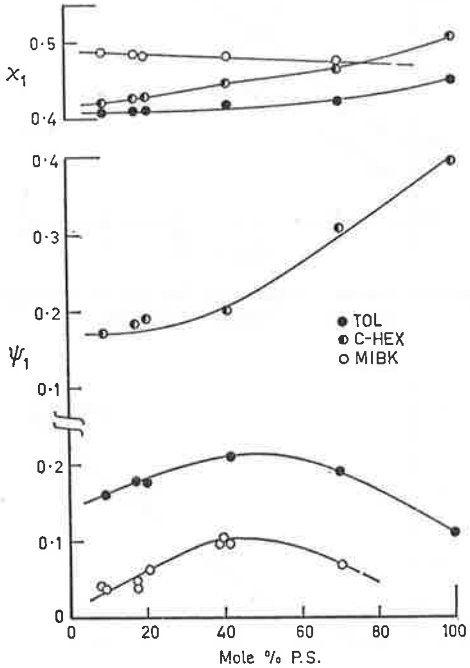

FIG. 6. The interaction parameter $\chi_1$ and entropy parameter $\psi$ for the block copolymers in toluene, cyclohexane and MIBK.

One might expect, intuitively, that $\theta$ for the blocks, determined by the extrapolation of $A_2$ to zero, may be composition dependent. Figure 4 shows theta temperatures for the blocks as a function of composition in four solvents. $\theta$ passes through a maximum in toluene, a good solvent for both types of segments and in MEK as well as MIBK, both poor solvents for polyisoprene and polystyrene; in the case of cyclohexane, a preferential solvent for polyisoprene, the plot of $\theta$ vs. composition is almost linear. The maximum in toluene occurs in the middle of the composition scale but is shifted towards the lower end of this scale in MEK and MIBK. At this point, it is encouraging to note the good correlation between the two methods of measuring $\theta$, the cloud point and osmometry. Of course, only poor solvents have been compared, but the results suggest that the theta temperature does represent a well defined configuration for the particular composition in the particular solvent. The results also suggest a basic difference in configuration depending upon the specific solvent. The preferential solvent displays linear change with composition from $\theta = 307°\text{K}$ for polystyrene to $\theta = 100°\text{K}$ for polyisoprene. Viscosity studies suggest that blocks in this solvent exhibit intramolecular phase separation(13-15) and therefore the contributions to $A_2$ from each kind of segment are simply additive with respect to the total. The maxima appearing in the other solvents suggest a random structure in which heterocontacts play an important role. In the very good solvent, the maximum is at the point at which the greatest number of heterocontacts would be expected, i.e. in the middle of the composition scale, where there are equal numbers of each type of segment.(16) The shift of the maximum to lower composition in the poor solvents may possibly be explained by partial domain formation. Finally, it can be noted that the $\theta$ temperature of the blocks appear to be independent of molecular weight.

Cleavage of the interaction parameter into its enthalpic and entropic elements for the purposes of discussion can be profitable. Figure 5 displays $\chi_H$ and Fig. 6 $\psi = \frac{1}{2} - \chi_S$ and $\chi_1$ as a function of composition. In toluene and MIBK, $\chi_S$ makes the major contribution to $\chi_1$ as is generally the case. Maxima occur in toluene and MIBK, as was found with the theta point, at the middle of the composition scale. The situation is quite different in cyclohexane; a rise in $\chi_H$ is observed from values approximating those in the solvent toluene to very high values with increasing styrene content, indicating that we are operating below the Flory point in this solvent when the composition exceeds about 30 per cent. The curvature may be real since the higher molecular weight blocks showed similar curvature. This molecular weight dependence of $\chi_H$ is consistent with the behaviour of homopolymers. The decreasing chain length of the styrene sequence, with lower composition for blocks of the same overall molecular weight, would be expected to show increasing solubility. The maxima occurring in $\chi_H$ in toluene and MIBK is considered to indicate the number of heterocontacts in a random coil configuration which, of course, should occur at the mid point on the composition scale when expressed as mole fraction or mole per cent. This brings out the point that $\chi_H$ is influenced by interactions other than the solvent/polymer system alone, and therefore might be expected to contribute to domain formation at higher concentrations. The entropy parameter $\psi$ would be expected to increase (or $\chi_S$ decrease) for the same reasons since the excess entropy of dilution, that is above that expected for the simple mixing of the segments and solvent, may be explained on the basis of the more restricted configurational freedom for this system than the equivalent homopolymer of the same molecular weight. Alternatively, the more expanded molecule, caused by heterocontacts, makes a greater volume available to the solvent than in the case with the homopolymer of equivalent molecular weight.

A closer examination of the data reveals that the enthalpy and entropy of dilution are molecular weight dependent. $\chi_H$ decreases with increasing $\bar{\text{M}}$ at least for toluene and cyclohexane; by contrast, in MIBK there is no observable dependence on molecular weight where all points fall on the same curve. In fact $\chi_H$ drops to 2/3 of its value in the former solvents with increasing $\bar{\text{M}}$ from 100,000 to 500,000. However, the overall shape of the plot of $\chi_H$ or $\chi_S$ with composition remains unchanged.

It seems clear that a proper theory, to explain the solution behaviour of block copolymers, must take account of the composition of the polymer but must also include the contributions to the entropy and enthalpy of dilution from the heterocontacts, which, at least in preferential solvents, give rise to intramolecular phase separation and therefore a change in the configuration of the molecule.

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## REFERENCES

(1) P. J. Flory, *Principles of Polymer Chemistry.* Cornell University Press (1953).
(2) H. Tompa, *Polymer Solutions.* Butterworths (1956).
(3) P. J. Flory, *Discuss. Faraday Soc.* No. 49 (1970).
(4) D. N. Cramond and J. R. Urwin, *Europ. Polym. J.* **5,** 45 (1969).
(5) D. N. Cramond and J. R. Urwin, *Aust. J. Chem.* **21,** 1835 (1968).
(6) D. N. Cramond, M. J. Hammond and J. R. Urwin, *Europ. Polym. J.* **4,** 451 (1968).
(7) H. G. Elias, *Makromolek. Chem.* **33,** 140 (1959).
(8) C. F. Cornet and H. Ballegooijen, *Polymer* **7,** 293 (1966).
(9) J. Brandrup and E. H. Immergut (Eds.), *Polymer Handbook.* Interscience, New York (1966).
(10) M. Kurata and W. H. Stockmayer, *Adv. Polym. Sci.* **3,** 196 (1963).
(11) T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami and H. Inagaki, *Polym. J.* **1,** 245 (1970).
(12) P. J. Flory, *Statistical Mechanics of Chain Molecules.* Wiley (Interscience), New York (1969).
(13) M. Girolamo and J. R. Urwin, *Europ. Polym. J.* **7,** 693, 785 (1971).
(14) M. Girolamo and J. R. Urwin, *Aust. J. Chem.* **24,** 729 (1971).
(15) M. Girolamo and J. R. Urwin, *Makromolek. Chem.* (in press).
(16) J. R. Urwin, *Aust. J. Chem.* **22,** 1649 (1969).

**Résumé**—On a examiné une série de dix copolymères séquencés de poly(isoprène/styrène) par osmométrie à différentes températures. On a utilisé plusieurs solvants; un bon solvant des deux séquences (toluène), un mauvais solvant des deux séquences (méthyl isobutyl cétone) et un solvant préférentiel (cyclohexane) qui est un bon solvant du polyisoprène et un mauvais solvant du polystyrène. On a déterminé les températures de Flory (ou theta) de tous les polymères dans les trois solvants. On a fait une comparaison entre les valeurs de $\theta$ déterminées par des méthodes de point de louche en utilisant la méthyl éthyl cétone comme solvant. On fait apparaitre la partie entropique et enthalpique du paramètre d'interaction $X_1$ et on l'examine en relation avec la composition et le poids moléculaire. On discute également la dépendance entre le poids moléculaire et le second coefficient du viriel. Le fait d'ajouter le paramètre de composition à ceux normalement utilisés pour les homopolymères ne permet pas une description complète des propriétés en solution des copolymères séquencés particulièrement dans le cas de solvants préférentiels où il est évident qu'il y aura une séparation de phase intramoléculaire.

**Sommario**—Si è esaminata una serie di dieci copolimeri in massa di poli(isoprene:stirene) per una gamma di temperature, mediante osmometria. Si sono impiegati diversi solventi; uno si è dimostrato un buon solvente per entrambe le sequenze (toluene); un altro, cattivo solvente per entrambe le sequenze (metil *iso*-butil chetone); e un altro ancora, solvente preferenziale (cicloesano) che è un buon solvente per la sequenza di poliisoprene ma cattivo per il polistirene. Per tutti i polimeri nei tre solventi, si sono determinate le temperature Flory (theta); si è eseguito un confronto dei valori di $\theta$ determinato mediante metodi a temperatura di intorbidimanto impiegando come solvente del metil etil chetone. Si è suddiviso il parametro di azione reciproca $\chi_1$ nelle sue parti entalpica e entropica, e lo si è esaminato per quanto riguarda la composizione e il peso molecolare. Si discute pure come dipenda il peso molecolare dal secondo coefficient viriale. L'inclusione del parametro di composizione, oltre a quelli normalmente impiegati per omopolimeri in questi sistemi, non è sufficiente per una descrizione completa delle proprietà in soluzione dei copolimeri in massa, particolarmente nel caso di solventi preferenziali con i quali si hanno ampie prove di separazione di fase intramolecolare.

**Zusammenfassung**—Eine Serie von zehn Block-Copolymeren von Poly(isopren: styrol) wurden durch Osmometrie über einen Temperaturbereich untersucht. Es wurden verschiedene Lösungsmittel verwendet; eines war für beide Sequenzen ein gutes Lösungsmittel (Toluol), ein anderes war für beide Sequenzen ein schlechtes Lösungsmittel (Methyl-*iso*butyl-keton) und ein anderes war ein bevorzuntes Lösungsmittel (Cyclohexan), welches für die Polyisoprensequenz ein gutes Lösungsmittel, für Polystyrol aber ein schlechtes Lösungsmittel ist. Für alle Polymeren wurden in den drei Lösungsmitteln die Flory (oder Theta)-Temperaturen bestimmt. Die mit Methyl-äthylketon als Lösungsmittel durch Trübungspunkt-Methoden bestimmten $\theta$ Werte werden verglichen. Der Wechselwirkungsparameter $x_1$ wird aufgetrennt in seinen Enthalpie- und Entropieanteil und in Bezug auf die Zusammensetzung und das Molekulargewicht untersucht. Die Molekulargewichtsabhängigkeit des zweiten Virialkoeffizienten wird ebenfalls diskutiert. Die Einbeziehung des Parameters der Zusammensetzung, zusätzlich zu denen, die normalerweise für Homopolymere in diesen Systemen verwendet werden, ist für eine vollständige Beschreibung der Lösungseigenschaften von Block-Copolymeren nicht geeignet, vor allem im Fall von bevorzugten Lösungsmitteln, wo ein starker Hinweis auf eine intramolekulare Phasentrennung besteht.

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# THE CONFIGURATION OF BLOCK COPOLYMERS OF POLYISOPRENE AND POLYSTYRENE IN DILUTE SOLUTION - PART I.

## UNPERTURBED DIMENSIONS

J.R. URWIN AND M. GIROLAMO*

Summary

The unperturbed dimensions of block copolymers of polystyrene and polyisoprene in dilute solution have been determined from measurements made under <u>theta</u> conditions, by application of the Flory-Fox theory to viscosity data. In other solvents, where <u>theta</u> temperatures preclude direct evaluation, the Stockmayer-Fixman method has been applied. The results show that unperturbed dimension determined under <u>theta</u> conditions, whether measured directly or by appropriate extrapolation procedures, vary linearly with composition. Thus the characteristic ratio for the block copolymer may be calculated from homopolymer data according to the relation

$$c_\infty^{\text{Block}} = x c_\infty^{\text{P.S.}} + (1 - x) c_\infty^{\text{P.I.}}$$

where x is the mole fraction and superscripts P.S. and P.I. refer to

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polystyrene and polyisoprene respectively. The steric factor $\sigma = r_o^2/r_{of}^2$ obeys a similar relation.

Short range interaction parameters have also been determined by application of equations relating osmotic second virial coefficients with the excluded volume and which have been shown to be reasonably successful when applied to homopolymers. Data from viscosity and osmometry methods are compared and discussed.

## INTRODUCTION

The concept of an expanded configuration of a linear chain molecule owes its existence to long range interactions and is peculiar to the environment afforded by dilute polymer solutions.(1 It may be recalled that the long range effect, which results in the expanded configuration, is the effective covolume for a pair of segments in the chain immersed in the given solvent. Furthermore, the effect is maximal in dilute solution. Thus, the expansion of the linear chain depends markedly on the solvent in which it is immersed.

The covolume is enhanced by the use of good solvents, but is diminished in a poor one. The judicious choice of both solvent and temperature allows the experimenter to adjust the medium to the point where the covolume is zero. At this point the excluded volume effect vanishes and the polymer chain assumes its 'unperturbed' configuration.(2 It is important to note that the dimensions of the chain represented by the end to end distance, under unperturbed or *theta* conditions, is the average or mean square of the end to end distance $\langle r^2 \rangle_0$, and collectively comprise the complete array of configurations which define the random coil. Thus $\langle r^2 \rangle_0$ denotes the second moment of the end to end distance, averaged over a statistical mechanical ensemble of unperturbed molecules, free of constraints.

In homopolymer theory the second moment of the end to end distance can be expressed by the relation

$$\langle r^2 \rangle = n\ell^2 + 2 \sum_{i<j} \langle l_i l_j \rangle \qquad (1)$$

where $\ell^2$ is the average squared bond length of the n bonds with fixed bond lengths. The first term represents the value for the freely jointed chain or random flight statistics. The summation term represents the sum of the correlations between a pair of bond vectors. The corresponding term for block copolymers contains cross correlations between different species of segments. At the *theta* point the correlations vanish. However, for block copolymers the cross correlations, which are responsible for the more expanded configurations in any other environment, due to interactions which are repulsive in nature, provide a poorer medium for the pair of polymer chain segments than is experienced by either homopolymer immersed in the given solvent. In short, the *theta* temperature may be anticipated to be higher near than the middle of the composition range, where correlations are greatest. This behaviour has in fact been observed and reported by us for these polymers.(3

Since the long range [illegible]ractions have been eliminated at the *theta* point, the 'unperturbed' dimensions, which depend only on bond lengths, bond angles, rotational torque and steric effects, should be a simple function of the number of segments of A and B. Flory recommends the adoption of the freely jointed chain as the reference state for linear molecules and the adoption of the characteristic ratio

$$C_n = \langle r^2\rangle_0/n\ell^2 \qquad (2)$$

for a chain of n bonds of average length ℓ, as the criterion for comparative study. Similarly, the end to end distance may be referred to the freely rotating chain in order to get a measure of steric effects. It would seem, therefore, that theory developed for homopolymers should be applicable to block copolymers, under *theta* conditions, with the introduction of one further parameter, i.e. the composition. The purpose of this paper is to explore this hypothesis.

## EXPERIMENTAL

A series of ten block copolymers of polyisoprene and polystyrene containing just two polymer sequences (AB type) were synthesised anionically by techniques described earlier.(4

The more important characteristics of this series of polymers have been set out in Table 1. Number average molecular weight was measured by high speed osmometry, composition by U.V. absorption spectrometry and heterogeneity ratio $\bar{M}_w/\bar{M}_n$ by G.P.C.(5 Viscometry data on the series was obtained using a number of viscometers constructed in these laboratories. Flared capillaries were adapted to the more usual Ubbelohde suspended level viscometers but which were fitted with an automatic timing device. Solvent flow times at 30.0°C ± 0.01°C were 215.73, 229.87 and 407.86 ± 0.05 sec. in toluene, methyl isobutyl ketone and cyclohexane respectively.

Non-Newtonian behaviour was investigated by comparing $\eta_{rel}$ measured in three viscometers having capillaries with flow times of 120, 215 and 450 sec. respectively for toluene at 30°C. Polymer solutions were measured at the highest concentrations used in the viscometry studies (i.e. $2.5-3.5 \times 10^{-3}$ g. $cm^{-3}$) in the solvents toluene, cyclohexane and methyl isobutyl ketone. Values of $\eta_{rel}$ agreed within 0.1% for particular solvents and it was therefore concluded that corrections would be unnecessary in this work.

Typical behaviour of these polymers, in the three solvents employed, is shown in Fig. 1. The plots represent $\eta_{sp}$ against concentration (full lines) from which the constant $k_H$ is obtained according to Huggins,

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c \qquad (3)$$

The dotted lines shown represent plots of ln $\eta_{rel}/c$ against concentration, from which the constant k' is derived, according to the relation of Kraemer

$$\ln \eta_{rel}/c = [\eta] - k'[\eta]^2c. \qquad (4)$$

These two equations are related such that the sum of the two constants is $\frac{1}{2}$, thus $k_H + k' = 0.5$.

Experimental values obtained on the whole series of polymers in toluene and methyl isobutyl ketone were in good agreement with the above prediction. This is in accord with results of other workers reported for block copolymers with two and three sequences.(6

Osmotic data were measured with a Hewlett-Packard membrane osmometer. Second virial coefficients were obtained from plots of $[\Pi/c]^{\frac{1}{2}}$ against concentration at specific temperatures. Theta temperatures were obtained by the usual extrapolation of $A_2$ against 1/T to $A_2 = 0$ where $\theta = T_{A_2=0}$.

## RESULTS AND DISCUSSION

Of the two principal methods currently in use to determine the dimensions of polymer chains, i.e. light scattering and viscometry, the latter is, strictly speaking, the only valid one for block copolymers. The difficulty in light scattering is the intractable problem associated with measurement of the radius of gyration from polymer solutions containing species with different refractive indices.

It is desirable to determine the unperturbed dimensions in each of several solvents, but since measurement at the *theta* temperature is often experimentally impractical it is necessary to resort to methods other than direct measurement under *theta* conditions. The method depends on the relationship(7

$$[\eta] = \Phi\langle r^2\rangle^{3/2} \Big/ M \qquad (5)$$

valid for random polymer coils of high molecular weight. Here $\Phi$ is assumed constant for all systems, and M is the molecular weight. If measurements are made under theta conditions it is appropriate to write Eq. 5 in the form

$$[\eta]_\theta = \Phi (\langle r^2\rangle_0/M)^{3/2} M^{1/2} \qquad (6)$$

in which $\Phi$ is given the limiting value $2.68 \times 10^{23}$, with r in cms. and $[\eta]$ in mls. per gram. For sufficiently long homologous chains the unperturbed end to end distance is proportional to M and Eq. 6 becomes

$$[\eta]_\theta = KM^{1/2} \qquad (7)$$

where K is constant for a given homologous series and we may write

$$(\langle r^2\rangle_0/M)_\infty = (K/\Phi)^{2/3} \qquad (8)$$

The intrinsic viscosity $[\eta]$ was measured for the whole series of polymers in the *theta* solvents previously reported.(3 The results are listed in Table I. Values of $K_\theta$, $r_0^2/M$, $r_0^2$ and $r_0^2/z$ were calculated according to the method described. Here, the symbol z represents the number of links which is a more appropriate parameter for blocks when examining the effect of composition. The question of how to express the composition arises from the different segmental molecular weights of styrene $M_0 = 104$ and isoprene $M_0 = 68$ as well as the different number of bonds and bond types occurring in these chains. Allowing for the 5% 3,4-polyisoprene in the isomeric composition and also the double bond, the value of z was calculated from the relation

$$z = \bar{M}_n [w\ 2/104 + (1 - w)3.8/68] \qquad (9)$$

in which w is the weight fraction. The composition may then be expressed as link fraction (or links percent) for comparative purposes.

A glance at values for $K_0$ shows that they are independent of molecular weight but vary with composition, in fact closer examination reveals that they vary linearly with composition, whether the composition range is expressed in weight percent or in terms of z. Extrapolation to each end of the composition range on the latter scale yields values of 13.0 for polyisoprene and 8.0 for polystyrene. Values of K reported for 100% cis polyisoprene (natural rubber) and 100% trans (gutta-percha) are $11.9 \times 10^{-4}$ and $23.2 \times 10^{-4}$ respectively.(8 Adjusting for a composition 80% cis, 15% trans and 5% 3,4 gives a value of 13.4 for the isomeric composition in the block. The agreement is most satisfactory. The extrapolated value using the weight fraction scale yields a value for polystyrene which is too high (9.7).

The other dimensional parameters behave similarly since they are calculated from the same data. The steric behaviour is most often expressed by the steric factor σ defined by

$$\sigma = \frac{\langle r^2 \rangle_0^{\frac{1}{2}}}{\langle r^2 \rangle_{of}^{\frac{1}{2}}} \qquad (10)$$

which relates the unperturbed dimension with reference to the freely rotating chain. A plot of the steric factor against z is shown in Fig. 2. It can be seen that values vary linearly from that of polyisoprene to the value for polystyrene.

The characteristic ratio $c_\infty$, in which the reference state is the freely jointed chain,(9 is preferred for comparison purposes and values of $c_\infty$, column 9, may be compared with those shown in brackets which have been calculated from

$$c_\infty^{Block} = x c_\infty^{P.S.} + (1 - x) c_\infty^{P.I.} \qquad (11)$$

where x is the mole fraction of polystyrene, thereby demonstrating the simple linear dependence of $c_\infty$ for the block on the composition. All values are ~~all~~ well within the experimental error which may be reasonably expected for the method.

In other solvents, particularly good solvents, direct measurement at the theta temperature is impracticable and it is therefore necessary to resort to indirect methods. A useful and well tried method is that due to Stockmayer and Fixman.(10 These authors using a simple closed expression for the viscosity expansion factor α, due originally to Fixman,(11 proposed the relation,

$$[\eta] = KM^{\frac{1}{2}} + 0.51\Phi BM \qquad (12)$$

where B is the long range interaction parameter related to the Flory interaction parameter $\chi_1$ by

$$B = \bar{v}^2 (1 - 2\chi_1)/V_1 N_A \qquad (13)$$

with $\bar{v}$ = specific volume of polymer, $V_1$ = molar volume of solvent, $N_A$ = Avogadro's number, or in terms of the binary cluster integral β

$$B = \beta/M_0^2 \qquad (14)$$

which we will explore in the next part of this paper. For the purpose of this enquiry, we need only concern ourselves with the first term in Eq. 12, i.e. the short range parameters. In order to evaluate the first term, plots of $[\eta]M^{-\frac{1}{2}}$ against $M^{\frac{1}{2}}$ must be constructed. The intercept gives the short range interaction parameter $K_\theta$ or the short range parameter A where A is defined by

$$A^2 = <r^2>_0/M \tag{15}$$

and Eq. 12 may be written in the form

$$[\eta] = \Phi A^3 M^{\frac{1}{2}} + 0.51\Phi BM \tag{16}$$

in which $\Phi$ has its limiting value $2.68 \times 10^{23}$. Equation 12 has been shown to yield correct values for $K_\theta$ in both good solvents and poor solvents alike. The results of the application of Eq. 12 to the block copolymers for the series 25/75 and 50/50 representing 25% P.S. and 50% P.S. by weight respectively are given in Table 2. The plots of $[\eta]M^{-\frac{1}{2}}$ against $M_n^{\frac{1}{2}}$, Fig. 3, were curved in the higher molecular weight region for the series 25/75 and therefore difficult to extrapolate, resulting in a corresponding loss of accuracy. The other plots were linear. According to experience with homopolymers,(12 the limit of applicability of Eq. 12 is $\alpha_\eta < 1.4$. The same limitations were found to apply to the block copolymers. This explains the curvature of the highest molecular weight I39 in cyclohexane where $\alpha_\eta = 1.68$. Values of $A = (<r^2>_0/M)^{\frac{1}{2}}$ and $K_\theta$ are tabulated in Table 2 along with values from determinations in theta solvents directly. The agreement is most gratifying, indicating that the two methods are equally applicable to block copolymers in dilute solution. It should be made clear at this stage that considerable caution must be exercised in applying these methods to 'preferential' solvents since intramolecular phase separation may invalidate the procedure(13 unless the temperature is well above the transition temperature, $T_p$. This was the reason for adopting $T = 46°C$ for cyclohexane in this investigation.

It is always desirable to complement, if possible, a particular method of measurement with an alternative method based on different basic principles. This approach is particularly valuable in our case where we are trying to assess the validity of the application of theories developed for homopolymers to block copolymer systems. Kurata and coworkers(14 have proposed using second virial coefficients from osmotic measurements for the determination of unperturbed dimensions. These workers derive an expression relating the second virial coefficient $A_2$ from osmometry and the excluded volume based on the Fixman relation.(11 Accordingly, Kurata et al. arrive at the expression

$$A_2\bar{M}_n^{1/2} = 1.65 \times 10^{23} A_\eta^3 + 0.968 \times 10^{23} B_\eta \bar{M}_n^{1/2} \qquad (17)$$

in which form the short and long range interaction parameters are clearly separated. Treatment of the data requires only that plots be made of $A_2\bar{M}_n^{1/2}$ against $\bar{M}_n^{1/2}$ from which $A_\eta$ may be obtained. The relation is valid when $\alpha_\eta > 1.2$, i.e. in good solvents only. That good linear plots were obtained can be seen from inspection of Fig. 3 although it must be admitted that only three points were available for each series.

An alternative expression, in which the Fixman relation for the excluded volume is replaced by one due to Ptitsyn,(15 has the same form as Eq. 17 with different constants thus:

$$A_2\bar{M}_n^{1/2} = 2.83 \times 10^{23} A_\Pi^3 + 1.67 \times 10^{23} B_\Pi \bar{M}_n^{1/2} \qquad (18)$$

Values calculated from osmotic data already published(3 are set out in Table 3. The subscript on $\Pi_1$ and $\Pi_2$ refers to values obtained from Eqs. 17 and 18 respectively. Polymers of the series coded 25/75 (25% P.S.) and 50/50 (50% P.S.) have been examined and the results may be compared with those from the [η]-M method. $A_\eta$ has been included to assist comparison. Only data measured from toluene and cyclohexane solutions are amenable to treatment, MIBK is outside the range of applicability. The discrepancies between $A_\eta$ and $A_\Pi$ are in line with experience gained with homopolymers.(16,17,18

The closer agreement between $A_\eta$ and $A_{\Pi_2}$ than between $A_\eta$ and $A_{\Pi_1}$ may be better appreciated by consideration of the osmotic dimensionless ratio defined as $A_2\bar{M}_n/[\eta]$. Eq. 17 predicts values should be about 60 whereas the use of Eq. 18 should yield values of about 110. Experimentally, values of $A_2\bar{M}_n/[\eta]$ ranging from 100-140 have been obtained from homopolymer studies.(3,19 Values calculated for the block copolymers in toluene and cyclohexane are shown in Table 4. It can easily be seen that the values in toluene are close to the predicted limit using Eq. 17 whilst those in cyclohexane are generally lower but lie between the two predicted values. This may provide a reason for the better correlation between $A_\eta$ and $A_{\Pi_2}$ and also may provide an explanation for the ratio $A_M/A_\eta$ being greater than unity using Eq. 17 and less than unity using Eq. 18 for the series 50/50 in cyclohexane.

The poor agreement between the $A_2$-M and [η]-M methods is in part due to the low sensitivity of $A_2$ to M but it also shows a need for refinement of the theory. Nevertheless the [η]-M method appears to inspire confidence for its general use with block copolymer systems provided caution is adopted in applying the method within the limits set by the theory.

On the basis of the arguments presented, it seems clear that unperturbed dimensions may be obtained in solutions where the excluded volume has vanished and which may be identified by the temperature and composition at which the second virial coefficient vanishes. To appreciate 'theta' conditions for a block copolymer containing two or more sequences comprised of different species it is illuminating to consider an analogous system, the three component 'theta mixture' of polymer-solvent-non solvent. In the block copolymer system, the non solvent is replaced by the other block, that is segments of one polymer chain are in an environment of solvent/segments of the second block.

In the microscopic system of a single chain the concentration of the poorly compatible segments may be quite high. The theta temperature must therefore be expected to show concentration, i.e. composition, dependence. That this is so is borne out by the behaviour of the viscosity constant $K_\theta$ which has been found to be independent of the solvent at the given temperature and composition. Thus the characteristic ratio of the block copolymer may be calculated directly from the corresponding values of $c_\infty$ measured for homopolymers, according to Eq. 11 and provided the composition is known.

In summary, the two parameter theories derived for homopolymers may be applied to solutions of block copolymers with the addition of one further parameter, namely the composition, and with the same degree of confidence. The theta point has the same meaning and can be defined in the same way as for homopolymers. The unperturbed dimensions may be calculated from data derived from the parent polymers with the addition of the composition parameter.

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## References

1. P.J. Flory, Statistical Mechanics of Chain Molecules, Interscience, 1969 pp 35.
2. Ibid. pp 34.
3. M. Girolamo and J.R. Urwin, European Polymer J. (in press).
4. D.N. Cramond and J.R. Urwin, Austral. J. Chem. 21 (1968) 1835.
5. D.N. Cramond, M.J. Hammond and J.R. Urwin, European Polymer J. 4 (1968) 451.
6. L.A. Utracki, R. Simha and L.J. Fetters, J. Polymer Sci. A2 6 (1968) 2051.
7. H. Tompa, Polymer Solutions, Butterworths, London 1956, pp. 275.
8. M. Kurata and W.H. Stockmayer, Fortsch. Hochpolym.-Forsch, 3 (1963) 196. omit
9. Ref. 1, pp 38.
10. W.H. Stockmayer and M. Fixman, J. Polymer Sci. C1 (1963) 137.
11. M. Fixman, J. Chem. Phys. 23 (1955) 1656.
12. M. Inagaki, T. Mijamoto and S. Ohta, J. Phys. Chem. 70 (1966) 3420.
13. J.R. Urwin and M. Girolamo, Die Makromolek. Chemie (in press); European Polymer J. __ (1971) ; Austral. J. Chem.24___ (1971)729
14. M. Kurata, H. Fukatsu, H. Sotobayashi and H. Yamakawa, J. Chem. Phys. 41 (1964) 139.
15. O.B. Ptitsyn, Vysokomol. Soedin. 3 (1963) 1673.
16. G.C. Berry, J. Polymer Sci. B4 (1966) 161.
17. G.C. Berry, J. Chem. Phys. 44 (1966) 4550; 46 (1967) 1338.
18. M. Iwama, H. Utijama and M. Kurata, J. Makromol. Chem. 1 (1966) 701.

19. T.A. Orofino and P.J. Flory, J. Chem. Phys. 26 (1957) 1067.

20. J.E. Mark, J.A.C.S. 88 (1966) 4354; 89 (1967) 6829.

# Captions

Fig. 1. Plots of reduced viscosity $\eta_{sp}/c$ (full lines) and $\ln \eta_{rel}/c$ (dashed lines) for a block copolymer in three solvents.

Fig. 2. Plot of the steric factor $\sigma = (r_o^2/r_{of}^2)$ against composition expressed as percentage links (Polystyrene %) in the backbone of the chain.

Fig. 3. Plots of $[\eta]\bar{M}_n^{-\frac{1}{2}}$ and $A_2\bar{M}_n^{\frac{1}{2}}$ against $\bar{M}_n^{\frac{1}{2}}$ for the series of polymers coded 25/75 and 50/50 in the solvents indicated.

Table 1

Intrinsic viscosity and unperturbed dimensions of the block copolymers of poly(isoprene-styrene) under theta conditions

| Polymer | $\bar{M}_n$ $\times 10^{-5}$ | $\bar{M}_w/\bar{M}_n$ * | Composition % P.S. wt.% | Links % | Mole % | $[\eta]_\theta$ ml/g | $K_\theta$ $\times 10^2$ | $\bar{r_o^2}/M$ $\times 10^{17}$ | $\bar{r_o^2}/n$ $\times 10^{17}$ | $C_\infty$ ** |
|---|---|---|---|---|---|---|---|---|---|---|
| I.S.1 | 1.02 | 1.08 | 13.5 | 5.1 | 9.2 | 41.3 | 12.9 | 6.15 | 120.8 | 5.20 (5.10) |
| I.S.2 | 1.02 | 1.10 | 24.7 | 10.1 | 17.6 | 40.3 | 12.6 | 6.05 | 129.2 | 5.56 (5.61) |
| I.S.3 | 1.01 | 1.09 | 28.2 | 11.9 | 20.4 | 39.1 | 12.3 | 5.95 | 130.7 | 5.62 (5.76) |
| I.S.4 | 1.04 | 1.08 | 52.2 | 27.3 | 41.6 | 37.5 | 11.6 | 5.73 | 155.9 | 6.70 (6.86) |
| I.S.5 | 1.03 | 1.08 | 78.2 | 55.2 | 70.1 | 33.5 | 10.4 | 5.33 | 195.9 | 8.40 (8.35) |
| I.S. 6 | 2.53 | 1.10 | 11.8 | 4.4 | 8.0 | 65.0 | 12.9 | 5.16 | 119.3 | 5.14 (5.12) |
| I.S.7 | 2.52 | 1.08 | 25.5 | 10.5 | 18.3 | 63.3 | 12.6 | 6.05 | 130.0 | 5.59 (5.65) |
| I.S.8 | 2.54 | 1.07 | 48.5 | 24.5 | 38.1 | 58.6 | 11.6 | 5.73 | 150.4 | 6.47 (6.60) |
| I.S.9 | 4.99 | 1.11 | 25.1 | 10.3 | 17.9 | 89.1 | 12.6 | 6.05 | 129.6 | 5.58 (5.63) |
| I.S.10 | 5.10 | 1.13 | 48.7 | 25.4 | 39.3 | 82.3 | 11.6 | 5.75 | 152.7 | 6.57 (6.74) |
| P.S. | – |  | 100 | – | – | – | 8.2 | 4.49 | – | 9.90† |
| P.I. | – |  | 0 | – | – | – | 11.9 | 6.89 | – | 4.70† |

* Calculated from standard deviation determined by G.P.C.(5 ** Values in brackets from eq. (11).

† From references 1, 20.

Table 2

Short range interaction parameters for the block copolymers calculated from the Stockmayer-Fixman relation (Eq. 12)

| Polymer series | Solvent | Temp. °C | $K_\theta$ $\times 10^2$ | A $\times 10^{11}$ |
|---|---|---|---|---|
| Code 25/75 | Toluene | 30 | 12.8 | 782 |
| | MIBK | 30 | 12.8 | 782 |
| | Theta (MEK) | 49 | 12.6 | 778 |
| 50/50 | Toluene | 30 | 11.5 | 754 |
| | MIBK | 30 | 12.4 | 773 |
| | c-Hex | 46 | 11.6 | 756 |
| | Theta (MEK) | 44 | 11.6 | 757 |

### Table 3

Short range interaction parameter $A_{\Pi}$ determined from second virial coefficients- molecular weight data

| Solvent | Polymers (code) | $A_{\eta}$ $\times 10^{11}$ | $A_{\Pi 1}$ $\times 10^{11}$ | $A_{\Pi 2}$ $\times 10^{11}$ | $A_{\Pi_1}/A_{\eta}$ | $A_{\Pi_2}/A_{\eta}$ |
|---|---|---|---|---|---|---|
| Toluene | 25/75 | 782 | 1059 | 885 | 1.35 | 1.13 |
| c-hexane | | 778 | 1018 | 850 | 1.31 | 1.09 |
| Toluene | 50/50 | 754 | 981 | 820 | 1.30 | 1.80 |
| c-hexane | | 756 | 823 | 687 | 1.09 | 0.91 |

Series coded 25/75 are I.S.2, I.S.7, I.S.9

50/50 are I.S.4, I.S.8, I.S.10

### Table 4

Osmotic dimensionless ratio of the block copolymers from data in the solvents toluene and cyclohexane

| | $A_2\bar{M}_n/[\eta]$ | | | $A_2\bar{M}_n/[\eta]$ | |
|---|---|---|---|---|---|
| Polymer | Tol. | c-hex. | Polymer | Tol. | c-hex. |
| I.S.1 | 118 | 96 | I.S.6 | 59 | 71 |
| I.S.2 | 112 | 93 | I.S.7 | 98 | 79 |
| I.S.3 | 119 | 97 | I.S.8 | 111 | 76 |
| I.S.4 | 106 | 80 | I.S.9 | 76 | 54 |
| I.S.5 | 115 | 70 | I.S.10 | 92 | 65 |

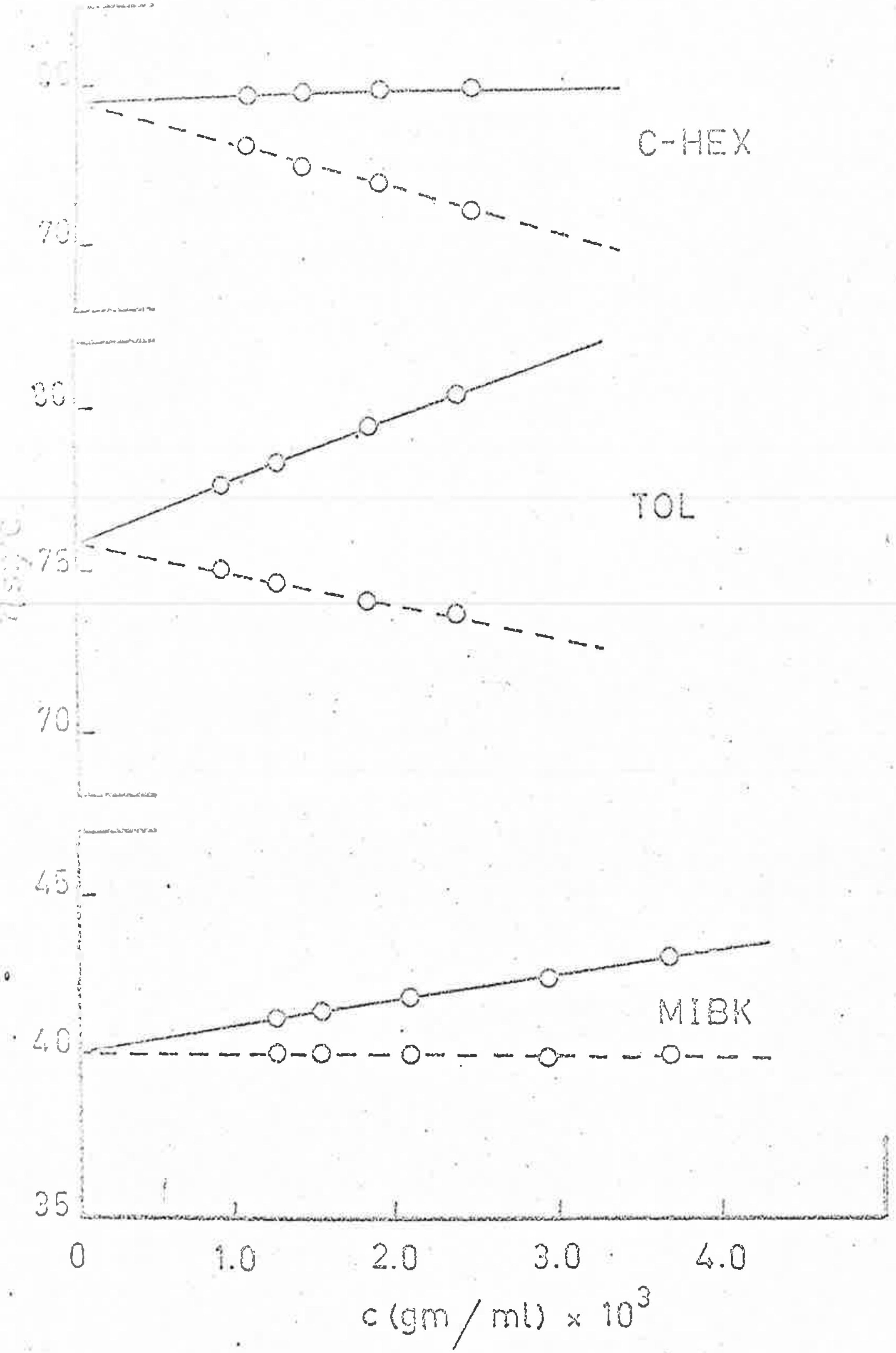

Fig. 1

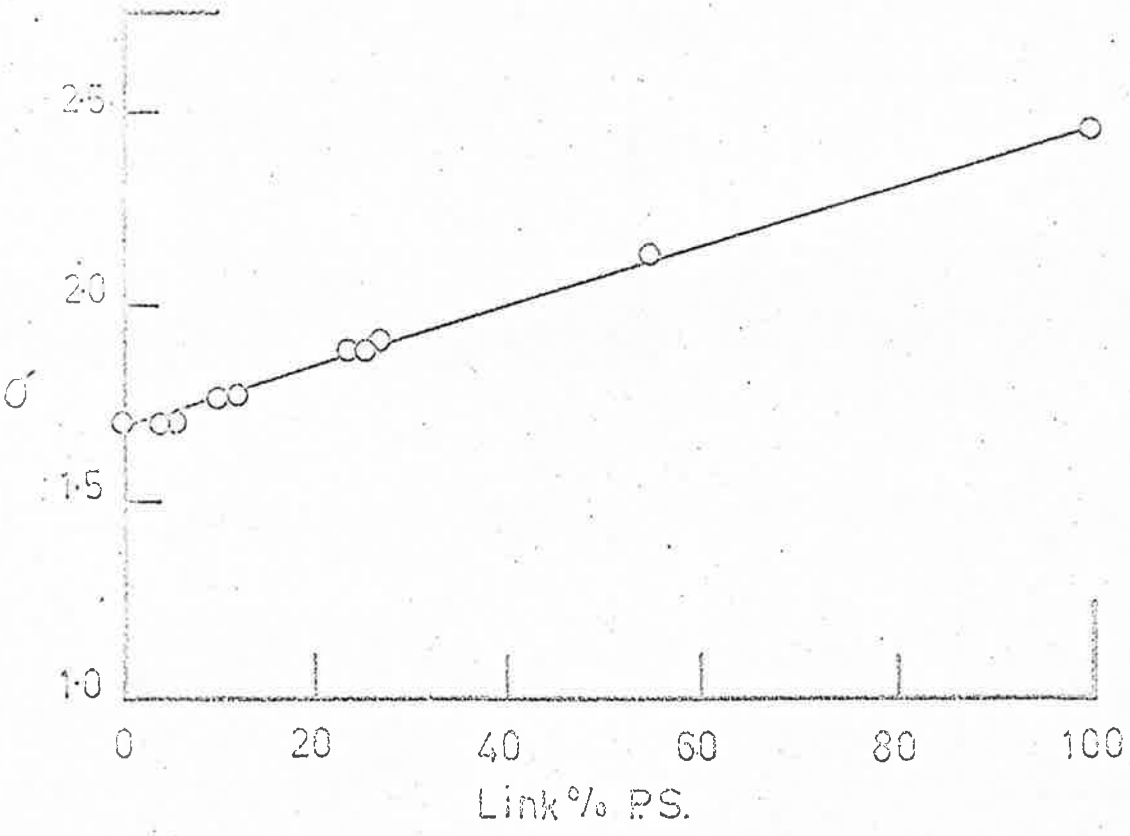

Fig. 2

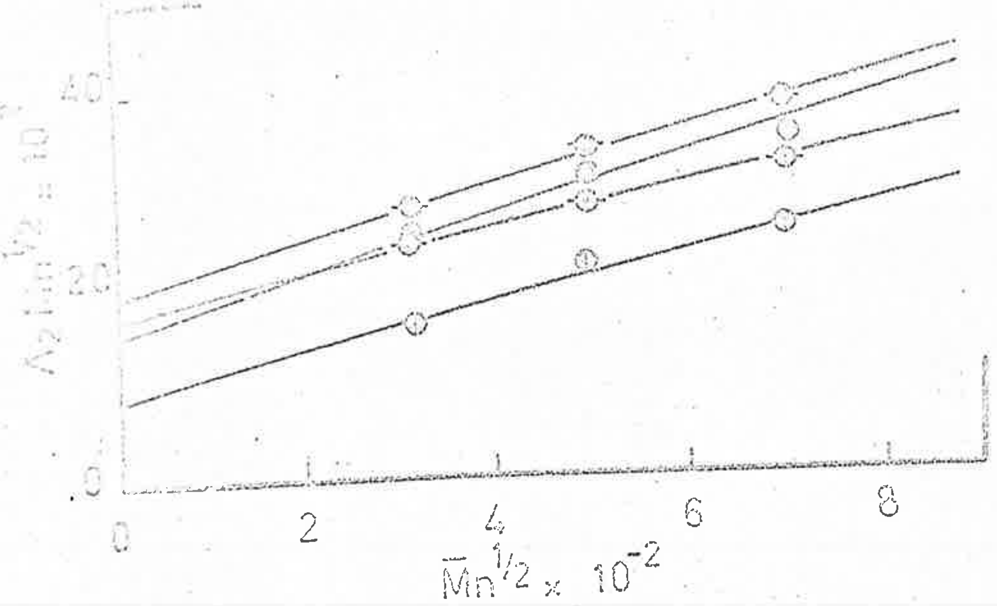

Fig.3

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# THE PREPARATION AND ANALYSIS OF HIGH PURITY ORGANO-LITHIUM INITIATORS

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(Received December 23rd, 1971)

## SUMMARY

The preparation and analysis of organolithium initiators with a high degree of purity, which is highly desirable for the synthesis of polymers, is described. The efficiency and accuracy of various analytical methods currently in use are compared and discussed.

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The importance of alkyllithium initiators in the synthesis of highly stereospecific polydienes has long been recognised[1]. Combined with the non-terminating character of anionic polymerization first recognised and exploited by Szwarc[2], these discoveries have provided the experimentalist with powerful tools for the synthesis of polymers containing a high percentage of *cis*-1,4-polydiene. Recently, much work has been directed towards the synthesis of triblockpolymers, particularly those which constitute the commercially important thermoplastic elastomers. In these polymers the central block is a polydiene and the two terminal sequences are polystyrene or a similar glassy polymer. Organolithiums of a high degree of purity are necessary to produce both the elastomeric character of the material and the overall structural perfection required to achieve their maximum potential.

Organolithiums are highly reactive towards atmospheric contaminants, in particular water and oxygen. Failure to achieve "clean" systems results in the production of non-initiating basic products according to the reactions:

$$\text{R–Li} + \text{O}_2 \rightarrow \text{ROOLi}$$

$$\text{ROOLi} + \text{R–Li} \rightarrow 2\,\text{ROLi}$$

$$\text{R–Li} + \text{H}_2\text{O} \rightarrow \text{RH} + \text{LiOH}$$

Basic impurities may be expected to be present to some degree in all samples of these initiators unless specific precautions are taken to exclude contaminants during preparation and subsequent handling. The presence of contaminants in the initiator is undesirable on two counts since lithium hydroxide affects polystyrene tacticity and both alkoxides and hydroxide reduce the *cis*-1,4-diene content. Furthermore, these

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impurities create problems in the analysis of the initiator since it is necessary for accurate predictability of molecular weight to know the amount of impurity present and to avoid further destruction of the initiator in subsequent steps. The importance of this is readily seen when one realises the dilution, *viz.* $10^{-5}$–$10^{-2}$ *M*, which is required for polymerization to high molecular weight and which is governed by the ratio of monomer and initiator charges. In this study of organolithiums it has been found possible to prepare lithium based initiators with a high degree of purity and to analyse them, without further contamination, by the use of long established vacuum line techniques.

High purity n-butyllithium and sec-butyllithium were prepared for this study by addition of the appropriate alkyl chloride to metallic lithium:

$$R{-}Cl + 2\,Li \rightarrow R{-}Li + LiCl$$

The absence of lithium chloride in the system, below detectable limits, has been established in this work. The alternative route involving the use of dialkylmercury was not considered a viable method because of the long duration of the reaction time required (*i.e.* several weeks)[3]. This would most certainly result in some decomposition of the alkyllithium. In this study we also describe the preparation of the dianionic initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane. A method for the removal of benzophenone from 1,1-diphenylethylene, which is essential to the preparation, is also described. Benzophenone is nearly always present in 1,1-diphenylethylene since it is an oxidation product of the reagent. The method of elimination described in this work offers an alternative to that proposed by Spach *et al.*[4] and is, we believe, faster and more efficient. Finally, a comparison has been made of the various methods of analysis ggested for alkyllithium compounds which are still in current use.

## EXPERIMENTAL

Proton magnetic resonance (PMR) measurements were conducted on a Varian DA 60 IL NMR spectrometer. All optical densities were determined on a Gilford model 2000 and a Shimadzu QH-50 UV spectrophotometer. Optical densities over the range of wave lengths 250–310 nm were checked, using mercury lines, according to the method proposed by Haupt[5].

### *Benzene*

A.R. grade benzene was refluxed over calcium hydride for 12 h, distilled through a 3 ft. fractionating column and the fraction boiling between 80–81° collected. Gas chromatograms were obtained on all samples and the results obtained indicated a pure product. Degassing of the solvent on the vacuum line was followed by flash distillation into a 1 l reservoir attached to the line. The distillation of the solvent was followed by the polymerization of styrene in the reservoir by n-butyllithium; the bright red colour served as an indicator demonstrating the complete absence of contaminants. Further samples of benzene were added to this vessel from time to time until the colour eventually faded. All charges of benzene were taken from this reservoir.

### *Purging solutions*

The preparation of purging solutions for the purging of all reaction vessels

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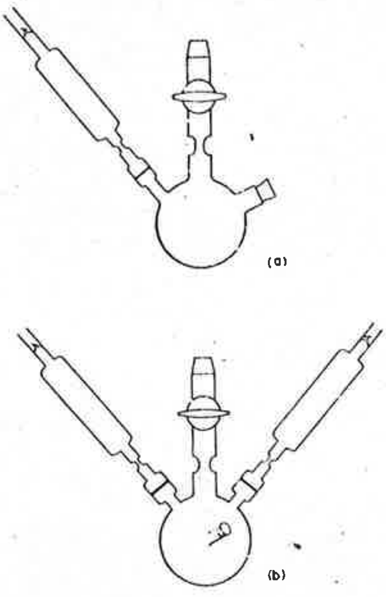
has been adequately described in an earlier publication[6]. The same procedures were adopted for this study.

*Concentrated initiator solutions*

(*a*). n-Butyl chloride and sec-butyl chloride were gently refluxed over calcium hydride for several hours and finally fractionated. The fractions boiling at 78–79° (n-butyl chloride) and 68–69° (sec-butyl chloride) were collected over fresh calcium hydride. Again, gas chromatograms indicated the complete absence of impurity.

Some of the solutions of alkyllithium compounds, previously used by Cramond and Urwin[6], were observed to become cloudy after a short period of storage. These were always discarded but because of this it was considered necessary to modify the procedure. A vessel fitted with a tap and stoppered side arm and sampling ampoule, Fig. 1(a), or for large volumes, with several sampling ampoules attached, Fig. 1(b), was flamed out under high vacuum. With the tap closed, the vessel was removed from the line and dry argon allowed slowly to fill it. With argon still flushing, lithium chips, cut under benzene, were added through the side arm. The surface remained bright throughout showing that the oxidation of the surface was minimal. This precaution was found necessary for starting the reaction; often it was found that reaction with the alkyl halide was inhibited by the absence of bright surfaces. The vessel was restoppered, evacuated, and a charge of benzene admitted from the reservoir (100–120 ml). This was followed by 30 ml of dry alkyl halide, after which the mixture was frozen down. After pumping to high vacuum, the vessel was removed from the line, thawed and left in an ice bath for 12 h. It was allowed to stand for three days at ambient



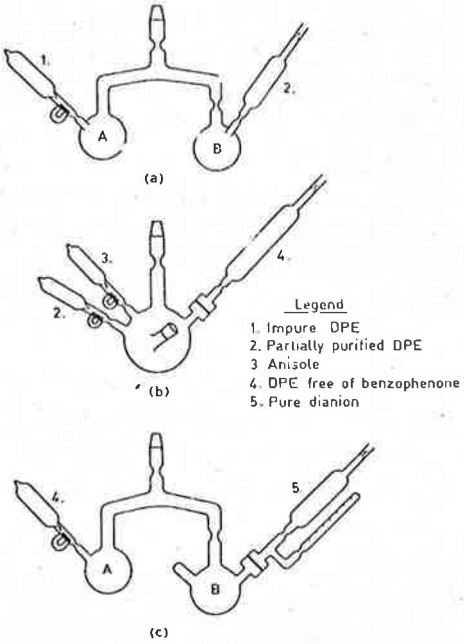


Fig. 1. Reaction vessel for the preparation of concentrated initiator solutions.

Fig. 2. Apparatus used in the preparation of the dianion.

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temperature to complete the consumption of the alkyl halide. To ensure that no unreacted alkyl chloride remained, all distillable materials were removed on the line and finally a fresh charge of benzene added. After freezing and pumping to high vacuum, the vessel was sealed off at the constriction, the mixture filtered through a No. 4 porosity filter and sampled. Storage at −10° minimized decomposition of the product. The concentration at this stage was about 2.5 *M*. Two grades of lithium were employed, (*i*), B.D.H. Lab. grade 98 % purity and (*ii*), Koch Light 2N8 99.8 % purity.

(*b*). 1,4-Dilithio-1,1,4,4-tetraphenylbutane (TPB)$Li_2$, the dianionic initiator, was prepared by reacting 1,1-diphenylethylene with lithium metal. The radical ion formed first but then rapidly dimerizes to yield the dianion. The preparation of a pure product is difficult owing to the presence of the oxidation product of diphenylethylene, benzophenone. Szwarc and coworkers[4] used a method involving a series of distillations of diphenylethylene onto previously prepared samples of the sodium salt of the dianion. The blue adduct between benzophenone and the dianion became progressively paler with successive distillations until all benzophenone was removed. We propose a method for removing benzophenone *in situ* as follows. The reaction vessel, Fig. 2(b), had attached an ampoule of anisole (30 ml) which is used to solubilise the dianion. Anisole was used because this ether least affected the *cis*-1,4 content of the polyisoprene. After an initial flash distillation of the 1,1-diphenylethylene, Fig. 2(a), into sealed ampoules, one of the ampoules was attached to the reaction vessel, lithium chips were added under argon gas, and the vessel was evacuated. Finally, a charge of benzene (200 ml) was admitted from the reservoir. After sealing off from the line, the impure diphenylethylene was broken in, with anisole, on to the lithium chips. In about 18 h a dark blue colour developed, which ultimately became masked by the deep red colour of the dilithio anion. The contents of the flask were filtered through a No. 4 porosity filter to separate the unreacted diphenylethylene, the benzophenone products and a small amount of the dianion from the lithium. In this way, most of the original diphenylethylene was retained. The ampoule from this step was then attached to bulb A, Fig. 2(c), lithium chips were admitted to bulb B under argon, as previously, the side arm was sealed off and the vessel evacuated. After sealing from the vacuum line, the ampoule on A was broken in. Benzene, anisole and diphenylethylene was distilled into B, leaving behind the non-distillable products of benzophenone and the previously formed dianion. Finally, bulb B was sealed off and the reaction allowed to proceed for three days. The red colour appeared within several hours but with no sign of the blue colour characteristic of the adduct. This was taken to imply that the benzophenone had been completely removed. After filtration, an ampoule of the dilithio initiator containing a concentration of about $10^{-2}$ *M* was obtained. Analysis was effected by acid titration, employing the calibrated side tube.

### *Dilution and sampling procedures*

In Fig. 3 the apparatus for dilution and sampling of the initiators n-butyl- and sec-butyllithium is shown Two ampoules, containing 100–120 ml of polystyryllithium in benzene, were attached to bulb A, whilst to bulb B was sealed a ½ to 1 ml sample of the concentrated (2.5 *M*) initiator solution. ~~Two solution~~. Two silica cells of 0.5 cm optical path were attached to the bulb, together with several pre-calibrated sampling tubes constructred from obolete Pyrex burettes and pipettes. Cell corrections for each cell with respect to its matched partner had previously been calculated at 285 nm

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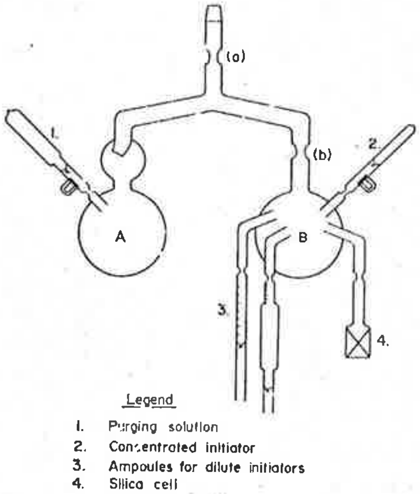

Fig. 3. Apparatus for dilution and sampling of initiators.

with benzene as solvent. (BuLi was found to obey Beer's Law at 285 nm)[7].

The vessel was flamed out and sealed off, under vacuum, at the constriction. The living polymer solution was broken into A and the complete apparatus purged. The purge solution was returned to A and the vessel rinsed with solvent distilled from this bulb. After several washings, with particular attention paid to the silica cells to remove small amounts of terminated polymer, the solvent was distilled from the polystyryllithium into bulb B. The concentrated initiator solution was broken into B and mixed with the solvent to give an approximately $10^{-2} M$ solution. A small quantity of this solution was tipped into one of the silica cells which was then sealed from B. The concentration was determined accurately by UV analysis and, if necessary, the concentration adjusted by distillation of solvent back into A. The analysis was then repeated, using the second cell attached to B. Bulb B was then sealed off at the constriction. The volumes of initiator required to polymerize a monomer charge of 13–16 g, for various molecular weights, were calculated and this volume tipped into pre-calibrated ampoules. The ampoules were sealed from bulb B and stored in the refrigerator.

The excess initiator was collected in a large calibrated ampoule, removed from B, broken open under water and the benzene evaporated off. The resulting hydroxide solution was analysed by acid titration using standard hydrochloric acid with phenolphthalein or bromothymol blue as indicator. This method of analysis was considered satisfacotry, particularly when coupled with the special preparative procedures adopted above, and the fact that no initiator losses were observed during dilution and sampling operations in prepurged vessels.

The same apparatus was used for dispensing samples of sec-butyllithium. Concentrations were therefore all determined by simple acid titration after demonstrating the efficacy of the procedures adopted. Accurate volumes of the sec-butyllithium were dispensed and also stored under refrigeration.

Similar apparatus was also used to convert the dianion 1,4-dilithio-1,1,4,4-tetraphenylbutane to polyisoprenyldilithium "seed". The object in using the seeding

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technique was to avoid precipitation due to the limited solubility of 1,4-dilithio-1,1,4,4-tetraphenylbutane. The "seeding" technique was achieved by mixing the sample of purged isoprene in bulb A, sufficient to convert all the dianion, attached to bulb B, to the low molecular weight "seed" ($M_n \approx 2000$).

*Lithium butoxide*

The NMR spectrum of lithium n-butoxide was determined to provide a routine check for the presence of this impurity in initiator samples. The butoxide was prepared by reacting n-butanol with n-butyllithium

$$\mathrm{BuOH + BuLi \rightarrow BuOLi + BuH}$$

A reaction vessel was evacuated and sufficient n-butanol to consume $\frac{1}{4}$ of the n-

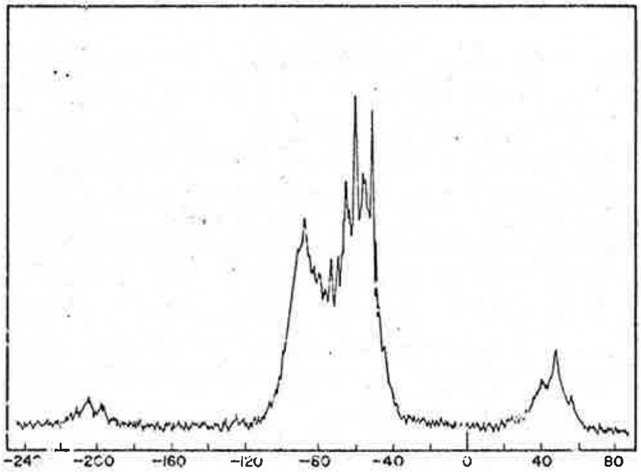

Fig. 4. PMR spectrum of n-butyllithium in benzene containing butoxide (in Hz referred to TMS).

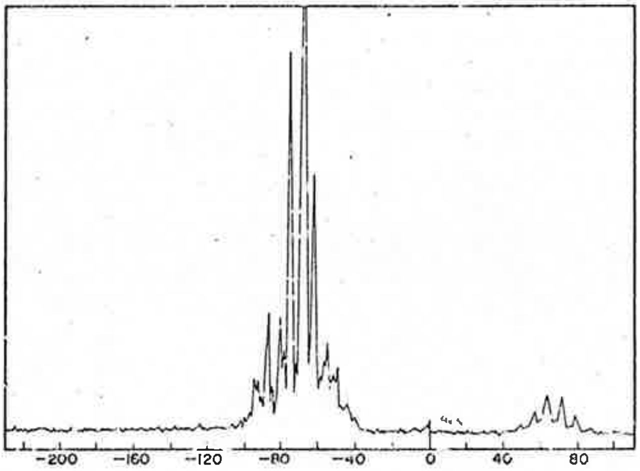

Fig. 5. PMR spectrum of sec-butyllithium in benzene (in Hz referred to TMS).

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butyllithium to be added was distilled in. The vessel was sealed from the line, n-butyllithium broken in and a vigorous reaction ensued. After reaction, samples were tipped into NMR tubes sealed to the reaction flask and sealed off from the vessel. The NMR spectrum (Fig. 4) showed a triplet, centre peak 206 Hz downfield from TMS. The n-butyllithium triplet was 48 Hz upfield from TMS. The areas of the two triplets showed the ratio 3/1 as expected, indicating complete consumption of the butanol. The wide separation of these peaks allowed rapid checks to be made on all initiator samples. No resonances were observed in the 200 Hz region in any sample, thereby indicating the absence of butoxide within the limit of detection of the spectrometer (*i.e.* 1 %).

The PMR spectrum of sec-butyllithium in benzene was examined in the same way. The sextet from the sec-butyllithium occurs at 66 Hz upfield from TMS, Fig. 5. Again no resonances attributable to butoxide could be observed in any of the samples prepared.

## RESULTS AND DISCUSSION

The purity of all organolithiums prepared in this study has been shown to be high. In the case of BuLi, the high degree of purity suspected was confirmed by carrying out several common methods of analysis in conjunction with a qualitative proton magnetic resonance (PMR) spectrum. The methods of analysis used were the acid titration procedure and the Gilman extension of this, the Volhard methyl iodide procedure and the Gilman extension of this, the Volhard methyl iodide procedure, the Clifford and Olsen iodine procedure and the quantitative PMR technique discussed by us in an earlier publication[7]. The results of these analyses, performed in a concentrated solution of BuLi in benzene, are shown in Table 1 below. It should be mentioned at this point that the Gilman, the Volhard and the Clifford and Olson procedures all involve the addition of a chemical reagent to the alkylmetal compound, converting it to a non-basic, titratable product. The added reagent must therefore be scrupulously contaminant-free (*i.e.* no oxygen or water), otherwise the subsequent titration will be in error to the extent of further organolithium destruction. This aspect, while important in the analysis of concentrated alkylmetal compounds, is clearly of critical importance in the determination of the very low metal alkyl concentrations required to polymer synthesis (*viz.* $10^{-4}$–$10^{-2}$ *M*). The methods of anal-

TABLE 1

ANALYSIS OF A CONCENTRATED n-BUTYLLITHIUM SOLUTION BY VARIOUS ANALYTICAL METHODS

| | *Method of analysis* | *Concentration of BuLi found* (mole · $l^{-1}$) |
|---|---|---|
| 1. | Acid titration (Std. HCl) | 2.63[a] |
| 2. | Gilman double titration | 2.61[a] |
| 3. | Volhard methyl iodide | 2.67[a] |
| 4. | Iodine titration | 2.40 |
| 5. | PMR method | 2.59[b] |

[a] Averaged value of two analyses. [b] Averaged value of four analyses.

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ysis involving chemical reagent addition, were therefore used only for concentrated alkylmetal determinations. Our previously reported analysis procedure involved addition of mesitylene to concentrated BuLi solutions, however, the addition was made under completely contaminant-free conditions since, as indicated, it was purged with polystyryllithium prior to analysis. Also, in regard to the PMR analysis, considerably less complex apparatus was eventually developed[12] than was previously described. Although an "absolute" method, reproducibility using the PMR technique was, in view of its complexity, less attractive than a simple titration method used in conjunction with the precautions outlined above.

The general agreement between the above methods, *cf.* 2.62 ± 0.05 (except for the iodine titration) is very satisfactory, especially when it is considered that all BuLi samples were dispensed under vacuum, from pre-calibrated break seals. The low result for the iodine titration is consistent with one of the shortcomings reported for this method of analysis, *viz.* a coupling reaction. Ideally, the reaction of iodine with the alkylmetal compound;

$$\text{R–Li} + \text{I}_2 \rightarrow \text{R–I} + \text{LiI}$$

is quick and quantitative, however, in practice a coupling reaction between the alkyl iodide and further alkylmetal compound may occur.

$$\text{R–Li} + \text{RI} \rightarrow \text{R–R} + \text{LiI}$$

In the above analysis the low result is therefore consistent with the expected coupling between BuLi and butyl iodide. None of the methods of analysis used are without some shortcomints. The acid and the methyl iodide methods, for example, do *not* account for the alkoxide and hydroxide impurities; they measure the total lithium and are therefore suitable only for analysis of alkylmetal solutions with high carbon-bound-lithium content. The Gilman procedure, although it accounts for basic impurities, likewise is inaccurate if alkoxide is present, because of reaction of the alkoxide with the added alkyl halide[13]. All three methods may therefore give too high a value for the alkylmetal concentration; they are satisfactory only when the basic impurity content is negligible. The latter, of course, can not be known *a priori*, and it was primarily for this reason (and because of the non-interference by basic impurities, in particular alkoxide) that we proposed the PMR analysis, which in conjunction with UV analysis, is a suitable alternative method.

Comparison of our PMR method and the acid titration results shows the latter to be higher by approximately 2 %, and this, we proposed in our earlier publication, is possibly due to lithium butoxide and lithium hydroxide being present. Since the basic impurity content has been demonstrated to be low, the somewhat more accurate Gilman procedure was at first preferred. Our comparison of the acid and Gilman methods now shows that the impurity levels in BuLi, using the precautions outlined here, are less than 1 % of the total lithium. High purity alkyllithium compounds may therefore be prepared by the procedure given above, and under these conditions, their purity is such that analysis by acid titration is quite acceptable and because of its obvious simplicity, preferable. The close agreement between the results of the Volhard and the acid titrations is of particular interest, since it precludes the presence of lithium chloride in BuLi solutions. Lithium chloride is not accounted for by the acid titration, but is involved in the Volhard procedure by reaction with silver nitrate. The absence

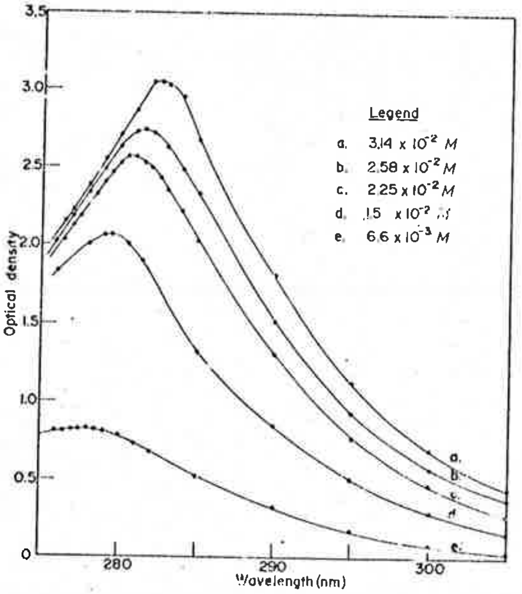

Fig. 6. UV spectra of n-butyllithium at various concentrations.

of lithium chloride removes any possibility that there can be complex formation, such as [R–Li . ClLi], which presumably can occur in certain initiating systems, and which may result in a loss of initiator efficiency.

The PMR method was used specifically in the calibration of dilute n-butyllithium solutions in benzene to allow an absolute determination of the extinction coefficient of carbon-bound-lithium. The UV absorption as a function of concentration is of some interest. The curves resulting from a series of concentrations are shown in Fig. 6. It can be seen that the maximum has shifted to higher wave lengths with increasing concentration. Nevertheless, concentrations of n-butyllithium showed an excellent linear Beer–Lambert plot over the range $2 \times 10^{-3}$ to $3.1 \times 10^{-2}$ *M* at 285 and 290 nm despite this shift in the peak. The extinction coefficient including maximum calculated error is $91 \pm 4$ ($l \cdot mole^{-1} \cdot cm^{-1}$) at 285 nm which was employed in this study. The excellent agreement between the UV and acid titration methods is most satisfactory and suggests that the maximum error may be lower than originally calculated. The results of titrations made under these conditions are shown in Table 2. The apparent agreement between these two results would indicate that the simple acid

TABLE 2

COMPARISON OF ANALYSES OF n-BUTYLLITHIUM IN THE UV WITH ACID TITRATION

| *Method of analysis* | *Concentration* ($l$ *mole*$^{-1}$) $\times 10^{-2}$ |
|---|---|
| UV analysis (calibration by NMR) | $1.06_2$ |
| Acid titration | $1.05_6$ |

40m 4/4/4.0

titration is, under conditions described above, as satisfactory as the UV analysis for determining low BuLi concentrations, nevertheless, the UV method is a quick and simple procedure.

The UV spectrum of n-butyllithium in benzene is difficult to explain. The shift in maximum, on casual inspection, would appear to suggest that more than one species is present in solution, however, the application of Beer's law provides conflicting evidence; the linear plot is indicative of a single species. A conjectural explanation for this shift is that the tail of the benzene peak significantly overlaps the n-butyllithium spectrum in the region 260 nm. This would have the effect of causing the solvent blank to "over compensate" at higher concentrations of n-butyllithium.

In conclusion, "high purity" organolithium initiators may be prepared, under high vacuum conditions, provided that strict attention is paid to the details of synthesis. PMR spectra can be qualitatively employed to detect the presence, or otherwise, of likely basic impurities, particularly alkoxide. Unfortunately, this method is not applicable to the case of the dianionic initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane, because of its low solubility in the benzene/anisole solvent mixture.

## ACKNOWLEDGEMENT

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## REFERENCES

1 F. W. Stavely *et al.*, *Ind. Eng. Chem.* 48 (1956) 778.
2 M. Szwarc, *Nature*, 178 (1956) 1168.
3 L. J. Fetters, *J. Res. Nat. Bur. Stand.*, 70A (1966) 421.
4 G. Spach, H. Moteiro, M. Levy and M. Szwarc, *Trans. Faraday Soc.*, 58 (1962) 1669.
5 G. Haupt, *J. Opt. Soc. Amer.*, 42(7) (1952) 441.
6 D. N. Cramond and J. R. Urwin, *Aust. J. Chem.*, 21 (1968) 1835.
7 P. J. Reed and J. R. Urwin, *J. Organometal. Chem.*, 15 (1968) 1.
8 H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, 66 (1944) 1515.
9 H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, 2 (1964) 447.
10 A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., p. 77.
11 A. F. Clifford and R. R. Olsen, *Anal. Chem.*, 32 (1960) 544.
12 P. J. Reed, M.Sc. Thesis 1971, University of Adelaide, S.A.
13 P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellstad, *Anal. Chem.*, 33 (1961) 468.
14 R. A. Finnegan and H. W. Kulta, *J. Org. Chem.*, 30 (1965) 4138.

yom 4144-10

Running Title: Molecular weight distribution by G.P.C. on block copolymers.

# MOLECULAR WEIGHT DISTRIBUTION OF BLOCK COPOLYMERS BY GEL PERMEATION CHROMATOGRAPHY

by J.R. Urwin* and M. Girolamo**

## Summary

Molecular weight distributions for block copolymers of polystyrene and polyisoprene have been determined by gel permeation chromatography for a series of well characterized polymers. Universal calibration curves from [η]M versus elution volume and by plots of unperturbed dimensions $(\bar{r}_0^2)^{\frac{1}{2}}$ versus elution volume have been constructed and examined. Normal-probability curves have been used to calculate the heterogeneity ratio $\bar{M}_W/\bar{M}_N$ and the results compared with values from light scattering measurements and from osmometry.

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# INTRODUCTION

In the short time since its introduction,(1 gel permeation chromatography (G.P.C.) has become widely accepted and used. The simplicity and speed of the method for determining molecular weight distribution is an attractive feature, particularly when compared with earlier fractionation techniques. It is preferable to other devices for expressing heterogeneity such as $\bar{M}_W/\bar{M}_N$ for the reason that skewed, bimodal and other distributions, normally occult, are openly displayed on the chromatograms. One disadvantage is the necessity to calibrate the instrument. To overcome the problem, which demands the use of well characterised, narrow distribution polymers of the type being investigated, has led to the search for a 'universal' calibration. One commonly adopted procedure is based on the assumption that fractionation is independent of column material or solvent and that separation occurs according to molecular dimensions. The exact mechanism of separation in the column is still unknown but the general consensus is that restricted diffusion(2 and steric exclusion from small pores(3 play a major role. Probably no single mechanism exists but rather that the true explanation must take account of a combination of these factors.

Obviously, it is important to collect and assess as much data pertinent to the problem as can be amassed. This is particularly true of well characterized polymers. In the case of block copolymers, it is necessary to determine beforehand that heterogeneity in composition is insignificant otherwise a correction will be required to compensate the drift in refractive index with molecular weight.(4 In this study, composition heterogeneity is examined by light scattering techniques.

Two methods of constructing 'universal' calibration curves will be investigated and the heterogeneity ratio $\bar{M}_W/\bar{M}_N$ will be compared with the equivalent quantity determined by G.P.C. from the standard deviation.

## EXPERIMENTAL

A series of diblock copolymers of polystyrene and polyisoprene were synthesized by sequential monomer addition initiated by n-butyllithium in benzene, using high vacuum techniques previously described.(5 The polymers have a range of molecular weight from 100,000-500,000 and compositions (expressed in per cent styrene) from 13% to 78%. The composition was determined by U.V. spectrophotometric analysis at λ = 262 nm and λ = 269 nm corresponding to the two main peaks in the spectrum of polystyrene. A Beckman D.U. spectrophotometer with matched cells previously calibrated against optical density standards was employed for the measurements. The microstructure of polyisoprene was investigated but overlap of a broad band from the polystyrene makes the investigation by the usual NMR method(6 difficult. An arbitrary correction based on measurements on a low polystyrene content polymer was applied and the microstructure of the block copolymers agreed with values obtained from polyisoprenes made by the same technique. An isomeric mixture, 81% cis-1,4;

14% trans-1,4; 5% 3,4, was assumed.

Light scattering data measured on a Sofica model 4200 photogoniometer was calibrated with high purity benzene assuming $R_{90} = 15.8 \times 10^{-6}$ at $\lambda = 546$ nm. A negligible angular dependence was found over the range 30°-150° after allowing for depolarization.(7 Refractive index increments ($\nu$) were determined on a Brice Phoenix differential refractometer. The values are shown in Table 1 along with calculated data assuming the relation:

$$\nu_{cop} = w_{ps}\nu_{ps} + (1 - w_{ps})\nu_{pi} \qquad (1)$$

where w is the weight fraction and subscripts signify the particular polymer. Light scattering data computed according to the method already described elsewhere are shown in Table 2.

Number average molecular weights were measured in toluene, cyclohexane and methylisobutyl ketone (MIBK) on a high speed membrane osmometer (Hewlett Packard Model 501).

The membranes were preconditioned in stages to pure toluene. When other solvents were used the same technique was adopted to change from toluene to new solvent. Before inserting membranes they were degassed by heating with agitation at 60° for about 30 mins.

Intrinsic viscosities in THF were determined in an Ubbelohde viscometer fitted with an electronic timer.(8 Viscosities were reproducible with high accuracy, e.g. flow times in excess of 200 sec ± 0.05 sec.

Gel permeation chromatography was carried out on a Waters Associates instrument. Three columns of gel permeabilities of $10^6$,

$10^5$ and $10^4$ Å were employed with THF as solvent (flow rate 0.5 $cm^3$/sec at 25°C). A 0.25% solution was injected over 1 minute, i.e. a total polymer weight of 1.25 mg injected. The detector was the differential refractometer. Counts correspond to an elution volume of 5 $cm^3$. Standard polystyrenes employed were supplied by the instrument manufacturer.

## RESULTS

The results from light scattering measurements in three solvents computed using a computer program based on one written for the Brice Phoenix instrument and adapted by us to the Sofica(9 are given in Table 2. $\bar{M}_W$ , and the heterogeneity parameters $P/\bar{M}_W$, $Q/\bar{M}_W$ where the quantities P and Q are given by

$$P = \sum_i \gamma_i M_i (x_i - x)$$

$$Q = \sum_i \gamma_i M_i (x_i - x)^2 \qquad (3)$$

in which $\gamma_i$ is the weight fraction of component i whose molecular weight is $M_i$ and composition $x_i$ are shown in the table. The two parameters indicate heterogeneity in composition. P relates to variation in composition and Q to distribution breadth. The parameters are related by the relation(10

$$M_{ap.} = \bar{M}_W + 2P(b/\nu) + Q(b/\nu)^2 \qquad (4)$$

where b is the refractive index increment difference between the two polymers. $\bar{M}_W$, P and Q are obtained by solving three simultaneous equations using three different values of $M_{ap.}$ obtained from measurements in three solvents of different refractive indices. The results show that the molecular weights obtained are fairly close in the three solvents chosen. This confirms the view of Bushuk and Benoit(10 that measurements on block copolymers in solvents of sufficiently high refractive index will not be greatly in error. MIBK seems particularly appropriate for use in single solvent determinations in this system. Involuted Zimm plots were not observed with any of these solvents but such behaviour has been observed in certain solvents(11 particularly in the so called 'preferential' solvents. The data indicate that these polymers are homogeneous with respect to composition. This means that the differential refractometer 'sees' the correct weight of polymer at all molecular weights.

It is of interest to examine the refractive index increment, $\nu$, measured for the blocks and to compare this with the calculated values which are often employed because of the tedious nature of $\partial n/\partial c = \nu$ measurements (Table 1). The deviations are significant and in view of the occurrence of $\nu$ in the light scattering equation as a squared term, the practice of employing claculated values should be discouraged as it may result in large errors. The heterogeneity ratio $\bar{M}_W/M_N$ is given in the table. Inspection of this parameter reveals that all polymers synthesized are of narrow molecular weight distribution and indicates that the method of synthesis is highly efficient, particularl in eliminating extraneous terminating species.

Chromatograms representative of the polymers are shown in Fig. 1 and show that only one single species occurs in each polymer. The concentration of homopolymer present may be deemed negligible. Peak counts are given (corresponding to the maximum of the curve) in Table 3. The normal plot of log $\bar{M}_W$ against peak counts for the polystyrene standards is constructed in Fig. 2. It can be seen that in the region 17.5-24 counts the slope is least and is linear. This corresponds to the region of best resolution for the series of columns employed, and, as we have seen, this is the region in which all peak counts for the blocks occur. The similarity in form of the chromatograms of blocks and standard polystyrenes is a qualitative indication that all polymers are unimodal and of narrow molecular weight distribution.

## DISCUSSION

By far the simples method for representing the data from G.P.C. chromatograms is the plot of the cumulative curve as a straight line on normal-probability paper. Other methods have been proposed(12 but are sufficiently tedious to require access to a computer. Another advantage of the normal-probability plot is that the results are so displayed that they may be scanned for inconsistency. If, as is usually the case, the plot is linear over most of the range then a Gaussian distribution may be assumed and the distribution width may be expressed in terms of the heterogeneity ration $\bar{M}_W/\bar{M}_N$.

Another very simple method has been proposed by Bly(13 in which the width of the base line formed by the tangents to the point of inflection on either side of the maximum is measured ($w_2$) and compared with the corresponding value of a standard sample ($w_1$) and in which the ratio $\bar{M}_W/\bar{M}_N$ = d may be known. Thus from the simple relation

$$w_1/d_1 = w_2/d_2 \tag{5}$$

the value of d for the unknown may be evaluated. The method is quick and convenient, particularly for analysis of new parameters. Application of this method to the block copolymers indicated narrow distribution in all samples.

The polymers were all examined by the normal-probability plot method. Fig. 3 shows representative plots of a standard sample and two of the block copolymers. The plots are linear over the same range. The region over which Gaussian distribution holds is easily seen and the standard deviation $\sigma$ may be determined from the difference in counts at the 50% and 16% marks. The value at 50% represents the geometric mean. Counts may be converted to molecular weight by means of a calibration curve. The ratio $M_W/M_N$ may then be evaluated from the relations(14

$$M_W = M_{W_g} \exp\left(\tfrac{1}{2}\sigma^2\right) \tag{6}$$

and

$$M_W/M_N = \exp(\sigma^2) \tag{7}$$

and

$$\sigma = \sigma_c/k \tag{7a}$$

where $M_{W_g}$ = geometric mean and k is the slope of the calibration curve.

One obvious advantage of this method is that $M_W/M_N$ may be compared with the heterogeneity ratio derived from light scattering and osmometry measurement

The most difficult problem which arises is how to construct a calibration curve. In the case of block copolymers, not only molecular weight is involved but composition also. Previously(15 we used calibration curves of the two homopolymers and assumed a simple linear relationship with respect to composition. A more desirable approach would be the use of a 'universal' calibration curve. Two well know methods have been applied to many polymers, the first due to Grubisic et a.(16 who suggest the use of the hydrodynamic volume for the calibration. Of course viscosity is proportional to the root mean square and to end distances $(\bar{r}^2)^{\frac{1}{2}}$ according to

$$[\eta] = \Phi(\bar{r}^2)^{3/2} / M \qquad (8)$$

and a plot of $[\eta]M$ against elution volume yields the desired result. Since viscosity measurements are easily made the method is a most attractiv one. In this work, viscosities in THF at 25°C were determined for all polymers. The calibration curve constructed from this data was used to calculate the heterogeneity ratio $M_W/M_N$ according to Eqs. 6, 7 and 7a.

An alternative approach, due to Dawkins,(17 proposes the use of unperturbed dimensions which may be easily evaluated from the published data on the parameter $(r_0^2/M)^{\frac{1}{2}}$. Again the required parameter may be obtained by direct measurement of $(\bar{r}_0^2)$ from viscosity measurements in theta solvents.

Calibration curves by both methods are shown in Fig. 4. Values of $[\eta]_{25}^{THF}$ and $[\eta]_\theta$ were measured for all polymers in the series and $\bar{M}_N$ was determined by osmotic measurements. The value for the standard polystyrenes were determined experimentally for $[\eta]_{25}^{THF}$ and by way of

$(\bar{r}_0^2/M)$ from the literature.(18 The value of $4.49 \times 10^{-17}$ was adopted in the present work. There is little difference between the methods from inspection of the plots. It may be that the unperturbed dimensions gave a better fit, this conclusion is reinforced by the observation that $\bar{M}_N$ calculated from Eq. 7 when compared with osmotic values shows a 5% drift to lower values when using the $[\eta]M$ plot. However, until the mechanism of separation is better understood there is little to commend one method over the other.

There can be little doubt about the excellence of G.P.C. as a qualitative analytical tool. On the other hand, the need for better calibration procedures is very obvious before the technique can be used quantitatively in solution property studies.

# REFERENCES

1 Moore, J.C., J. Polym. Sci. (1964) Part A, 2, 835.

2 Ackers, G.K., Biochemistry (1964) 3 (5), 723.

3 Laurent, I.C. and Killander, J., J. Chromatography (1964) 14, 317.

4 Urwin, J.R. and Cramond, D.N., Austral. J. Chem. (1968) 22, 543.

5 Cramond, D.N. and Urwin, J.R., Austral. J. Chem. (1968) 21, 1835.

6 Chen, H.Y., Anal. Chem. (1962) 34, 1793.

7 Coumon, D.J., J. Coll. Sci. (1960) 15, 408.

8 Steel, B.J., J. Sci. Instr. (1965) 42, 751.

9 Urwin, J.R. and Girolamo, M., Makromol. Chem. (1971) 161, 142.

10 Bushuk, W. and Benoit, H., Compt. rend. (1958) 246, 3167; Canad. J. Chem. (1958) 36, 1616.

11 Prud'homme, J., and Bywater, S., Macromolecules (1971) 4, 543.

12 Tung, L.H., J. Appl. Polym. Sci. (1966) 10, 375; Smith, W.N., ibid. (1967) 11, 639; Hess, M. and Kratz, R.F., J. Polym. Sci. (1966) Part A-2, 4, 731.

13 Bly, D.D., J. Polym. Sci., Part C (1968) 21, 13; Anal. Chem. (1969) 41, 477.

14 Herdan, G., Small Particle Statistics, Butterworths (1960), 2nd Edn. p. 95.

15 Cramond, D.N., Hammond, J.M. and Urwin, J.R., Europ. Polym. J. (1968) 4, 451.

16 Grubisic, Z., Rempp, P., and Benoit, H., J. Polym. Sci. (1967) Part B, 5, 753.

17 Dawkins, J.V., J. Macromol. Sci. - Phys. (1968) B2 (4), 623.

18 Polymer Handbook, Interscience (1966), p. IV, 48.

<u>TABLE 1</u>

Specific refractive index increments of the block copolymers determined in toluene, cyclohexane and methyl isobutyl ketone

| | | $\nu_{546}$ | |
|---|---|---|---|
| Polymer | Tol. | c-Hex. | MIBK |
| IS1 | 0.036 (0.038) | 0.109 (0.113) | 0.144 (0.148) |
| IS2 | 0.044 (0.047) | 0.115 (0.120) | 0.150 (0.155) |
| IS3 | 0.050 (0.050) | 0.117 (0.123) | 0.152 (0.157) |
| IS4 | 0.065 (0.070) | 0.130 (0.139) | 0.165 (0.173) |
| IS5 | 0.084 (0.091) | 0.142 (0.156) | 0.178 (0.190) |
| IS6 | 0.035 (0.037) | 0.108 (0.112) | 0.143 (0.146) |
| IS7 | 0.047 (0.048) | 0.116 (0.121) | 0.152 (0.155) |
| IS8 | 0.062 (0.067) | 0.129 (0.136) | 0.164 (0.170) |
| IS9 | 0.045 (0.047) | 0.114 (0.121) | 0.149 (0.155) |
| IS10 | 0.062 (0.068) | 0.127 (0.137) | 0.163 (0.171) |

Values in brackets calculated from Eq. 1

## TABLE 2

Weight average molecular weights of the block copolymers and the heterogeneity parameters from light scattering data computed as in ref. 9 from measurements in toluene, cyclohexane and methyl isobutyl ketone

| Polymer | $\bar{M}_W$ $\times 10^{-5}$ | $P/\bar{M}_W$ | $Q/\bar{M}_W$ | $\bar{M}_W/\bar{M}_N$ |
|---|---|---|---|---|
| IS1 | 1.06 | 0.015 | 0.026 | 1.04 |
| IS2 | 1.07 | 0.009 | 0.056 | 1.05 |
| IS3 | 1.08 | -0.018 | 0.232 | 1.07 |
| IS4 | 1.07 | 0.028 | 0.116 | 1.03 |
| IS5 | 1.08 | 0.021 | 0.163 | 1.05 |
| IS6 | 2.68 | -0.002 | 0.026 | 1.06 |
| IS7 | 2.62 | 0.036 | 0.015 | 1.04 |
| IS8 | 2.62 | 0.023 | 0.021 | 1.03 |
| IS9 | 5.34 | 0.014 | 0.013 | 1.07 |
| IS10 | 5.41 | 0.034 | -0.007 | 1.08 |

# TABLE 3

Data from G.P.C. chromatograms of the block copolymers

(THF at 25°C. Flow rate 0.5 cm$^3$/min.)

| Polymer | $\bar{M}_N$* × $10^{-5}$ | Comp.** wt. % P.S. | Peak count | Std.Dev. $\sigma$ | $M_W/M_N$ |
|---|---|---|---|---|---|
| IS1 | 1.02 | 13.5 | 21.23 | 0.287 | 1.08 |
| IS2 | 1.02 | 24.7 | 21.38 | 0.312 | 1.10 |
| IS3 | 1.01 | 28.2 | 21.56 | 0.230 | 1.05 |
| IS4 | 1.04 | 52.2 | 21.36 | 0.277 | 1.08 |
| IS5 | 1.03 | 78.2 | 21.84 | 0.285 | 1.08 |
| IS6 | 2.53 | 11.8 | 19.40 | 0.317 | 1.10 |
| IS7 | 2,52 | 25.5 | 19.53 | 0.287 | 1.08 |
| IS8 | 2.54 | 48.5 | 19.85 | 0.272 | 1.07 |
| IS9 | 4.99 | 25.1 | 18.10 | 0.327 | 1.11 |
| IS10 | 5.01 | 48.7 | 18.35 | 0.352 | 1.13 |

* $\bar{M}_N$ by osmometry.

** Composition from U.V. measurements.

## Captions for the figures

Fig. 1. G.P.C. chromatograms of several block copolymers and a standard polystyrene.

Fig. 2. Plot of log $\bar{M}_w$ for the standard polystyrenes against elution volume in counts.

Fig. 3. Normal-probability plot of the cumulative weight data for a standard polystyrene and two block copolymers.

Fig. 4. Plots of $[\eta]M$ and $\log (\bar{r}_0^2)^{\frac{1}{2}}$ against elution volume. Universal calibration curves.

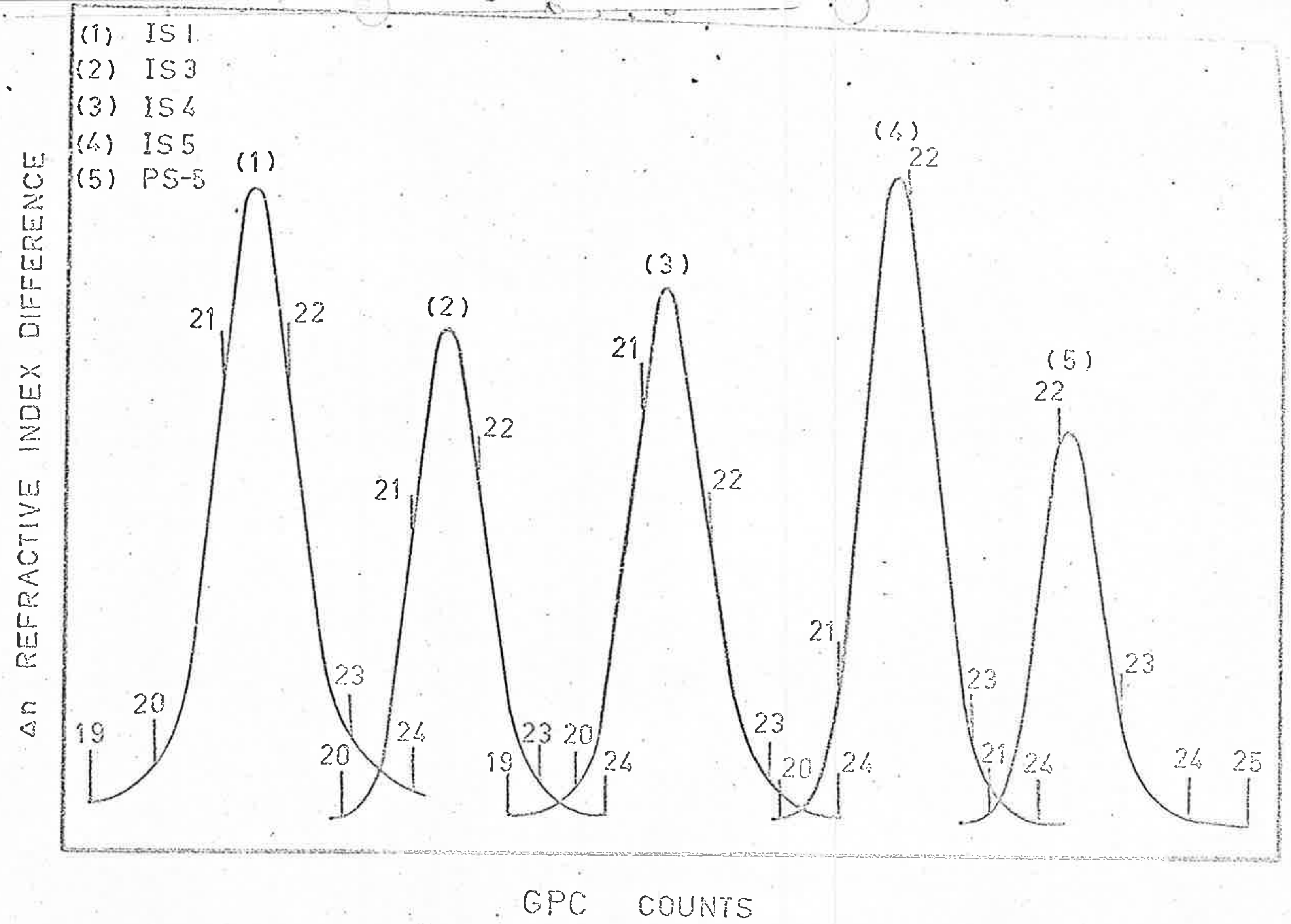
(1) IS1
(2) IS3
(3) IS4
(4) IS5
(5) PS-5
Δn REFRACTIVE INDEX DIFFERENCE
GPC COUNTS
(1)
(2)
(3)
(4)
(5)
19
20
21
22
23
24
25

Fig. 1

# THE CONFIGURATION OF BLOCK COPOLYMERS OF POLYISOPRENE AND POLYSTYRENE

## PART II.* MOLECULAR DIMENSIONS

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Abstract - Thermodynamic parameters and unperturbed dimensions for block copolymers of polyisoprene and polystyrene have already been discussed. In this part of the work the hydrodynamic factor $\alpha_\eta$ was determined directly from viscosity data (in three solvents) referred to $[\eta]_\theta$ measured under theta conditions. The displacement length parameter $(\bar{r}^2/Z)^{\frac{1}{2}}$, is reported for the series of copolymers, Z being the number of links corrected for isomeric composition and weight fractio of the polystyrene block. Long range interactions have been investigated from viscosity and osmotic data; the binary cluster integral has been computed. The results are discussed in relation to the composition of the copolymer and its molecular weight. The results show the general applicability of two parameter theories derived for homopolymers with the addition of one further variable, i.e. composition.

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## INTRODUCTION

The environment, peculiar to dilute solutions of linear polymers in good solvents, is responsible for the expanded configuration of linear chain molecules. The long range effects, resulting from the effective covolume of pairs of segments, are minimal in concentrated solution and maximal at infinite dilution. The covolume reduces to zero in poor solvents at a particular temperature viz. the theta point where the molecule assumes its unperturbed dimensions.(1

In part I(2 we argued the existence of an unperturbed configuration for block copolymers in single and mixed solvents despite the fact that the solvent is not a theta solvent for either block under these conditions. The theta temperature was shown to display composition dependence, interpreted to mean that the block copolymer behaves as a ternary system consisting of solvent-block (1)-block (2), within the domain occupied by the copolymer. Thus the unperturbed dimension of the block copolymer depends only on bond angles, bond lengths, rotational torque, steric effects and composition.

The degree of linear extension attributed to the so called excluded volume effect, is defined by the linear perturbation factor

$$\alpha = (\bar{r}^2/\bar{r}_0^2)^{\frac{1}{2}} \qquad (1)$$

i.e. the ratio of perturbed to unperturbed end-to-end distance, and may be measured directly from viscosity data in various solvents relative to data under theta conditions. According to the Flory-Fox treatment of viscosity the intrinsic viscosity is given by

$$[\eta] = \Phi(\bar{r}^2)^{3/2}/M \tag{2}$$

where $\Phi$ was originally assumed constant for all systems. Where measurements are made under theta conditions this expression is more appropriately written

$$[\eta]_\theta = \Phi[(\bar{r}_0^2)/M]M^{\frac{1}{2}} \tag{3}$$

For sufficiently long chains when $(\bar{r}_0^2)$ is proportional to the chain length and therefore M we may write

$$[\eta]_\theta = KM^{\frac{1}{2}} \tag{4}$$

where K may be regarded as characteristic of a polymer homologous series. Hydrodynamic considerations indicate that $\Phi$ must depend on the form of the spatial distribution of the segments of the chain. The volume effect distorts not only the average dimensions but, to some extent, the form of the distribution as well.(1

In order to retain Eq. (2) $\Phi$ must be adjusted slightly downward. Thus the experimentally determined hydrodynamic expansion factor

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \tag{5}$$

is related to the linear perturbation factor by(3

$$\Phi = \Phi_0(\alpha_\eta/\alpha)^3 \tag{6}$$

We have adopted the value

$$\Phi_0 = 2.68 \times 10^{23}$$

for measurements made under theta conditions and for all other conditions, the value

$$\Phi = 2.2 \times 10^{23}$$

in which r is in cm and $[\eta]$ in $cm^3$ per g. In the present work the value of $[\eta]_\theta$ was measured directly in theta solvents and the values of $\alpha_\eta$ evaluated from viscosity data in the various solvents at specific temperatures according to Eq. (5). We believe the method quite valid for systems other than those in preferential solvents, near or below the value of $T_p$ where there is a neomorphic change which we consider to be an intramolecular phase transition.(4

The first attempts to quantify long range interactions, responsible for the expanded configuration of the linear chain, are due to Flory. He introduced the empirical interaction parameter, $\chi$, which in modern theory(5 becomes the reduced residual chemical potential and which may then be separated into an enthalpic and entropic part, i.e. in the more recent approach $\chi$ does not simply represent exchange interactions alone as originally defined. An ingenious formulation due to Fox, Flory and Schaafgen, derived from Flory's excluded volume treatment, relates $\chi$ to viscosity data thus

$$[\eta]^{2/3}/M^{\frac{1}{2}} = K^{2/3} + C(1 - 2\chi)K^{5/3}(M/[\eta]) \qquad (7)$$

but the method has been shown to lead to underestimation of the viscosity constant K and is not recommended for use with good solvents.(6

Probably the best approach is due to Stockmayer and Fixman(7 leading to formulation of the simple expression

$$[\eta] = K_\theta M^{\frac{1}{2}} + 0.51\Phi_0 \, BM \qquad (8)$$

where the long-range parameter B is related to the Flory parameter $\chi$

by the relation

$$B = \bar{v}^2 (1 - 2\chi_1)/V_1 N_A \tag{9}$$

in which $\bar{v}$ is the specific volume of polymer, $V_1$ the molar volume of solvent and $N_A$ Avogadro's number. The separation of short and long range interactions is attractive; treatment of the data requires simply the plotting of $[\eta]M^{-\frac{1}{2}}$ against $M^{\frac{1}{2}}$ and B is obtained from the slope. Furthermore, this relation has been shown to be valid in good and bad solvents. The equation describes the dilute solution properties of flexible linear polymers with the one restriction that drainage effects are minimal.

Attempts to use the second virial coefficient of osmotic pressure measurements in an alternative approach to the determination of B are due to Kurata et al.(8 Adopting an expression for the excluded volume due to Ptitsyn, a two parameter formulation yields an equation similar in form to the $[\eta]$-M treatment, i.e.

$$A_2\bar{M}_N^{\frac{1}{2}} = 2.83 \times 10^{23} A_\Pi^3 + 1.67 \times 10^{23} B_\Pi \bar{M}_N^{\frac{1}{2}} \tag{10}$$

in which $A_\Pi$ is the short range parameter defined by

$$A_\Pi^2 = \bar{r}_0^2/M \tag{11}$$

and the subscript $\Pi$ signifies the use of osmotic pressure data. As with the $[\eta]$-M expression the treatment is simple and a plot of $A_2\bar{M}_N^{\frac{1}{2}}$ against $\bar{M}_N^{\frac{1}{2}}$ yields $B_\Pi$ from the slope.

Finally, the contributions from the several types of long range interactions possible in a copolymer may be approached through the binary cluster integral ($\beta$) which, in the case of the block copolymers, will contain three types of interaction between segmental pairs, i.e. $\beta_{11}$, $\beta_{22}$ and $\beta_{12}$ representing the usual excluded volume for a pair of segments of the same kind and of different kinds; the latter are of greatest significance in block copolymer studies. This part of the report seeks to explore the application of two parameter homopolymer theories to the block copolymer system chosen with the addition of the one further parameter, namely the composition expressed in an appropriate form.

## EXPERIMENTAL

An earlier, preliminary study of this particular system led to inconclusive results; it seemed prudent to attempt to extend our knowledge of the operative parameters by a full investigation. Consequently, anionic methods(9 were used to synthesise a series of ten block copolymers, which would enable studies of the effects of composition at constant molecular weight and the influence of molecular weight at constant composition. Briefly, the polymers were prepared by sequential addition of monomers initiated by n-butyl lithium; benzene was used as solvent because of the requirement that the polyisoprene block contains a high cis 1,4 isomer content (about 80%), that is a high degree of structural perfection.

The determination of microstructure in the polymers employed in the study is important particularly when examining dimensions, since the characteristic ratio of the cis and trans structures is so markedly different in polyisoprenes.(10 Analysis by I.R. spectroscopy has proved ineffective principally because of the overlap of bands in polystyrene and polyisoprene. In any case, N.M.R. spectroscopy is now widely used for polyisoprene and has proved to be very satisfactory for determining the cis-trans ratio. The 1,2 isomer seems to be entirely absent in polymers produced by this method and therefore the remaining polymer is the 3,4 structure. Application of the method to block copolymers of polystyrene and polyisoprene presents a problem. A broad absorption band due to polystyrene occurs in the same region as polyisoprene and cannot be satisfactorily separated. The microstructure within the block copolymer was therefore assumed to coincide with that of polyisoprene, synthesized by the same method. Actually, a compensatory method which allows for the existence of polystyrene composition according to the formula

$$\% \text{ cis } 1,4 = \frac{A5a \times 100}{A5(1 - 0.6w)} \qquad (12)$$

where A5a and A5 are the areas under peaks 5a and 5 (according to Chen's(11 assignment) and w is the weight fraction of polystyrene in the block copolymer, gave values of 81% ± 2% cis conformation for all of the polymers examined, in excellent agreement with the results from polyisoprene samples.

A Varian D.P. 60 N.M.R. spectrometer equipped with an H.A. 60

probe and operating at 30°C was employed for all determinations. Benzene was adopted as the internal lock and areas under peaks were evaluated using the integrator provided with the instrument. The microstructure so obtained shows cis 1,4 (82%); trans 1,4 (14%); 3,4 (4%).

The composition of each block, in terms of polystyrene content, was obtained by measuring U.V. absorptions at 262 nm and 269 nm on a Beckman DU Spectrophotometer.(12,13 Comparison of predicted and actual compositions shown in Table 1 indicate that the method of synthesis is sufficiently satisfactory to allow tailoring to order within about 3%.

Number average molecular weights were obtained from high speed osmometry (Hewlett Packard model 501). As expected, values obtained in toluene, cyclohexane and methyl isobutyl ketone (MIBK) were in good agreement. The predicted values, calculated from kinetics, are listed under $M_k$. On the basis of the general agreement of $M_k$ and $\bar{M}_N$, it is expected that molecular weight distributions should be narrow.

Whilst the number average molecular weight is unambiguous, the weight average molecular weight normally measured is an apparent value, as pointed out many years ago by Bushuk and Benoit.(14 Results in this work were obtained from measurements made on a SOFICA photogoniometer model 4200. Actually, $\bar{M}_W$ was obtained from the results in the three solvents used in osmometry. Values were computed using a computer program as previously discussed by us(15 and based on one developed by Evans et al.(16 The refractive index increments were measured directly on a Brice-Phoenix differential refractometer. It is clear from the values shown in Table 2 that apparent values in a solvent with sufficiently high refractive index, such as MIBK, will yield values of $M_{app}$ which are very close to $\bar{M}_W$ and which, in view of the large errors involved, can be safely taken to be equivalent to $\bar{M}_W$. This may not be the case where distributions of molecular weight and/or composition are broad.(17

Gel permeation chromatography gives a more comprehensive characterization, but of course the method is not absolute and some form of calibration is necessary. In this study, a 'universal' calibration based on a plot of log $[\eta]M$ versus elution volume, as suggested by Grubisic et al.,(18 was used. The results were obtained on a Waters Associates instrument using T.H.F. at 25°C and three columns of $10^6$, $10^5$, $10^4$ A.U. permeabilities. The chromatograms were all unimodal, narrow in molecular weight distribution and indicated the absence of homopolymer. Except for the calibration procedure, the treatment of data was similar to that previously described.(19 The standard deviation $\sigma$ and heterogeneity ratio derived from it (in brackets) are given in Table 1 for comparison.

## RESULTS AND DISCUSSION

Intrinsic viscosities obtained in the solvents toluene, cyclohexane, methyl isobutyl ketone and under theta conditions (discussed in part I)(2 are set out in Table 3. The hydrodynamic expansion factors were calculated directly from these results according to Eq. (5) and the linear perturbation factor $\alpha$ determined by way of Eq. (6). Only values of the former appear in the table although $\alpha$ was used in later calculations.

It is of interest to note that values of $\alpha_\eta$ in toluene and cyclohexan are very similar over the whole series of polymers but much smaller in MIBK, indicating that this is a poor solvent for both block copolymers and homopolymers. Generally, the values lie between homopolymer values in a particular solvent. The increase in $\alpha_\eta$ with molecular weight in toluene and cyclohexane is in accord with observations on homopolymers. The results in MIBK show that there is little sensitivity to chain length.

Polymer dimensions are usually expressed in terms of either the root mean square end-to-end distance or root mean square radius of gyration. The latter is difficult, if not impossible, to obtain in the case of block copolymers. $(\bar{r}^2)^{\frac{1}{2}}$ was calculated for the series from Eq. (2). A more characteristic quantity is the displacement length parameter in which the normalizing factor is the number of links Z in the chain. In homopolymers this parameter is more often expressed as $(\bar{r}^2/M)^{\frac{1}{2}}$ since M is proportional to Z. Similarly, the number of segments could be used. However, in block copolymers, the use of M as the normalizing factor gives too much weight to one block if the molecular weights of the segments $M_0$ are very different, e.g. $M_0 = 104$ (styrene) compared with $M_0 = 68$ (isoprene). Even the use of number of segments needs some qualification, since the number of bonds per segment is two for polystyrene and the 3,4 isomer of polyisoprene but is four for the cis and trans isomers, one of which is a double bond. We have adopted the expression

$$Z = \bar{M}_N \left(w \frac{2}{104} + (1 - w) \frac{3.8}{68}\right) \qquad (13)$$

in order to account for the composition and to allow for the isomeric content found by NMR analysis. This allows a plot of $(\bar{r}^2/Z)^{\frac{1}{2}}$ versus Z, free from the distortion caused by difference in $M_0$ for the different blocks. Plots of the displacement length against composition expressed as links % are shown in Fig. 1 for the three solvents. A positive deviati from linearity occurs in all solvents with the maximum deviation at about mid-scale for toluene and MIBK. This may be attributed to extra repulsions from hetero contacts, which would be greatest at 50% composition due to the greater probability of cross interactions. This implies sufficient mixing of segments to give rise to the phenomenon. It is also consistent with thermodynamic behaviour shown by this system. The similarity of the curves in these two solvents indicates a similar configuration.

The results in cyclohexane, a preferential solvent, are quite different. The dimensions of the block copolymer are such that, at this temperature, they are greater than for either constituent homopolymer. It should also be observed that the values for the copolymer show little composition dependence.

To investigate the problem further, it is necessary to examine the long range interactions. The long range parameter B in the Stockmayer-Fixman relation, Eq. (8), is shown in Table 4. This parameter is obtained from the slopes of plots of $[\eta]/M^{\frac{1}{2}}$ versus $M^{\frac{1}{2}}$. The alternative method for calculating B, proposed by Kurata et al.,(12 involves plotting $A_2M^{\frac{1}{2}}$ versus $M^{\frac{1}{2}}$. To distinguish between them, we use the subscripts $\eta$ and $\Pi$ respectively. The results from both methods appear in the table for the series 25/75, i.e. 25% P.S. with molecular weights $1.0 \times 10^5$; $2.5 \times 10^5$; $5.0 \times 10^5$ and similarly for the series 50/50 containing equal weights of each polymer in the block. In each case, values have been measured in toluene and cyclohexane. The agreement between the two methods (about 10%) is of the same order as that reported for homopolymers, and the accuracy and limitations are similar to those experienced with homopolymers.(20,21,22 $A_2$-M expressions are limited to relatively good solvents ($\alpha > 1.2$) so invalidating their use for the solvent MIBK. In fact, two $A_2$-M expressions have been proposed, one based on Fixman's equation(23 for the excluded volume and the other on an alternative derivation due to Ptitsyn.(24 These equations take the same form but with different coefficients. The region of applicability may be gauged from the value of the so called osmotic dimensionless ratio (ODR) $= A_2\bar{M}_N/[\eta]$. These values are about 60 for the former and 110 for the latter. It was shown in part I of this series that the second expression had greater validity in the present system and that most values of the ODR determined for the blocks in toluene fell close to that predicted. In cyclohexane, the values of the ODR were generally lower but still fell between the two limits. The results indicate a need for further refinement in theory generally but the low sensitivity of the second virial coefficient to molecular weight makes the $A_2$-M approach less attractive than the $[\eta]$-M method.

Another widely used approach to the investigation of long range effects is the determination of the binary cluster integral $\beta$ defined by the relation

$$\beta = \int_0^\infty [1 - e^{-w(r)/kT}]4\Pi r^2 dr \qquad (14)$$

where w(r) is the pair potential, which represents the potential energy for solute-solute interactions. However, $\beta$ is not independent of solvent, i.e. solute-solvent interactions are involved as well. Higher order of clusters may be safely neglected, in good solvents at least, when measurements are made in dilute solution.

An expression due to Kurata et al.(25 (KSR equation) is useful for this purpose if values of $\alpha$ are known. The relation in its amended form(26 (the equation originally appeared incorrectly in both summary and in the text but was subsequently corrected by Kurata) is given by

$$(\alpha^3 - \alpha)(1 + 1/3\alpha^2)^{3/2} Z^{-\frac{1}{2}} = (4/3)^{5/2}(3/2\Pi a^2)^{3/2}\beta \qquad (15)$$

in which $a = \overline{r_0^2}/Z$. In this expression, $\beta$ may be taken to be the excluded volume for a pair of segments. Values of $\beta$ balculated from the linear expansion factors, corrected from $\alpha_\eta$ determined experimentally, are shown in Table 5. The values of $\bar{r}_0^2/Z$ are to be found in Table 1 of Part I. A plot of β for the series of polymers in the three solvents is shown in Fig. 2. The curves for toluene and MIBK fall on a smooth curve between values for the two homopolymers in the same solvents, which means that they follow a form similar to that expected from the relation originally proposed by Zimm(27 thus

$$\beta = \beta_{11}x^2 + \beta_{22}(1 - x)^2 + 2x(1 - x)\beta_{12} \qquad (16)$$

in which the subscripts refer to contacts between species of the same kind and heterocontacts and x is the mole fraction. The expression applies strictly to a random distribution of segments. In cyclohexane, β is virtually independent of composition, which may mean that the expansion of the chain is due almost entirely to the isoprene block and that, in this solvent, interpenetration of the blocks is virtually absent, i.e. a high degree of intramolecular phase separation exists at this temperature, as is suggested by the thermodynamic results.(28

In the preliminary study of this system, the original but incorrect form of the KSR equation was used and led to distortion of the β-composition curve and therefore to incorrect interpretation. Use of the correct form of the equation would by itself justify the present more detailed study. Finally, β may be calculated from the long range interaction parameter directly, according to

$$B = \beta/M_o^2 \qquad (17)$$

for a homopolymer. The corresponding expression for a copolymer is

$$B = \beta/M_{oc}^2 \qquad (18)$$

where

$$M_{oc} = \sum_i M_{oi}x_i \qquad (19)$$

and $x_i$ is the mole fraction of each species. Calculations for the series, computed from B determined in toluene, showed that values of $\beta$ for the series 25/75 and 50/50 were 1.51 and $2.44 \times 10^{-24}$ cm respectively which compares favourably with 1.49 and $2.25 \times 10^{-24}$ cm calculated from results shown in Table 5.

Evaluation of $\beta_{12}$ is of considerable interest in block copolymer studies. The use of Eq. (16) for this purpose demands a random structure approximating the random coil. This may be presumed in the case of toluene and MIBK, at least when there are about equal numbers of segments present. Calculation of $\beta_{12}$ from Eq. (16) showed considerable variation but the averages were $1.36 \times 10^{-24}$ cm in toluene and $0.30 \times 10^{-24}$ cm in MIBK. The value in MIBK for IS5 was in fact negative. The method is only approximate at best.

Froelich and Benoit(29 have proposed a more elegant solution to this problem which assumes a knowledge of the segmental distribution function. However, the relation is applicable only when $\alpha$ approaches unity. In this study, therefore only results in MIBK are strictly applicable. Actually comparison of the two sets of results shows reasonable correlation, particularly in the region 25-52% by weight. It is interesting to note that the value for IS5 is again negative only much more so.

To summarize, the application to block copolymers of two parameter theories, derived for homopolymers, appears to be quite valid in the regions prescribed by theory. The degree of accuracy is comparable to that found experimentally in homopolymer studies. It would appear, therefore, that the evidence indicates considerable interpenetration of the blocks particularly in good solvents, but probably also in poor solvents for cases where the covolume is similar for each block. In preferential solvents, intramolecular phase separation is already in evidence at temperatures below the theta point for the least soluble polymer. Under these conditions, the validity of their application seems doubtful, to say the least, and should be approached with great caution.

Acknowledgement. We express our gratitude to the A.R.G.C. for provision of light scattering and osmometry equipment.

# REFERENCES

1. P.J. Flory, Statistical Mechanics of Chain Molecules, Interscience, 1969, p. 34-37.
2. J.R. Urwin and M. Girolamo, Makromolek. Chem. (in press).
3. M. Kurata and W.H. Stockmayer, Adv. Polym. Sci., 3, 196 (1963).
4. J.R. Urwin and M. Girolamo, Makromolek. Chem., 150, 179 (1971).
5. P.J. Flory, Disc. Farad. Soc., 49, p. 14 (1970).
6. E.F. Casassa, Ann. Rev. Phys. Chem., 11, 477 (1960).
7. W.H. Stockmayer and M. Fixman, J. Polym. Sci., C1, 137 (1964).
8. M. Kurata, M. Fukatsu, H. Sotobayashi and H. Yamakawa, J. Chem. Phys., 41, 139 (1964).
9. D.N. Cramond and J.R. Urwin, Aust. J. Chem., 21, 1835 (1968).
10. J.E. Mark, J. Am. Chem. Soc., 88, 4354 (1966); 89, 6829 (1967).
11. H.Y. Chen, Anal. Chem., 34, 1793 (1962).
12. R.C. Hirt, R.W. Stafford, F.T. King and R.G. Schmitt, Anal. Chem., 27, 226 (1955).
13. J.E. Newell, Anal. Chem., 23, 447 (1953).
14. W. Bushuk and H. Benoit, Canad. J. Chem., 36, 1616 (1958).
15. J.R. Urwin and M. Girolamo, Makromolek. Chem., 142, 161 (1971).
16. J.M. Evans, M.B. Huglin and J. Lindley, J. App. Polym. Sci., 11, 2159 (1957).
17. J.R. Urwin and D.N. Cramond, Aust. J. Chem., 22, 543 (1969).
18. Z. Grubisic, P. Rempp and H. Benoit, J. Polym. Sci., B, 5, 753 (1967).

19. D.N. Cramond, M.J. Hammond and J.R. Urwin, Europ. Polym. J., 4, 451 (1968).

20. G.C. Berry, J. Polym. Sci., B4, 161 (1966).

21. G.C. Berry, J. Chem. Phys., 44, 4550 (1966); 46, 1338 (1967).

22. M. Iwama, H. Utijama and M. Kurata, J. Makromolek. Chem., 1, 701 (1966).

23. M. Fixman, J. Chem. Phys., 23, 1656 (1955); 36, 3123 (1962).

24. O.B. Ptitsyn, Vysokomol. Soedin., 3, 1673 (1961).

25. M. Kurata, W.H. Stockmayer and A. Roig, J. Chem. Phys., 33, 151 (1960).

26. Ref. 3, p. 208.

27. B. Zimm, J. Chem. Phys., 14, 164 (1946).

28. M. Girolamo and J.R. Urwin, Europ. Polym. J., 8, 299 (1972).

29. D. Froelich and H. Benoit, Makromolek. Chem., 92, 224 (1966).

Footnotes to Table 3

† $^{a}\eta$ in toluene calculated from data on polystyrene and polyisoprene for M.Wts. (a) $1.0 \times 10^5$, (b) $2.5 \times 10^5$, (c) $5.0 \times 10^5$, from refs. (1) Polymer Handbook, Interscience (1966); (2) Krigbaum and Carpenter, J. Phys. Chem., 59, 1166 (1955); (3) Wagner and Flory, J.A.C.S., 74, 195 (1952).

†† Ref. Part 1.

## Table ~~I~~ 1

General characteristics of the series of di-block copolymers of polyisoprene and polystyrene

| Polymer | Composition wt. % polystyrene | | Molecular Weight × $10^{-5}$ | | | $\bar{M}_W/\bar{M}_N$ | G.P.C. Std.Dev. σ |
|---|---|---|---|---|---|---|---|
| | Predicted† | Found†† | $M_k$* | $\bar{M}_N$ | $\bar{M}_W$ | | |
| IS1 | 11.8 | 13.5 | 1.00 | 1.02 | 1.06 | 1.04 (1.08) | 0.287 |
| IS2 | 25.0 | 24.7 | 1.00 | 1.02 | 1.07 | 1.05 (1.10) | 0.312 |
| IS3 | 28.6 | 28.2 | 1.00 | 1.01 | 1.08 | 1.07 (1.05) | 0.230 |
| IS4 | 50.0 | 52.2 | 1.00 | 1.04 | 1.07 | 1.03 (1.08) | 0.277 |
| IS5 | 77.8 | 78.2 | 1.00 | 1.03 | 1.08 | 1.05 (1.08) | 0.285 |
| IS6 | 11.8 | 11.8 | 2.50 | 2.53 | 2.68 | 1.06 (1.10) | 0.317 |
| IS7 | 25.0 | 25.5 | 2.50 | 2.52 | 2.62 | 1.04 (1.08) | 0.287 |
| IS8 | 50.0 | 48.5 | 2.50 | 2.54 | 2.62 | 1.03 (1.07) | 0.272 |
| IS9 | 25.0 | 25.1 | 5.00 | 4.99 | 5.34 | 1.07 (1.11) | 0.327 |
| IS10 | 50.0 | 48.7 | 5.00 | 5.01 | 5.41 | 0.08 (1.13) | 0.352 |

* Based on monomer charge-initiator concentration ratio.

†† From U.V. analysis.

† From ratio wt. of styrene to total charge.

## TABLE 2

Weight average molecular weight calculated from the apparent molecular weights determined by light scattering measurements in three solvents

| Polymer | Apparent M.Wt. ($\times 10^{-5}$) | | | $\bar{M}_W$* $\times 10^{-5}$ |
|---|---|---|---|---|
| | Tol. | c-Hex | M1BK | |
| IS1 | 1.27 | 1.06 | 1.08 | 1.06 |
| IS2 | 1.29 | 1.10 | 1.09 | 1.07 |
| IS3 | 1.63 | 1.14 | 1.12 | 1.08 |
| IS4 | 1.30 | 1.14 | 1.10 | 1.07 |
| IS5 | 1.29 | 1.14 | 1.12 | 1.08 |
| IS6 | 3.00 | 2.71 | 2.69 | 2.68 |
| IS7 | 3.00 | 2.75 | 2.71 | 2.62 |
| IS8 | 2.80 | 2.70 | 2.67 | 2.62 |
| IS9 | 5.78 | 5.46 | 5.42 | 5.34 |
| IS10 | 5.64 | 5.60 | 5.53 | 5.41 |

* Computed according to the method of Bushuk and Benoit.(18

TABLE 3

Intrinsic viscosities, hydrodynamic expansion factors and displacement length parameters in toluene, cyclohexane and methyl isobutyl ketone (M1BK)

| Polymer | Composition % P.S. |  |  | $[\eta]_{30°C}$ $cm^3/g$ |  |  | $[\eta]_\theta$ | Expansion factor at 30°C $\alpha_\eta$ |  |  | $(\bar{r}^2/Z)^{\frac{1}{2}} \times 10^8$ cm |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Wt. % | Mole % | Links % | Tol. | c-Hex. | M1BK | MEK†† | Tol. | c-Hex. | M1BK | Tol. | c-Hex. | M1BK |
| IS1 | 13.5 | 9.2 | 5.1 | 88.0 | 92.1 | 43.2 | 41.3 | 1.29 | 1.31 | 1.02 | 4.85 | 4.92 | 3.83 |
| IS2 | 24.7 | 17.6 | 10.1 | 80.1 | 89.8 | 42.9 | 40.3 | 1.26 | 1.31 | 1.02 | 4.90 | 5.09 | 3.98 |
| IS3 | 28.2 | 20.4 | 11.9 | 75.7 | 79.0 | 40.2 | 39.1 | 1.25 | 1.26 | 1.01 | 4.89 | 4.96 | 3.96 |
| IS4 | 52.2 | 41.6 | 27.3 | 75.5 | 63.7 | 42.8 | 37.5 | 1.26 | 1.19 | 1.05 | 5.41 | 5.11 | 4.48 |
| IS5 | 78.2 | 70.1 | 55.2 | 59.2 | 41.6 | 34.6 | 33.5 | 1.21 | 1.07 | 1.01 | 5.80 | 5.16 | 4.85 |
| IS6 | 11.8 | 8.0 | 4.4 | 201.0 | 237.0 | 78.7 | 65.0 | 1.46 | 1.54 | 1.07 | 5.45 | 5.76 | 3.99 |
| IS7 | 25.5 | 18.3 | 10.5 | 172.0 | 178.5 | 74.1 | 63.3 | 1.40 | 1.41 | 1.05 | 5.47 | 5.52 | 4.12 |
| IS8 | 48.5 | 38.1 | 24.5 | 139.0 | 144.2 | 65.3 | 58.6 | 1.33 | 1.35 | 1.04 | 5.61 | 5.67 | 4.36 |
| IS9 | 25.1 | 17.9 | 10.3 | 345.5 | 426.7 | 94.5 | 89.1 | 1.57 | 1.69 | 1.02 | 6.13 | 6.58 | 3.98 |
| IS10 | 49.7 | 39.3 | 25.5 | 263.5 | 272.0 | 84.8 | 82.3 | 1.47 | 1.49 | 1.01 | 6.23 | 6.30 | 4.27 |
| P.S.† |  |  |  |  |  |  |  | 1.22a<br>1.31b<br>1.38c | 1.00 | 1.07 | 5.91 | 4.83 | 5.16 |
| P.I.† |  |  |  |  |  |  |  | 1.32a<br>1.50c | 1.36 | 1.04 | 4.54 | 4.66 | 3.55 |

# TABLE 4

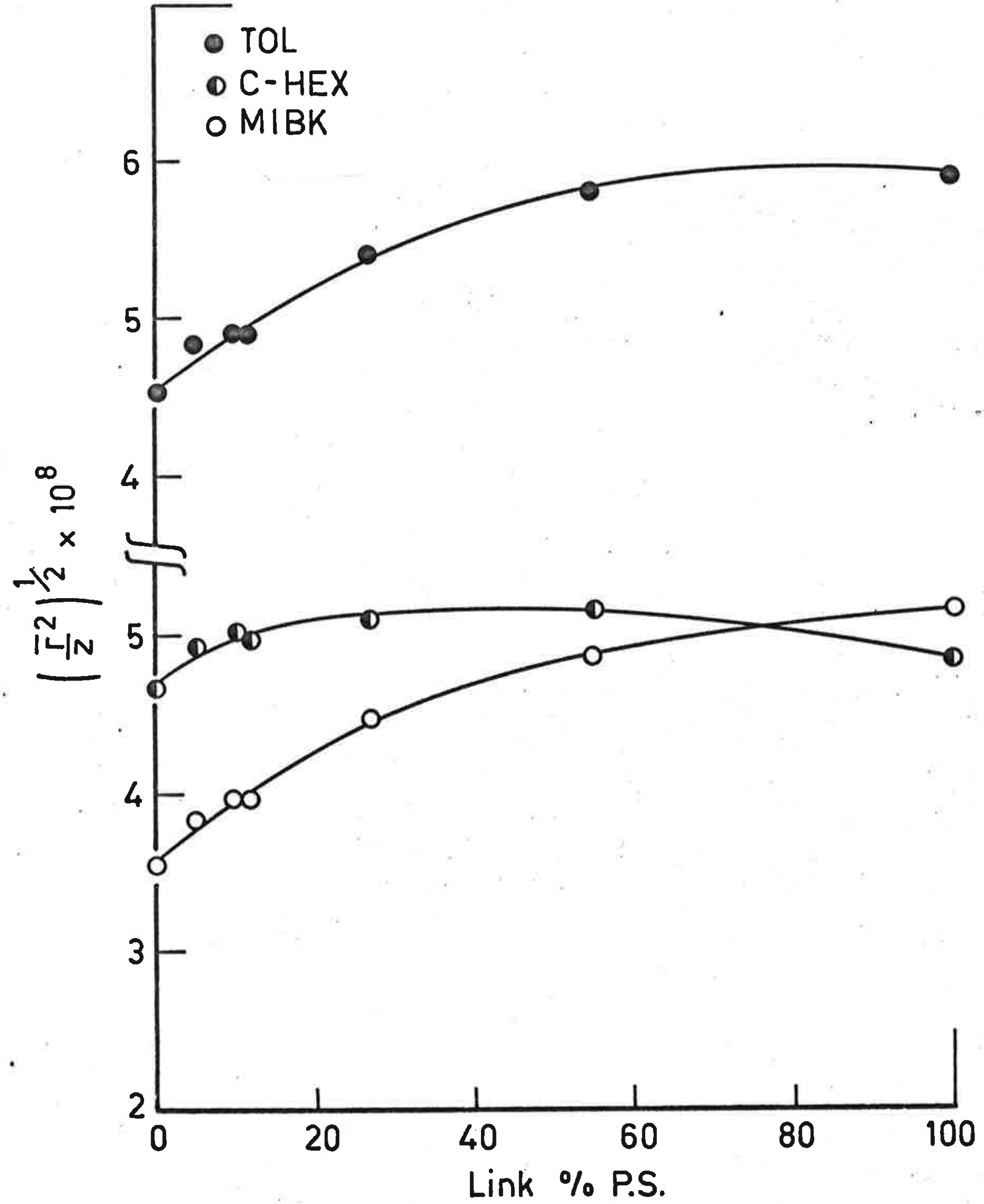
The long range interaction parameter B for the block copolymers from [$\eta$]-M and $A_2$-M relations Eq. (8) and Eq. (10) respectively for the series coded 25/75 (25% P.S.) and 50/50 (50% P.S.)

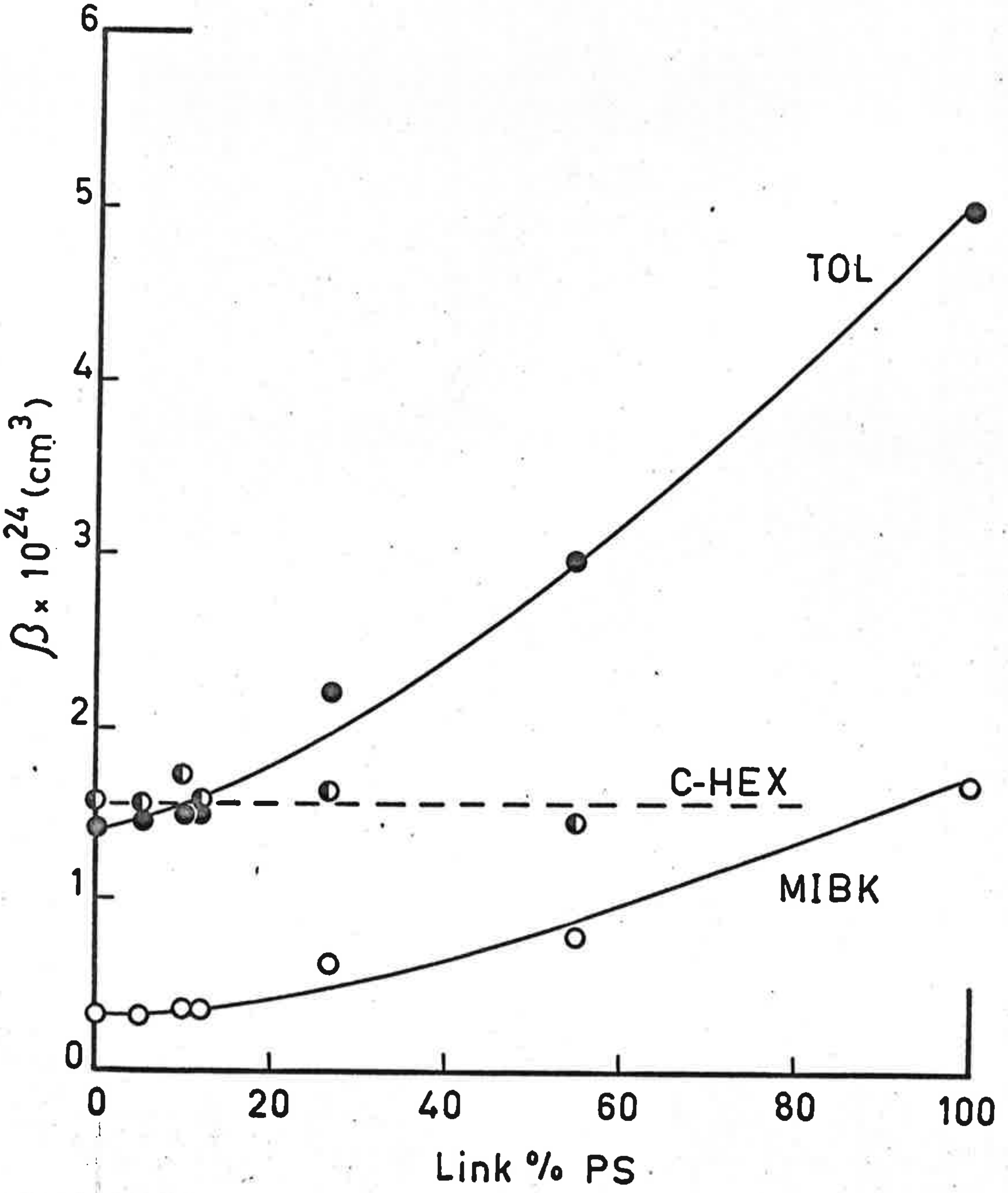
| Polymer Code | Solvent | $B_\eta$ $\times 10^{28}$ | $B_\Pi$ $\times 10^{28}$ | $B_\Pi/B_\eta$ |
|---|---|---|---|---|
| 25/75 | Toluene | 26.3 | 27.2 | 1.03 |
| | c-Hex. | – | 22.5 | – |
| 50/50 | Toluene | 25.6 | 28.7 | 1.12 |
| | c-Hex. | 24.8 | 23.3 | 0.94 |

## Legends for Figures

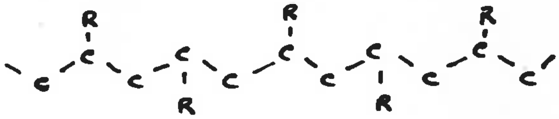
Fig. 1. Plots of displacement length parameter against composition (links %) in toluene, cyclohexane and MIBK.

Fig. 2. Plots of binary cluster integrals β against composition (links %) in toluene, cyclohexane and MIBK.


● TOL
◐ C-HEX
○ MIBK
$\left(\frac{\bar{r}^2}{z}\right)^{\frac{1}{2}} \times 10^8$
6
5
4
5
4
3
2
0
20
40
60
80
100
Link % P.S.


6
5
4
3
2
1
0
$\beta \times 10^{24}$ (cm$^3$)
TOL
C-HEX
MIBK
0
20
40
60
80
100
Link % PS

# POLYMER TOPICS



*This feature, published on behalf of the Polymer Division, briefly surveys current thinking on aspects of polymer science. The articles, which are intended to be of general as well as specialist interest, are contributed by guest authors under the general direction of Dr. J. H. O'Donnell. Relevant comment and suggestions may normally be addressed direct to Dr. O'Donnell, C/- Chemistry Department, University of Queensland, St. Lucia, Qld. 4067. Dr. O'Donnell is at present overseas, and in his absence mail may be addressed to the Editor.*

## The Development of Polymer Science in Australia

### A proposal to establish an Institute of Polymer Science in Australia

*Contributed by* J. R. URWIN, Department of Physical and
Inorganic Chemistry, University of Adelaide.

Polymer science provides the theoretical background for a wide range of economically important industries. It is an exact science in the strictest sense and is advancing on an ever-widening front; in fact, high polymers form one of the major growth areas of scientific knowledge. It is linked quite logically with other established branches of science such as chemistry, physics and materials science. However, the very nature of polymer science is such that the type of training required for the development of polymer scientists cuts right across the traditional scientific disciplines. Some scientists believe that the criticism, so often levelled at universities, of the extremely disparate assistance given to the industry is, in no small way, due to the interdisciplinary nature of the science.

Some industrial groups have attempted to bridge this gap by setting up their own institutions. One of the better known of these in the U.K. is the Rubber and Plastic Research Association, known as RAPRA. With financial aid from the Science Research Council, RAPRA has recently up within the Association the Polymer Supply and Characterization Centre, which aims to supply well characterized polymers for research in industry, universities or, for that matter, any laboratory requiring polymers for research programmes. The Centre proposes to collect and collate all relevant information on rubber and plastics gathered from every possible source, as a *general service* to the whole industry.

The larger industries have long recognized the need for interdisciplinary training groups. ICI's Petrochemical and Polymer Laboratory is just such a specialist laboratory which, by contrast with RAPRA, attempts to span the *whole spectrum of research*, from the fundamental to technological studies, on polymers in which they have direct interests. The aim is to provide a team of excellence with interdisciplinary interaction, which, because these scientists return to the body of the industry after three to five years, is a training ground within the specific industry at the same time. Of course, the expertise so gained is injected into that particular industry and does nothing to promote the *general level* of excellence within the industry as a whole.

### The Growth of the Polymer Industry

The chemical industry is now the second largest in the U.K. Its growth rate is double that of the national economic growth rate and shows no signs of abating. At its present rate of increase, about 9 percent per annum, it will soon become that country's largest single industry. The growth of organic polymers is reliably predicted to dominate the industrial chemicals scene by 1980, and organic-based plastics, elastomers, synthetic fibres, etc., will by then consume over one-half of all available organic materials. In view of this conclusion, many scientists in the U.K. deplore the fact that no Organic Chemistry Department in the country devotes any real effort to the specific study of the organic chemistry of polymers. Quite candidly, the study of inorganic polymers can be said to be almost non-existent. Nevertheless, the most spectacular indication of the importance of the growth in the polymer industry is the prediction, based on conservative estimates, that in the U.S.A. in the mid 1970s, we will see the production volume of 'plastics' overhaul the volume output of steel. It can be confidently expected that the trend will continue further and that a similar growth rate will extend into all the technically advanced countries with a minimal time lag.

These observations only serve to underline the need, that must inevitably arise, for trained manpower in this huge industry. The situation as it stands is that, in the U.S.A., more than one-third of all active scientific

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personnel are employed in the 'polymer' industry. The U.K. survey of 1965 showed that between 4,000 and 5,000 out of a total of 7,000 scientifically trained personnel were directly employed in the plastics, fibres and rubber industries. Up to the present time in Australia, most of the technology in the fields of plastics, rubbers and fibres has been developed on processes originating from overseas research and carried out under licensing arrangements. How long this will continue cannot be accurately gauged, but one suspects that the increasing cost of licensing in Europe and the U.S.A. will encourage an increased Australian-based technology content, possibly accelerated by encouragement from the Treasury. Apparently, the practice of 'buying' overseas technology was adopted in Japan at first, but the Japanese-based contribution, in the form of original research, is now quite large.

Only a few firms in Australia are large enough to conduct their own developmental research on anything like a satisfactory scale. This points to a need for some organization which may be able to carry out developmental work of a short-term nature, preferably where it can be fitted into existing programmes and on a contractural basis. As a colleague in materials science has pointed out, there is no laboratory in Australia which would be capable of undertaking the maintenance of standards within the industry or of competently performing the functions of arbitrator in a dispute which might arise between manufacturer and customer. In the light of overseas trends, it seems entirely reasonable to assume that, with the growth of the petrochemical industry here and increasing sophistication in the manuturing processes, the immediate development in Australia must follow the same pattern as overseas. The needs, in numerical terms and in the kind of training required, must therefore be properly evaluated now. Students seeking to take higher degrees should be alerted to where they are most likely to find employment. Universities have a responsibility to these students to see that the employment outlook is squarely placed before them and that they are properly informed of the various options and where the relative opportunities exist for employment.

## The Training of Polymer Scientists

We can assume, on the basis of overseas experience, that a high proportion of all scientists trained for research and development in the future will enter industries manufacturing plastics, fibres, rubbers and elastomers, or those using polymers in the manufacture of such products as adhesives, coatings, finishes, tyres, etc. In all reason, this must be taken into account in planning the future training programme of scientists.

Some universities in Australia have recognized the need for such training during undergraduate studies. For example, in the School of Chemical Technology, University of N.S.W., a full-time B.Sc. degree course has been offered since 1960 which included about 80 hours of lectures and about 120 hours of practical work spread over three terms during the third year; this was boosted by 25 percent in the fourth year and included a small research project. This course is being scaled down in the future because of past lack of interest in the subject, and a revised version will be offered as an elective in Industrial Chemistry. Perhaps the course was too ambitious, even for a city of over two million. At Adelaide, which operates unit courses of 15–16 hours of lectures plus 54 hours practical, a unit in macromolecular chemistry, equally divided between synthetic polymers and biopolymers, is offered in the third year. Of course, those students who achieve a reasonable level of competence may then elect to study for an honours degree covering topics which include reaction kinetics or solution properties of synthetic polymers and topics in biopolymers.

It would be of considerable interest to know what is being done in other university departments to foster an interest in polymer science. One correspondent suggested a universal panacea, namely, that the more industrial aspects of polymer chemistry could be left to the University of N.S.W., and biopolymers to Adelaide. This rather shortsighted view would ignore aspiring polymer scientists in all the other universities.

Quite naturally, *postgraduate training* only reflects the specific interests of the professors and lecturers who supervise the postgraduate students. As able as this training may be, in no way does it continue the process of integration of disciplines required to train the polymer scientist. As a matter of interest, many of the present managers of research teams, now responsible for policy formulation in the industries they lead, were originally trained as polymer chemists. These men found that they had to retrain themselves in physics, engineering materials and materials science in order to cope with the complex business of handling real materials. Few, if any, would recommend this method of acquiring the necessary training. A different approach seems to be required. At the undergraduate level, the polymer scientist-elect must acquire certain basic disciplines but, at the same time, be introduced to some aspects of the physics of polymers as well as gaining a working knowledge of the science of materials and the problems of materials engineering.

At the University of Sussex, the need for interdisciplinary training was recognized from its inception, and from the second-year level instruction in polymer chemistry is given in the physics, engineering and materials science schools as well as in chemistry. The structure of the course is still in the melting pot but a proper interdisciplinary approach at the undergraduate level is gradually emerging.

The real problem, though, emerges at the postgraduate level. Of course, properly trained Ph.Ds and M.Scs should be *fundamentally* problem solvers and, although some research projects lend themselves to this approach more readily than others, it should be the broad aim. There is, however, a difference in approach between disciplines to which some attention should be drawn. If one might be forgiven for such a crude analogy, the average chemist 'sees' the stretching of rubber as an entropic process involving molecular perturbations, whereas the engineer is more inclined to 'see' it in terms of the thermomechanical spectrum. It is the same phenomenon. The difference in approach is the microscopic versus macroscopic view; the polymer scientist must be able to reconcile the two. There is a growing need for men capable of applying their problem-solving ability to the complex interdisciplinary problems which arise today, and which will become even more complex as the methods of engineering of the newer and far more sophisticated organic-based polymers are evolved.

To illustrate the point, one might draw attention to one of the more recent arrivals on the polymer scene, that is, the invention of thermoplastic elastomers. These are materials which are unusual in that they have the properties of both rubbers and thermoplastics. Firstly, the discovery is already encouraging the search for a wider range of the new materials. Secondly, studies of the new materials raise fundamental questions as to what constitutes an elastomer. The new materials are already being used as models in an effort to solve such questions. Thirdly, a critical examination of their properties, ranging from the most fundamental to the technological handling on the factory floor, must be made. Fourthly, new demands for variations in properties will arise. So it goes on. Even the discards may become useful products in time.

The most important point to grasp, at this time, is that a research and development capability cannot be gained secondhand; one must take an active part in the process. Even at the expense of being less 'expert' than others, some men must be capable of handling the overall problems. A reliably based estimate is that one-quarter of any research and development team should have this kind of background.

The responsibility for undergraduate training rests squarely with the universities. On the other hand, the existing Institutes of Polymer Science throughout the world seem to offer one proven method of providing the postgraduate training ground which brings together the multiplicity of disciplines that make up polymer science. The Institutes have demonstrated their research capability to generate new ideas, but it is not always consciously realized that the feedback process, so familiar to research groups, also operates on the wider canvas. One may confidently predict that many of the new materials, based on high polymers, will in the near future replace those materials in current use. This will bring in its wake a crop of problems for the whole industry which will make many present-day production problems *seem* elementary. But, then, part of the function of the Polymer Institute is to provide effective consultation covering the whole field of polymer activity; the need for consultation will grow rapidly.

## An Institute of Polymer Science in Australia

Institutes of polymer science have been established in nearly all the scientifically advanced countries in the world, such as the U.S.A., the U.S.S.R., the leading countries of Europe and, of course, Japan. In the U.S.A., recent statistics show that more than 20,000 trained scientists, 3,000 students and research assistants, and over 300 mature scientists devote their whole time to fundamental and applied polymer research. In Japan, more than 3,000 scientists are engaged on fundamental research with more than 200, classified as mature scientists, working in the field. In the U.S.S.R. and other Iron Curtain countries, the figures are at least as great, if not greater. These figures indicate that polymer science is a major interest of governments and industry in all of these countries.

If the funds allocated by the A.R.G.C. to polymer research can be taken as a guide, the interest in Australia is on a far smaller scale, relatively. This may not entirely indicate a lack of interest but rather reflect the broad lines of interest which have developed during the fairly recent rise of the Australian university community. However, this may point to a possible area for remedial action in future development. One often gains the impression that many industries are unaware of the full economic potentiality of PhDs. In this context, the mediocre salaries paid, in even the well-established sections of the polymer industry, to men with higher degrees and often with overseas experience should be noted. One also wonders to what extent the industry is aware of research being done in universities by present polymer groups. To be fair, though, the responsibility for this lack of dialogue may well lie equally with both sides.

Institutes of polymer science have firmly established themselves as major sources of new ideas in polymer science and as the main training ground for the newer polymer scientists. They do not train undergraduates.

As stated earlier, this role must remain the prerogative of the universities but, being integrated within the university structure, they must take a part in the postgraduate training, *i.e.*, be degree conferring at the M.Sc. and Ph.D. levels. They are staffed with multidiscipline personnel with the firm aim of promoting constant interaction between the disciplines, often to the point of initiating multidiscipline projects. The interdisciplinary approach is thus the norm among their postgraduates, postdoctoral and research fellows.

Regarding the establishment of an Australian Institute of Polymer Science, certain points might be raised for general discussion at this time. It seems to the author that the Institute should be a postgraduate research organization with teaching and consultative roles. It should in no way usurp the universities' undergraduate teaching function, but it might attempt to encourage and foster a greater polymer science content. It should not compete with university research groups for financial assistance. It should be attached to a university but be financially independent of it. In fact, the Institute should be free from any Commonwealth–State financial arrangements. It should be able to carry out fundamental and applied research, on a contractural basis where this can be fitted into existing programmes. In the first instance, it would have to be financed out of Commonwealth funds but should aim to improve its earning capacity and eventually become self supporting if possible. It should aim to encourage industry to make greater use of the research potential of graduates with higher degrees, and of their problem-solving capability. It should aim to improve production standards of polymers and polymer products by providing appropriate testing procedures.

At this stage, any comments, criticisms or suggestions would be most welcome. The whole point of this article is to encourage thoughtful discussion and to alert all interested persons, scientists and lay public alike, to the tremendous growth that is taking place in the polymer field and the implications this has for the advancement of polymer science in Australia.

**Acknowledgments**

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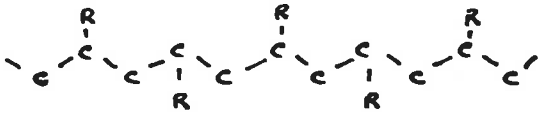
# POLYMER TOPICS



This feature, published on behalf of the Polymer Division, briefly surveys current thinking on aspects of polymer science. The articles, which are intended to be of general as well as specialist interest, are contributed by guest authors under the general direction of Dr. B. A. Bolto. Relevant comment and suggestions may be addressed direct to Dr. Bolto, C/o CSIRO Division of Applied Chemistry, Box 4331, G.P.O., Melbourne, Vic. 3001.

# The New Generation of Rubbers

*Contributed by* J. R. URWIN, Department of Physical and Inorganic Chemistry, The University of Adelaide.

> *It is from ignorance of causes that operation fails . . . all depends on keeping the eye steadily fixed upon the facts.*
>
> Francis Bacon*.

Rubber has had a long and fascinating history of development[1]. The discovery of vulcanization by Goodyear (1839) allowed the conversion of the crude material, so ably investigated by Gough (1806), into the useful material we recognize as pure gum vulcanizate today. The thermodynamic description of rubber elasticity was formulated 100 years after vulcanization was first demonstrated and still remains basically unchanged. The molecular interpretation of the almost entirely entropic retractile force, which gives rise to the snap in rubber, had to await the enunciation of the macromolecular hypothesis by Staudinger. The effect on vulcanizates of the addition of fillers, notably carbon black, can at least be plausibly explained at the present time. However, since the late 1940s, synthetic rubber has largely supplanted natural rubber and the stereoregular *cis*-1,4-polyisoprene must now be considered as the equivalent of the natural product.

To get a better perspective, it might be profitable briefly to recall the general properties of rubber[2]. Natural rubber is entirely *cis*-1,4-polyisoprene of broad molecular weight distribution and with an average molecular weight of about 5,000. Mastication of the raw rubber is the first step in processing. This is a form of degradation (including oxidative degradation) designed to produce a thermoplastic material with low melt viscosity. Vulcanizers and fillers, including oils and antioxidants, are added to produce a stock which, after moulding, must be cured.

Vulcanization causes a degree of crosslinking, thereby removing the properties so necessary for moulding and extrusion, and replaces the thermoplastic with a three-dimensional network which, in its unperturbed state, is a randomly oriented structure well above its glass transition at ordinary temperatures. The material at this stage of production contains chains interconnected at the crosslinks by covalent bonds, except for a relatively small proportion of chains with only one end fixed and which therefore contribute nothing to the rubbery properties. Originally, the curing process was time-consuming, but with the introduction of organic vulcanizers and accelerators the curing time has been greatly reduced.

The synthetic rubber industry produces a wide range of elastomers, from copolymers of styrene and butadiene (SBR) to stereoregular polybutadiene (BR) and polyisoprene (IR) manufactured by anionic methods, a process which, incidentally, allows fairly strict control over molecular weight distribution. Blends of all types have also been made available by the industry. Other rubbers, such as butyl rubber, have special properties, such as low permeability to gases, which make them important in the manufacture of certain specialized products, *e.g.*, inner tubes for tyres. The polymer industry has also produced rubberlike or flexible thermoplastic materials, mainly plasticized

*Dr. Urwin's research interests lie in the field of polymer science. He is the author or coauthor of 30 scientific papers and articles, most of which have been concerned with the synthesis, analysis and solution properties of block copolymers. In recent years, this has been confined to blocks containing polystyrene and polyisoprene and the research has been aimed at elucidating the conformation of these polymers in solution.*

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* *The Great Instauration.*

PVC and polyethylene-PVA copolymer which, while satisfying some of the requirements of elastomers, cannot compete with the high extension and snap of rubber[3].

## A Novel Development

Since 1965 a new elastomer has been marketed[4] which has the remarkable property of being both thermoplastic, and therefore capable of being moulded to the required shape, yet which on cooling becomes a true elastomer with the characteristics of reinforced rubber (*i.e.*, conventional vulcanizates which contain filler or possess the ability to crystallize upon elongation). As shown in Figure 1, the new material has a tensile strength of 5,000 psi (350 kg cm$^{-2}$) and achieves greater than 800% elongation at break, its behaviour being comparable to that of a vulcanized natural rubber. The new material may be recycled since it is a thermoplastic, but it always returns to the elastomeric state on cooling. Because of this dual behaviour, the material is generally referred to as a thermoplastic elastomer. It has also been described as a virtually crosslinked elastomer[5], since crosslinking is necessary for rubbery properties but no chemical crosslinks in fact exist.. Obviously there is a new principle involved here which allows the formation of crosslinking by other means than the conventional formation of covalent bonds by vulcanization.

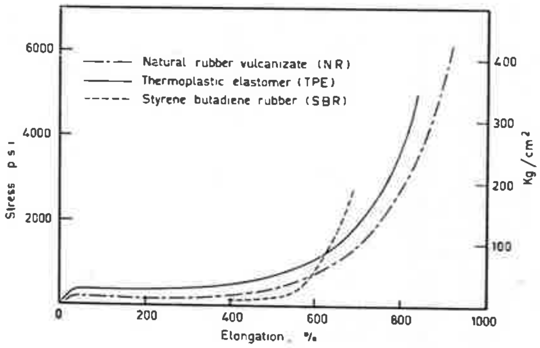

*Figure 1.*

## Synthesis

The new elastomers, to which attention was first drawn in the patent literature[6] in 1963, are block copolymers of the traditional materials used in the rubber industry — styrene, butadiene and isoprene. It is important that these block copolymers have at least three sequences or blocks arranged in a particular order, *e.g.*,

1. SSSSSSSSSBBBB . . . BBBBBSSSSSSS
2. SSSSSSSSSIIII . . . . . . IIIIISSSSSSS

where S is a styrene segment, B is butadiene and I is isoprene. The polymers are simply designated SBS or SIS where S, B and I stand for one sequence. Other arrangements such as SBSBS or SISIS have not shown any improvement in properties over the three-sequence type. On the other hand, SB, SI or BSB polymers do not exhibit the same properties for reasons which will become clear as we proceed.

Anionic polymerization is the most acceptable method of manufacture of these polymers and one which allows synthesis in one of two ways. In the first, the sequential method, lithium metal or lithium alkyls initiate chains which propagate from one end only. As an example, consider a lithium alkyl, $Li^-A^-$, as initiator[7,8]; the reaction proceeds as follows:

$$Li^+A^- + S \rightarrow AS^-Li^+ \qquad \textit{Initiation}$$

$$AS^-Li^+ + S \rightarrow AS_2^-Li^+$$

$$AS_2^-Li^+ + S \rightarrow AS_3^-Li^+ \qquad \textit{Propagation}$$

. . . . . . . . . . . .

$$AS_n^-Li^+ + S \rightarrow AS_{n-1}^-Li^+$$

If the system is anhydrous and oxygen, carbon dioxide and certain organic molecules such as alcohols are all absent, the reaction is terminationless and transfer free. The absence of termination means that another monomer may be added after the first has been exhausted and propagation of the new monomer continued.

$$\sim\sim\sim\sim S^- + B \rightarrow \sim\sim\sim\sim SB^-$$

(cross propagation)

$$\sim\sim\sim\sim SB^- + B \rightarrow \sim\sim\sim\sim SB_2^-$$

$$\sim\sim\sim\sim SB_2^- + B \rightarrow \sim\sim\sim\sim SB_3^-$$

(propagation of monomer 2)

Once again, the first monomer may be reintroduced after the second has been consumed. The same amount of monomer is added for the third sequence as was used for the first, so that the chain is symmetrical, thus: $S_xB_yS_x$. Dianionic initiators have also been used but their application is in the experimental stage[9]. These lithium-based initiators produce a diene dianion propagating from both ends, and when the diene is exhausted the polymer may then be capped with the glassy styrene. For practical purposes the total molecular weight must be kept to about 120,000 since higher molecular weight material will have a higher viscosity and therefore be more difficult to work.

Other experiments have amply demonstrated that the molecular weight distribution of the sequences must be kept as narrow as possible, but for different reasons for each block. The middle rubbery block has, however, to be several times larger than the end blocks[10]: the range of molecular weights may be varied between 10,000 and 20,000 for the end sequence and 40,000-80,000 for the rubbery sequence.

The theory of tensile strength in rubbers is based, at the molecular level, on the underlying assumption that, on stretching, the short network chains become stressed first. A break would then cause catastrophic failure 'initiated' by overloading connecting chains. On this assumption, the rubbery block in the thermoplastic elastomer should be as near to uniform chain length as possible. The smaller the molecular weight, the more difficult this is to achieve kinetically. The method of control lies in the relative rates of initiation and cross propagation when compared with propagation rates. When the initiation is fast compared with propagation, the distribution approaches the Poisson distribution predicted by Flory[1].

Although the use of ethers such as THF has been found rapidly to accelerate initiation, the effect upon the 1,4-isomer content is disastrous. However, it has been shown that certain ethers such as anisole or diphenyl ether have the desired effect of accelerating initiation with only minimal reduction of the 1,4-microstructure. The effect of the presence of vinyl structures is to raise the glass transition temperature, thereby limiting the utility of the elastomer.

## The Effects of Impurities

The presence of adventitious terminating material in the system will introduce unwanted amounts of polystyrene, polyisoprene and SB block in the final product. It has been demonstrated that addition of SB block will lower the tensile strength of an SBS block quite markedly[11]. In one experiment an SBS polymer, molecular weight 21,000-63,000-21,000, to which was added an SB polymer (21,000-63,000) showed a loss of tensile strength as follows: initial tensile strength 319 kg cm$^{-2}$, falling to 308 kg cm$^{-2}$ on addition of 1% SB polymer, and to 244 kg cm$^{-2}$ after adding 5% SB polymer, *i.e.*, losses of 3.5% and 23% respectively. Clearly the implication is that strict control over the purity of all materials in the reaction is essential for successful synthesis.

Morton has shown that the addition of polystyrene to a block copolymer such as SBS results in behaviour almost identical to that of a similar block with higher styrene content, *e.g.*, addition of 10% polystyrene to a block containing 20% polystyrene raises the stress-strain curve but not the tensile strength[12]. The result is the same as for a block containing 30% polystyrene. The homopolymer must therefore combine with the styrene domains. There are limitations though: addition of polystyrene with molecular weight greatly in excess of that of the styrene block sequences causes serious incompatibility. The material loses its clarity and becomes opaque and a definite loss of tensile strength is observed. On the other hand, the addition of a polymer with high glass transition temperature and of the appropriate molecular weight can give rise to enhanced tensile strength. This is an interesting side development, the reason for which will emerge later.

When polyisoprene homopolymer is mixed into the block copolymer, there is a drop in tensile strength corresponding to that which follows the addition of a diluent. The homopolymer cannot, of course, add to the strength of the polymer since it is not fixed at the ends as are the chains in the block.

The two-sequence block is damaging because the polystyrene end is included in the domains of polystyrene with one rubber end attached but free at the other end. The result is a network defect which has been shown experimentally to affect seriously the strength of the elastomer in the manner described earlier.

## Intramolecular Phase Separation

Phase separation between mixtures of chemically dissimilar polymers is a well-known phenomenon[1]. Block copolymers, such as those discussed, have been examined by differential thermal analysis and microcalorimetric methods and the existence of two glass transition temperatures demonstrated. The $T_g$ corresponding to polyisoprene is well defined, but the transition for polystyrene is much less so. For example, in the case of the SIS polymers a glass transition of good definition appears at -64°C, corresponding to pure polyisoprene, and another much smaller transition at temperatures between 80°C-100°C, which is the region where polystyrene is expected to show a glass transition. $T_g$ for polystyrene depends on molecular weight and molecular weight distribution; it approaches 100°C at high molecular weight and narrow distribution. Most experimenters report a $T_g$ of 94-96°C for polystyrenes of narrow molecular weight distributions. In block copolymers with a preponderance of isoprene, such as is the case in thermoplastic elastomers, it has been shown by phase microscopy and electron microscopy that spherical domains of polystyrene occur in a matrix of polyisoprene. The reverse situation is found in polymers with high styrene content. The dimensions of the polystyrene domains have been measured[13] and, on average, appear to be about 200-400Å in diameter[10]. This accounts for the fact that the material is transparent, since light is scattered from the interface between materials of different refractive index but scattering is negligible when the dimensions of the scattering particle are small compared with the wavelength of the incident light.

The existence of the glassy polystyrene domain provides the key to the elastomeric behaviour of the thermoplastic material. It also explains the reason for the requirement of a three-sequence block copolymer. On cooling the melt crosslinking occurs due to intramolecular phase separation. since each end of the rubbery centre block is anchored by van der Waals forces between the aggregated polystyrene chains in the glassy domain. Some chains will be anchored in two different domains, some simply looped and anchored in the same domain. A pictorial representation of the situation in a small region is shown in Figure 2. Attention should be drawn to the presence of the usual entanglements which exist in vulcanizates as well. The molecular weight between crosslinks has been estimated to be several times smaller than the diene chain length and therefore, by inference, entanglements are considerable[13].

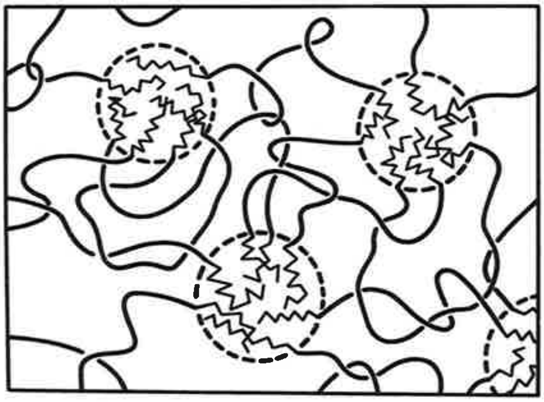

*Figure 2.*

Phase Separation in a Thermoplastic Elastomer

〰 Polystyrene

∞ Polyisoprene

The size and amount of the styrene component in the block copolymer appear to be critical for good results. Compatibility of the two polymers is an important factor in domain formation. Experiments with SIS and SBS polymers have demonstrated that when the molecular weight of the polystyrene sequence is less than 5,000 no phase separation is observed. The addition of homopolymer to blocks of this size has no effect whatsoever; domains simply do not form. In fact domain formation is only observed when the molecular weight exceeds 8,500, but normal tensile strength is not achieved until the molecular weight exceeds 10,000 [12].

## The Theory of Domain Formation

Meier[14] has formulated a theory of domain formation based on thermodynamic arguments. He has argued that the considerable loss in configurational entropy, due to the constraints of the spatial displacement of chains in a domain type of structure, requires that the critical molecular weights of sequences necessary for domain formation are much greater than the molecular weights required for phase separation in a simple mixture of the components.

To evaluate the difference in free energy between random mixing of the block copolymer molecules and the phase-separated domain system, Meier separates the entropic and enthalpic contributions into several easily recognized components, *e.g.*, the entropy decrease due to restricting the junction at glassy and rubbery sequences to the surface of a domain, the restriction of glassy sequences to the glassy domain and rubbery sequences to the rubbery matrix (restricted volume), and, lastly, the perturbation of chain dimensions in the domain system from random-flight values. The enthalpy may be separated into two components, firstly, the difference between domain and random mixture, and, secondly, the interaction at domain surfaces, which is treated as a problem in surface energy. The hopeless task of using a lattice model to calculate the placement entropy is overcome by using the diffusion equation and treating the constraints as a boundary value problem.

Meier concludes that the critical molecular weight for the styrene block will be from 5,000-10,000 for a butadiene block of 50,000. This result is in good agreement with experiment. The minimum value calculated for the block is 2.5-5 times that required for simple phase separation in mixtures.

## Hysteresis and High Elongations

The stress-strain curves of thermoplastic elastomers, such as that shown in Figure 1, represent the behaviour on first stretching; a high modulus is observed at low elongations, followed by a distinct draw period. This phenomenon of yield and draw is attributed to a molecular redistribution of the glassy phase as a result of the applied stress. At high elongations, there is an alignment of the glassy polystyrene in the direction of the applied stress. A rapid increase in stress is observed as a result of this phenomenon. Polystyrene has itself been shown to exhibit cold draw at high elongation[15,16], the evidence for which has been furnished by electron microscopy. It has been claimed that the ability of the particles of polystyrene to yield under stress delays the onset of rupture by absorbing energy and produces the unusually high tensile strength shown by the block copolymers.

Subsequent stress-strain cycling causes increased stress softening. Stress hysteresis decreases in magnitude after the first stretching and ultimately an equilibrium value is reached. This usually takes several cycles to attain. The decrease in stress on cycling might lead one to assume some sort of breakdown of the reinforcement mechanism had occurred. However, heat treatment or annealing at elevated temperatures, relaxation over long periods, or heating in hot water result in the recovery of the original stress-strain behaviour. It has been demonstrated that the original properties may be recovered either by recasting from solvents or by remoulding the material. The phenomenon has only been demonstrated on styrene-diene polymers, but it is highly probable that it applies to other blocks as well. Obviously, the breakdown does not involve the rupture of primary bonds in any way, as recovery is complete.

## The Role of the Filler

The addition of carbon black to natural rubber or synthetic polyisoprene increases the tensile strength and modulus or stiffness. On the other hand, addition of filler to the thermoplastic elastomer makes no real improvement to the physical properties. The reason for this behaviour seems to be that the polystyrene domains perform at least part of the role of the filler, *i.e.*, the thermoplastic elastomer behaves as though there is filler already present[5]. This can best be understood on the basis of the Bueche model[17]. When a rubber is stretched, the particle of carbon acts as a point of stress distribution. In the absence of the filler, rupture of a single chain will mean others attached to this point, whether by crosslinking or entanglement, will be more highly stressed, which may begin a series of ruptures until the stress is finally relieved. When the filler is present, the increased stress due to rupture at one point may be distributed among a much greater number of other chains which are physically bonded to the carbon particle; the increased stress is therefore much smaller on individual chains and no rupture occurs[18].

We can see here that we now have an entirely new concept in rubber structure, with the role of physical crosslinking and filler performed by the glassy domain, a most important step forward in the development of rubbers. From the structural point of view, the rearrangement of the segments of the random copolymer of styrene-butadiene into a three-sequence block copolymer has produced a new and versatile engineering material, one which may be processed by the conventional methods of the thermoplastics industry with the elimination of the rather cumbersome treatment required for conventional rubber. The new rubber has already found uses in footwear manufacture as a replacement for plasticized PVC and particularly in adhesives, where its solubility in a broad range of solvents is an advantage[19]. The SIS polymers have found particular use in the field of pressure-sensitive adhesives because of their superior retention of aggressive tack.

## Operational Temperatures

The low-temperature properties of thermoplastic elastomers are markedly superior to those of plasticized PVC in that the elastomer is flexible down to -50°C for SIS and -70°C for SBS. However, with these particular polymers a limitation for certain applications is that the upper operating temperature cannot exceed 60°C, *i.e.*, similar to the limit for plasticized PVC. This temperature is fixed by the glass transition temperature of the glassy domain, in this case polystyrene. The domains acts as a heat sink and above 60°C polystyrene chains may suffer creep, which allows the chains to pull out from the glassy domain with deleterious effects on physical properties.

Natural rubber still has the edge on synthetic polyisoprene, a fact which, surprisingly, appears to be due to the slight difference in the *cis* content. For most purposes this difference is insignificant but for certain uses, such as giant tyre treads, where the operating temperature is high and usually set at 100°C, the natural product is marginally superior[20]. Blends of natural, isoprene and butadiene rubber have shown that a 10% natural rubber content in the blend improves the physical properties to the point where the difference becomes insignificant.

Morton and coworkers[12] have attempted to remedy the low operating temperature of thermoplastic elastomers by replacing the styrene domain with a α-methyl styrene which has a glass transition at 173°C. A marked improvement in the upper useful temperature results. With styrene in the glassy domain, the tensile strength is reduced to zero at 80°C whereas with α-methyl styrene domains the tensile strength is still as high as 1,000 psi. However, this must be considered only as a first step in raising the upper limit as decomposition occurs at the temperatures required for processing due to the low ceiling temperature of α-methyl styrene.

## Alternative Structures

Very few developments outside the styrene-diene systems have been reported, although signs of alternatives to these are beginning to appear. Block copolymers of polyester-urethane, polyether-urethane, where the physical crosslinking seems to be due to hydrogen bonding between the hard aromatic urethane sequences[21], have been reported to exhibit the domain structure. Blocks of poly(bisphenol-A carbonate) + polyoxyethylene have been investigated and are said to show a degree of ordering in the polycarbonate but none in the polyoxyethylene. Similarly, ABA block copolymers of propylene-ethylene contain crystalline and amorphous regions; the crystallization of the polyethylene blocks on application of stress is interpreted as the evidence of physical crosslinks. The centre block, a random copolymer of polyethylene and polypropylene, remains amorphous. At the present time, however, most of the information on thermoplastic elastomers has been confined to the styrene-diene systems but there is little doubt that others will be developed.

## Conclusion

This dissertation is not intended to be a full-scale review but simply to give the reader a glimpse of one aspect of the fascinating growth of polymer science. Whilst much has been achieved in a short space of time, the rapid expansion in the effort being devoted to the development of this new category of materials, which combine the extraordinary properties of rubber with the processing versatility of thermoplastics, is very likely to produce a rash of new engineering materials in the very near future and, as a bonus, lead us to a better understanding of the properties that define the behaviour of rubber.

## References

1. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, N.Y., 1953.
2. F. W. Billmeyer Jr., "Textbook of Polymer Science", Wiley, N.Y., 1962.
3. J. T. Bailey, E. T. Bishop, W. R. Hendricks, G. Holden and N. R. Legge, *Rubber Age*, October 1966.
4. Kraton 1101, 1102 (a high and medium viscosity SBS block copolymer) and 1107 (a SIS block copolymer) marketed by Shell Chemical Co.
5. R. F. Fedors, *J. Polymer Sci.* **C26,** 189 (1969).
6. G. Holden and R. Milkovich, Belg. Pat. 627,652 (1963).
7. S. Bywater, *Adv. Polymer Sci.*, **4,** 66 (1965).
8. R. C. P. Cubbon and D. Margerison, *Progr. Reaction Kinetics*, **3,** 405 (1965).
9. L. J. Fetters, *J. Polymer Sci.*, **C26,** 1 (1969).
10. M. Morton, J. E. McGrath and P. Juliano, *J. Polymer Sci.*, **C26,** 99 (1969).
11. L. J. Fetters and M. Morton, *Macromolecules*, **2,** 435 (1969).
12. M. Morton, L. J. Fetters, F. C. Schwab, C. R. Strauss and R. F. Kammereck, Fourth International Rubber Symposium, London, Sept.-Oct., 1969.
13. G. Holden, F. T. Bishop and N. R. Legge, *J. Polymer Sci.*, **C26,** 37 (1969).
14. D. J. Meier, *J. Polymer Sci.*, **C26,** 81 (1969).
15. J. F. Beecher, L. Marker, R. D. Bradford and S. L. Agarwal, *J. Polymer Sci.*, **C26,** 117 (1969).
16. H. Hendus, K. H. Illers and E. Ropte, *Kolloid Z.Z. Polymere*, **216,** 110 (1967).
17. F. Bueche, *J. Appl. Phys.*, **7,** 1165 (1963).
18. E. T. Bishop and S. Davison, *J. Polymer Sci.*, **C26,** 59 (1969).
19. J. T. Bailey, *J. Elastoplastics*, **1,** 2 (1969).
20. L. H. Krol, *Rubber and Plastics Age*, **45,** 1341 (1964).
21. S. B. Clough and N. S. Schneider, *J. Macromol. Sci., Pt. B2*, **4,** 553, 641 (1968).

## 18

# MOLECULAR WEIGHT DISTRIBUTIONS BY TURBIDIMETRIC TITRATION

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# I Introduction

## A FRACTIONATION AND TURBIDIMETRY

A rapid and reliable method for the determination of molecular weight distributions has long been the goal of polymer chemists for a number of reasons. In the field of reaction kinetics, the choice between rival mechanisms may be made by examination of the chain length distribution (Cotton and Schneider, 1963; Flory, 1953). Thermodynamic parameters which are based on the chemical potentials of polymer species, as in the case of phase relationships, require that the distribution be known for their proper appreciation (Tompa, 1956). Virial coefficients show a molecular weight dependence which, strictly speaking, should be related to molecular weight distributions rather than some average molecular weight (Casassa, 1960). Similarly, conformational parameters and also certain physical and mechanical properties of polymers depend on distributions (Bawn, 1948), all of which has made the search for easy methods of determining the molecular weight distribution one of high priority. Analytical fractional precipitation by turbidimetric analysis is commonly known by its abbreviated title Turbidimetric Titration, derived from the practice of adding incrementally a nonsolvent or precipitant to a solution of polymer. The method has attracted the attention of many workers because of its relative simplicity and apparent reproducibility. However, opinions on the reliability and usefulness of this method have ranged, over the years, from favourable to the most pessimistic. The lack of any proper theoretical basis has hampered development of the technique in the past but, with more attention now being paid to the scattering theory of large spherical particles (Tabibian *et al.* 1956) and size distributions in polydisperse systems, the situation has shown some improvement. The application of computer programming to Turbidimetric Titrations has not been attempted for routine analyses but, correctly applied, it could do much to remove the tedium from calculations which plague the method where the Mie theory must be applied.

## B EARLY DEVELOPMENT

From its conception (Brönstead, 1938; Morey and Tamblyn, 1945) Turbidimetric Titration seemed to show considerable promise as a useful analytical method of fractionation from which molecular weight distributions could be obtained without the necessity for the usual procedure of evaporating and weighing the dried samples of polymer. It was assumed that, with the addition of each increment of precipitant to a solution of polymer, molecules within a narrow range of molecular weight would precipitate leaving all molecules of lower molecular weight in solution. It was further assumed that the increase in turbidity occasioned by the precipitation of these molecules was related in a simple way to the mass of polymer precipitating. A plot of turbidity against the volume of precipitant added would then yield a curve closely related to the solubility distribution. The first assumption is not in accord with the theory of phase relationships and the second completely ignores the effects due to change in size of precipitated particles on the scattering pattern and to changes in the swelling volume. At best, only qualitative changes in molecular weight distribution were observed in the early work or the presence of different species in a mixture detected (Campbell *et al.* 1954; Harris and Miller, 1951; Morey and Tamblyn, 1945; Morey *et al.* 1951; Oth, 1949; Oth and Desreux, 1951). An exact measurement of the amount of polymer present would seem to be very difficult indeed, despite the successful application of the Mie theory to the scattering of light from colloidal spheres by a number of workers (Heller and Pangonis, 1957; Tabibian *et al.* 1956).

An early attempt to examine the kind of particulate phase resulting from the slow addition of a non-solvent to a solution of polymer under isothermal conditions was made by Hastings and Peaker (1959), who examined the system polystyrene in benzene precipitated by dry methanol. In the early stages of the precipitation (less than 5 per cent precipitated), the average particle size appeared to be small and the scattering pattern close to that for spherical particles with the ratio of diameter to wavelength, $D/\lambda$, equal to 0·44. As the titration progressed, the dissymmetry measured over the angular range 40 to 140° showed an increase in magnitude, and the plot of dissymmetry versus angle of scatter showed a decrease towards the forward angle. In an attempt to explain this apparently anomalous behaviour, the precipitated polymer was examined in the electron microscope, where large linear aggregates as well as spherical particles were found. Obviously, this would make any quantitative evaluation impossible. Recently, Beattie (1965) has questioned this interpretation of the decrease in dissymmetry at low angles and has shown that the dissymmetry, calculated on the basis of a simple distribution having a range of $D/\lambda$ from 1·9 to 2·3, actually has the same general shape as the curve of Hastings and Peaker. It seems feasible, on this basis, that the observed aggregation might have occurred during the preparation of the specimen.

Certain assumptions are inherent in the method. These are that: (a) Fractionation is according to polymer solubilities, under conditions approaching equilibrium, at every stage of the titration. (b) The particulate phase is in the form of spherical liquid particles, the spherical shape being a consequence of the requirement of minimum surface energy at the interface. (c) Particle size or distribution of sizes remains sensibly constant during the titration unless aggregation is deliberately encouraged. (d) Providing the solvent–precipitant system is isorefractive, the refractive index of the particle is proportional to the volume fraction of polymer. Implicit in this, is the assumption that the particle refractive index increment is independent of both concentration and molecular weight. (e) The weight of polymer precipitating at each stage of the titration is directly calculable or can be obtained by resort to empirical relationships. Apart from (d) these assumptions are unlikely to be strictly valid although (a) and (b) are probably good approximations when the appropriate solvent/non-solvent system is chosen. The validity of (c) and (e) will be discussed in detail later in this chapter.

### C APPLICATION AND SCOPE OF THE METHOD

Until recently Turbidimetric Titration (T.T.) has been used almost exclusively as a qualitative method of characterization (Allen *et al.* 1956; Bishoff and Desreux, 1951; Dunn *et al.* 1954; Melville and Stead, 1952). Solubility relationships were investigated and empirical equations relating the point of precipitation to the concentration of polymer and molecular weight were described (Hengstenburg, 1956). Various ways of presenting the distribution using well known as well as empirical distribution functions have been employed. A number of polymers of widely different characteristics have been examined and, in the case of polystyrene, several different solvent-precipitant systems have been employed in these investigations (cf. Table 1). This table

**Table 1**

Molecular weight distributions by turbidimetric titration

| Method of representing data | Polymer | Solvent/Precipitant system | | Authors |
|---|---|---|---|---|
| Graphical nomograms DWD. | Cellulose Acetobutyrate | Acetone/Ethanol + Water | IP | Morey and Tamblyn (1945) |
| M.T. DWD. exponential functions | Polymethyl methacrylate | Acetone/Water | IP | Harris and Miller (1951) |
| M.T. DWD. | Polyvinyl acetate | Acetone/Water | IP | Morey *et al.* (1951) |
| M.T. DWD. | Polystyrene | Butanone/Acetone | IP | Hengstenburg (1956) |
| Claesson Grid. modified. DWD. | Polystyrene | Benzene/Methanol | IP | Gooberman (1959) |
| Claesson Grid. DWD. | Polystyrene | Toluene/Methanol | IP | Mathieson (1960) |
| Graphical differentiation. DWD. | Polystyrene | Butanone/iso-propanol | IP | Urwin *et al.* (1964) |
| Absolute method. Cumulative sol. dist. | Polystyrene | Butanone/iso-propanol | IP | Beattie (1965) |
| M.T. Claesson Grid. Wesslau function. | Polyvinyl pyrrolidone | Water/$Na_2SO_4$ | IP | Scholtan (1957) |
| M.T. DWD. | Polyvinyl pyrrolidone | Water/$Na_2SO_4$ | IP | Campbell *et al.* (1954) |
| Method of slopes. Width of dist. Wesslau function. | Polyethylene | Chloronaphthalene and 30% dimethyl-phthalate | TGP | Taylor and Tung (1962) |
| Probability graph Log normal dist. | Polypropylene | Tetralin/Butyl-cellosolve | IP | Tanaka *et al.* (1965) |
| Curve fitting. Tung exponential function | Nylon 66 | *m*-Cresol/cyclohexane hexane | IP | Howard (1963) |
| Method of slopes. Width of dist. | Ethylene-co-propylene | Heptane/n-propanol | TGP | Gamble *et al.* (1965) |

M.T. Based on the method of Morey and Tamblyn. IP Isothermal Precipitation. DWD. Differential weight distribution curves. TGP Thermal Gradient Precipitation.

contains published studies to date for handy reference and shows the methods employed, both practically and in displaying the molecular weight distribution. It can be seen that the number of polymers investigated is quite small. However, polymers made under different conditions have been compared by examining their individual T.T. curves and changes in the breadth of distribution were found to be easily recognized by inspection (Gooberman, 1959). Unimodal or bimodal distributions could be distinguished at a glance, provided of course, that the average molecular weight was sufficiently different (Cotton and Schneider, 1963). Examination of the products from block and graft copolymer synthesis by T.T. clearly showed the presence of homopolymer as well as the copolymer where this occurred (Molyneux, 1960; Shen and Eirich, 1961). As a rapid and simple method of demonstrating the existence of extraneous polymer species in a product, the efficacy of T.T. has been amply demonstrated (Elias and Gruber, 1964) and it has long been recognized as a useful tool in the selection of solvent-precipitant systems for conventional fractional precipitation.

The application of T.T. to the quantitative determination of molecular weight distribution has not been so encouraging. In view of the difficulty of devising convincing tests of accuracy for molecular weight distributions (Channen, 1959) all attempts to date must properly be regarded with caution and the best of them must be considered as only reasonable approximations of the distributions. The so-called "absolute" method (Beattie and Jung, 1968; Meehan and Beattie, 1961) seems to offer the best chance of success to date, or at any rate, as has already been observed, the attempt to place T.T. calculations on a proper theoretical basis is commendable (Kratohvil, 1964).

The use of T.T. for purposes other than molecular weight distributions is an interesting departure from the accepted role. The determination of theta conditions is a perennial problem in the study of solution properties and the need for a simple rapid method for establishing theta temperatures in single solvents has long been recognized. Cornet and Ballegooijen (1966) have used T.T. for this purpose, basing their approach to establishing theta compositions in mixed solvents on the method of Elias (1959). Theta compositions are obtained by isothermal addition of precipitant until phase separation is first observed. A plot of the volume fraction of non-solvent against the logarithm of the corresponding volume fraction of polymer extrapolated to pure polymer gives the theta composition. Cooling of a solution until phase separation occurs has been employed to determine the theta temperature. A plot of the reciprocal of the temperature at incipient turbidity against volume fraction of polymer, extrapolated to pure polymer, yields the theta temperature. The method of Cornet and Ballegooijen differs from that of Elias only in that the extrapolation is extended to pure polymer, rather than the arbitrary unit concentration employed by the latter.

The determination of polymer solubility parameters ($\delta_3$) by application of turbidimetric titrations (Suh and Clark, 1967) has further extended the usefulness of the method. The technique is a valuable adjunct to the swelling and viscosity techniques. Two non-solvents are chosen such that one has a higher solubility parameter ($\delta_2$) than the other. Titration of a series of solvents of different $\delta_1$ value yields the volume fraction of non-solvent necessary to produce a standard turbidity and hence the $\delta_m$ of mixing. The solubility parameter of the polymer is obtained by plotting $\delta_m$ for a number of solvents and each particular non-solvent, taking the mid-points between the two and intersecting with the line of $\delta_3 = \delta_1$ plotted on the same graph.

### D RECENT DEVELOPMENTS

During the last few years a new approach has been proposed (Beattie, 1965; and Jung, 1968; Meehan and Beattie, 1961), which attempts to place T.T. on a quantitative basis. This method uses the technique that eliminates the continuous or incremental titration and replaces it with a sequential method similar to that used by Howard (1963). A series of precipitations containing progressively greater amounts of precipitant is allowed to reach maximum turbidity, at which point the turbidity is readily calculated, in principle at least. At the maximum, the weight of polymer precipitated is determined for a known solvent-precipitant ratio. The solubility distribution is then readily constructed and, if the relationship between molecular weight and solubility is also known, the molecular weight distribution can be obtained without resort to empirical methods. The "absolute" method must therefore be seen as an important contribution to the evolution of the turbidimetric titration technique.

## II Phase Separation

### A THEORY OF SEPARATION

The primary objective in T.T. is identical with all other fractional precipitation methods, namely to sort out the polymer species according to their chain lengths (Schneider, 1965). The precipitation process must properly be regarded as a separation into two liquid phases, the one rich in polymer being referred to as the precipitate. An ideally sharp separation is one in which all polymer below a certain mole weight is in one of the fractions and all the rest in the other. Phase relationships however, show just how far the actual separation by two phase equilibrium is from the ideal one. A detailed discussion of phase relationships would be out of place in this chapter but an understanding of the broad principles is essential to good fractionation practice.

The basis for discussion of the separation by fractional precipitation is the well known equation, derived from consideration of the chemical potentials of polymer and solvent in two phase equilibrium

$$\ln(\phi'_x/\phi_x) = \sigma_e x \qquad (1)$$

where $\phi$ is the volume fraction of the species $x$ in the solution the prime representing the particulate phase, and $x$ is actually the ratio of the molar volumes of polymer and solvent, but may be taken to be the number average degree of polymerization. The quantity $\sigma_e$ may be considered, on the basis of simple energetics, to represent the gain in energy when polymer is transferred from one phase to another. Equation (1) shows that every species of the polymer is more soluble in the precipitate or concentrated phase and that the ratio ($\phi'_x/\phi_x$) increases exponentially with $x$. To improve this rather inefficient separation, the dilute phase must be made large relative to the concentrated phase. The larger partition factor for the longer molecules is the reason that the higher mole weight species are selectively transferred to the concentrated phase despite the relatively small volume.

## B METHOD OF SEPARATION

Two methods of fractional precipitation are employed in T.T. Either (i) a non-solvent is added slowly to a solution of the polymer under isothermal conditions or (ii) a solution in a poor solvent, just above the precipitation threshold, is allowed to cool over a convenient temperature range. If a single solvent is employed in the latter method, the phase relationships are relatively simple. However, in general, the mixed solvent is the rule and the familiar triangular phase diagram is necessary to describe the behaviour of the system. The hyperbola shaped spinodial divides the stable and meta-stable regions from the unstable. The tie lines show that, except at the critical point, two phases appear when the temperature is lowered or the solvent/non-solvent composition is made sufficiently poor for the solution to support the polymer. One phase contains a considerable proportion of polymer with varying amounts of solvent and non-solvent such that this phase is a swollen polymer and the other phase is practically pure liquid (Tompa, 1956). The solvent composition of the two phases is therefore very different. In both cases, aggregation will take place ultimately, although properly adjusted stirring may delay the process for some time.

The most widely used technique in T.T. is the isothermal addition of a non-solvent to a well stirred and very dilute solution of polymer. The addition of non-solvent is made by incremental or continuous addition from a pipette injection device into specially constructed cells. If the rate of addition of precipitant is too fast, the conditions under which phase separation takes place will be far removed from equilibrium, with deleterious effects on the fractionation. In the alternative method, a solvent/non-solvent mixture with a theta point at a convenient temperature is chosen, so as to precipitate the whole range of molecular species over a preferably narrow span of temperature (Channen, 1959; Cornet and Ballegooijen, 1966).

### C AGGREGATION AND SWELLING

After a sufficient lapse of time, the particulate phase will, in all cases, aggregate to form a uniform whole. Aggregation is always fully established in normal fractionation procedures but is not encouraged in T.T., where adequate stirring is generally employed to keep the precipitate suspended. Too rapid stirring can often have the opposite effect and then aggregation is enhanced. Generally, it is necessary to establish that aggregation of particles has been negligible during the time of measurement (Kratohvil, 1964), although in the "absolute" method, aggregation to particular particle size is encouraged (Beattie, 1965; Beattie and Jung, 1968).

It must be remembered that the particulate phase is a swollen polymer and that during the course of the titration, there will be a change in the degree of swelling as the non-solvent/solvent ratio is changed. At first, the volume of the precipitate increases on adding non-solvent but reaches a maximum and finally there is a decrease in the swelling volume as non-solvent content increases. On the other hand, the basis of the turbidimetric technique is the assumption that the degree of swelling in a given solvent/non-solvent mixture is independent of the molecular weight (Boyer, 1952; Krozer *et al.* 1960; Schulz, 1937). Accepting this as demonstrated, we can determine its dependence on the solvent/non-solvent ratio once and for all and make use of the derived relationship to calculate the amount of polymer in the precipitate.

## III Turbidity and Scattering Theory

### A CHOICE OF THEORY

Three theories have relevance to the discussion of light scattering in disperse systems (Heller and Pangonis, 1957; Tabibian *et al.* 1956). The choice is limited to the region in which a particular theory is applicable. This region is clearly defined by the limitations imposed on two parameters, (i) the size parameter $\alpha_s = (2\pi a)/\lambda$ where "$a$" is a dimension of the order of the size of the particle and $\lambda$ the wavelength in the medium, and (ii) the relative refractive index $\tilde{n}_r = \tilde{n}_2/\tilde{n}_1$ where $\tilde{n}_2$ and $\tilde{n}_1$ are the refractive indices of particle and supporting medium respectively. As a general rule, only the theory as applied to the particular case of isotropic non-absorbing spheres is considered in discussions of turbidity and scattering theory, consequently the energy removed from the incident beam is equal to the total scattered.

### B RAYLEIGH SCATTERING

This is the simplest of the theories and applies to the case where the particles are small compared to the wavelength (Heller and Pangonis, 1957). The particles may have any practically conceivable $\tilde{n}_r$ provided $\alpha_s$ is small. For light in the visible region $\alpha_s \leqslant 0{\cdot}4$, which limits the usefulness of Rayleigh scattering to a very small fraction of the colloidal range. The familiar polar diagram of scattered intensity, often referred to as *the* Rayleigh scattering diagram, is applicable only to the particular case of isotropic spheres irradiated by incident natural light.

The introduction of the limitation in size of the particle simplifies the problem to the extent that the particle may be treated as an oscillating dipole in a homogeneous field. The electric polarization thereby modifying the particle's own field. The extent of polarization is determined by the orientation of the applied field with respect to the oscillating particle. The oscillating dipole radiates in all directions, but the angular distribution of the scattered intensity for isotropic particles is illustrated by the polar diagram for incident unpolarized light where, at the angle of observation $\theta = 90°$, the light scattered is completely polarized. The scattered intensity $i$ for incident natural light of intensity $i_0$ is given by the formula

$$i = \frac{(1+\cos^2\theta)8\pi^4|\alpha'|^2}{r^2\lambda_0^4} i_0 \tag{2}$$

where $\lambda_0$ is the wavelength of light *in vacuo*; $r$ is the photometric distance, that is, the distance from the particle to the point of observation, such that $r \gg \lambda_0$ and $\alpha'$ is the polarizability of the particle. The Lorenz formula for spheres with radius $a$, volume $V$ is

$$\alpha' = \frac{3(\tilde{n}_r^2-1)}{4\pi(\tilde{n}_r^2+2)} V = \frac{\tilde{n}_r^2-1}{\tilde{n}_r^2+2} a^3 \tag{3}$$

independent of direction. The special cases where $\tilde{n}_r$ is very large or close to unity are treated in Van der Hulst's book (1957). The use of the Rayleigh equation outside the range of practical validity has been discussed by Heller (1965).

### C RAYLEIGH–GANS REGION

For particles which cannot be considered small, i.e. $\alpha_s > 0{\cdot}4$ for visible light, the previous theory is no longer applicable. However, the limitation of $\tilde{n}_r$ to values approaching unity (in practical terms this means limiting $\tilde{n}_r \leqslant 1{\cdot}05$ and $\alpha_s \leqslant 10$) leads to a relatively simple treatment based on Rayleigh scattering. Strictly the limits are $|\tilde{n}_r - 1| \ll 1$, $2\alpha_s(\tilde{n}_r - 1) \ll 1$ which means that the smaller the relative refractive index the greater the ratio of size to wavelength. This approach was developed by Rayleigh in 1911 and independently by Gans in 1925 (Heller and Pangonis, 1957). A further restriction in the Rayleigh–Gans theory is that the phase shift is small (Van der Hulst, 1957). Thus the applied field does not differ appreciably from the original and the scattered radiation is unaffected by the other volume elements present. Each volume element behaves as a Rayleigh scatterer independently of the others, but the scattered waves in a given direction interfere because of the different positions in space. Polarization therefore remains exactly the same as for Rayleigh scattering. The scattering at $\theta = 90°$ for natural incident light is still completely polarized. The intensity of scattered light is then the same as for Rayleigh scattering multiplied by a factor which depends on the shape of the particle.

The Rayleigh ratio or reduced intensity for unpolarized light at the angle $\theta$ is found according to the formula for a suspension of spherical particles (Van der Hulst, 1957)

$$R_{\theta u} = \frac{2n\pi^2V^2}{\lambda_0^4}(\tilde{n}_r - 1)^2 P(\theta)(1 + \cos^2\theta) \tag{4}$$

where the particle scattering factor $P(\theta)$ is calculated from the following equation

$$P(\theta) = [3/X^3(\sin X - \cos X)]^2 \tag{5}$$

where

$$X = \frac{4\pi a}{\lambda_0}\sin(\theta/2) \tag{6}$$

Numerical values of the particle scattering factor may be found in many texts. In eqn. (4), $n$ refers to the number of particles per ml of particulate phase. It has been shown that the upper limit of the size parameter may be usefully extended by employing vertically polarized light. The resulting formula (Beattie and Jung, 1968) is:

$$R_{\theta v} = \frac{4n\pi^2V^2(\tilde{n}_r - 1)^2}{\lambda_0^4}P(\theta) \tag{7}$$

## D MIE THEORY

The treatment of scattering without restriction of $\tilde{n}_r$ or $\alpha_s$ is due to Mie's work in 1908 (Van der Hulst, 1957). Based on the classical electro-magnetic theory the scattering particle is considered as an assembly of interdependent dipoles. In contradistinction to the other two theories, excitation depends not only on the primary field but on the total field as affected by other dipoles in the same assembly. With increasing $\alpha_s$ the multipolar contributions, both electric and magnetic, make the computations very laborious. However, electronic computation has made available data over a wide range of the parameters (Tabibian, 1956). Some simplifications have been attempted but with a corresponding loss of accuracy. The Mie equations reduce to the simple Rayleigh equation when $\alpha_s$ is small (Heller and Pangonis, 1957), since then, only the electric dipole need be considered. Similarly, when $\tilde{n}_r$ approximates to unity the Mie equations closely approximate to the Rayleigh-Gans equations.

The scattering of a single particle may be expressed in the form

$$J_{\perp} = (\lambda_0^2/4\pi^2r^2)i_{\perp} \tag{8}$$

$$J_{\parallel} = (\lambda_0^2/4\pi^2r^2\ i_{\parallel} \tag{9}$$

$J_\perp$ and $J_\parallel$ are the total intensities scattered by a single sphere in a direction defined by the angle of observation when the incident wave is of unit intensity and plane polarized with the electric vector vibrating perpendicularly ($\perp$) or vertically ($\parallel$) in the plane of observation. The Mie scattering functions $i$ are complex functions pf $\tilde{n}_r$, $\alpha_s$ and $\theta$. These intensity functions $i_\perp$ and $i_\parallel$ are expressed in terms of infinite series (Gucker and Egan, 1961)

$$i_\perp = |\sum_{n=1}^{\infty} a_n \Pi_n(\cos\theta) + b_n T_n(\cos\theta)|^2 \tag{10}$$

$$i_\parallel = |\sum_{n=1} a_n T_n(\cos\theta) + b_n \Pi_n(\cos\theta)|^2 \tag{11}$$

where the augmented angular functions, $\Pi_n$ and $T_n$ are formed from the first and second derivatives of argument $\cos\theta$. $a_n$ and $b_n$ are amplitude functions derived from Riccarti–Bessel functions of arguments $\alpha_s$ and $\tilde{n}_r\alpha_s$. Computations of $i_\perp$ and $i_\parallel$ are laborious but tabulated values are, nevertheless, available for a wide range of the parameters. The total light scattered by one sphere can be obtained by integrating both $J_\perp$ and $J_\parallel$ over the surface of a sphere of unit radius and halving the sum. Division of the total scattering by the geometrical cross section of the sphere $\pi r_s^2$ where $r_s$ is the radius of the scattering sphere, yields the scattering coefficient $K_s$. In terms of the Mie theory, eqn. (7) becomes

per limit
shifted

$$R_{\theta v} = \frac{n\lambda_0^2}{4\pi^2} i_\perp \tag{12}$$

Plots of the scattering coefficient against $X$ for particular values of $\tilde{n}_r$ are instructive. $K_s$ increases at first with increasing $\tilde{n}_r$ but reaches a maximum at some value of $\alpha_s$. The larger the value of $\tilde{n}_r$ the sooner the maximum appears. It turns out that $K_s$ is an oscillating function with a series of maxima and minima which eventually coalesce until $K_s$ becomes independent of $n_r$ at large values of $\alpha_s$. Determination of the number of maxima and the angles at which they appear forms the basis of one method of particle size determination.

## E TURBIDITY AT THE FIRST MAXIMUM

Calculation of the amount of polymer precipitating from T.T. data is a formidable task since the continuously changing size distribution is unknown. The use of the approximate Rayleigh–Gans theory with corrections based on dissymmetry can only be considered as a rough approximation at best because the calculation requires the knowledge of the size distribution and an accurate measurement of $\tilde{n}_r$ at every stage of the titration.

It has been proposed recently (Beattie, 1965) that the precipitate should be allowed to grow up to the first maximum in the turbidity where, as Meehan and Beattie (1961) have shown, the ratio $K_s/\alpha_s$ is almost constant with respect to $\alpha_s$. Consequently if the distribution of particle sizes is narrow or the breadth of the distribution can be determined from a curve fitting procedure using known distributions (Beattie and Jung, 1968), the turbidity becomes directly proportional to concentration. For the purpose of turbidimetric titration, it is more convenient to plot $K_s/\zeta$ for various values of $\tilde{n}_r$ against $\zeta = 2\alpha_s(\tilde{n}_r - 1)$. The quantity $K_s/\zeta$ is observed to increase from zero to a maximum at $\zeta \cong 3$, and then to fall and oscillate about a slowly decreasing value. The advantage of using $K_s/\zeta$ against $\zeta$ curves over plots of $K_s/\alpha_s$ against $\alpha_s$ is that the former have only a small dependence on $\tilde{n}_r$ in the region of the maximum.

## IV Solubility–Molecular Weight Relationships

### A Molecular Weight–Concentration Function

Solubility relationships have been established in a number of polymer/solvent/precipitant systems using Isothermal Precipitation (I.P.) or Thermal Gradient Precipitation (T.G.P.) as shown in Table 1. To demonstrate the general method employed, an example from the author's own work on polystyrene has been chosen (Urwin *et al.* 1964). In the example chosen, the molecular weight of polymer precipitating at any moment is assumed to depend on (i) the saturation composition of the solution appropriate to that molecular weight. However, the saturation value will depend in some way on the initial concentration of the solution $C_0$. The molecular weight precipitating will also depend on (ii) the particular stage of the titration; this may be represented by the volume fraction† of non-solvent in the mixture, $\gamma$, where

$$\gamma = V/(V_0 + V) \tag{13}$$

and $V$ and $V_0$ denote the volumes of non-solvent and solvent respectively. We have then that the molecular weight precipitating is a function of $C_0$ and $\gamma$,

$$M = M(C_0, \gamma) \tag{14}$$

Evaluation of the saturation concentration at every stage of the precipitation is difficult to achieve with any degree of accuracy and therefore the choice of the initial concentration seems more convenient. A problem immediately arises when a point on the titration curve must be selected to represent the saturation point corresponding to a given molecular weight. Some authors have arbitrarily chosen the initial onset of precipitation but this weights the value too far towards the high molecular weight region. The point at which 50 per cent of the polymer has been precipitated, $\gamma_p$, is probably a

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† There is a rather confusing diversity of notation in the literature for the solvent/non-solvent composition under different conditions. The following are utilized systematically in the text here:

$\gamma$ when the selection of the precipitation point is unspecified.
$\gamma_p$ when the mid-point of the curve is used
$\gamma^*$ when onset of turbidity is employed
$\gamma'$ when 1 per cent of maximum turbidity is developed.

better choice although it must be admitted that this does not correspond to any of the usually measured averages.

### B SOLUBILITY–CONCENTRATION DEPENDENCE

The next step is to examine a number of samples of the polymer, preferably narrow fractions, over a range of concentrations for a particular molecular weight. Since the advent of anionic polymerization, narrow distribution polymers may be synthesized for the specific purpose and whole polymer used for the calibration. The polymers are precipitated from a range of initial concentrations all with a given molecular weight. Satisfactory linear relationships of the form

$$\log C_0 = a - b\gamma_p \tag{15}$$

**Table 2**

Solubility relationships for Polystyrene in various systems
(Equations are mainly in the form in which they appear in the papers quoted. Several of the symbols are referred to in the text, but the reader should consult the original references for a more detailed explanation.)

| Authors | Solubility equations and experimental constants | Solvent/ precipitant system |
|---|---|---|
| Hengstenberg (1956) | $\gamma = \gamma_\infty + \beta/M^{0\cdot5}$<br>$\log M = a - b\gamma$ | Butanone/ Acetone+ water |
| Gooberman (1959) | $\gamma^* = \mu - K\log(c^*/c_0)$<br>$K_{(\theta_n=0\cdot5)} \equiv \bar{M}_w$<br>$K = 12\cdot9\bar{M}_w^{-0\cdot565}$<br>$c_0 = 2\cdot4\times10^3$<br>$\mu = 0\cdot2306$ | Benzene/ Methanol |
| Mathieson (1960) | $(v_2)_0^i = 0\cdot210 - k\log c^i$<br>$\log c^i/c^i_{(v_2)_0} = -3\cdot3\log\left\{\frac{1\cdot23v_2}{(v_2)_{\frac{1}{2}}}\right\}$<br>$(v_2)_0^i = 0\cdot210 - (0\cdot147 + 0\cdot0230\log 1/M^i)\log C^i$ | Toluene/ Methanol |
| Urwin *et al.* (1964) | $\log c_0 = a - b\gamma_p$<br>$\gamma_p = X + \gamma\bar{M}_n^{0\cdot5}$<br>$\gamma_p = 0\cdot108 + \frac{(218\cdot13 - 57\cdot85\log[c_0 \,.\, 10^5])}{\bar{M}_n^{0\cdot5}}$ | Butanone/ Isopropanol |
| Elias and Gruber (1964) | $\log\phi = \phi_{\text{crit}} - K_1\log c_p$<br>$\phi_{\text{crit}} = K_2 + K_1\log\bar{M}_n$<br>$\log K_1 = K_4 - a\log M_{\text{tr}}$<br>$M_{\text{tr}} = \frac{1}{2}(\bar{M}_w + \bar{M}_z)$<br>$K_2 = 44\cdot1$ vol %<br>$K_3 = -1\cdot8$<br>$K_4 = -0\cdot44$<br>$a = 0\cdot250$ | Benzene/ Isopropanol |

have been found for the example taken (Urwin *et al.* 1964) where $a$ and $b$ are constants which can be obtained directly from the graphs of log $c$ against $\gamma$. Scholtan (1957) has employed $\gamma = \gamma_0 + a \log c$ for polyvinyl pyrrolidone precipitated from aqueous solutions by sodium sulphate. Elias and Gruber (1964) have used $\log \phi = \log \phi_{\text{crit.}} - K_1 \log c_p$ for polyisoprene in benzene precipitated by isopropanol. Mathieson (1960) adopted the relation $(v_2)^i_0 = \text{const.} - k \log c_i$ for polystyrene in toluene with methanol as precipitant whilst Gooberman (1959) used $\gamma^* = \mu - K \log (c^*/c_0)$ for almost the same system (note that in this case $c_0$ simply denotes a constant). In Table 2 are shown the solubility relationships for polystyrene in several systems employed by the various authors who have studied this polymer. The reader should refer to the original papers for a detailed explanation of the symbols used in these relationships. The experimental constants for the several systems are given where these have been published. Allowing for the differences in defining the precipitation point, concentrations and expressing the molecular weight, there is a fair measure of agreement at least on the form the relationship $\gamma = \gamma(c)$ should take if not on the constants found.

### C SOLUBILITY–MOLECULAR WEIGHT DEPENDENCE

Finally, it is necessary to find a relationship between $\gamma$ and the molecular weight. Mathieson (1960) reports that a number of polymers conform to the equation

$$\gamma^* = k \log c + f(M) \tag{16}$$

where $\gamma^*$ is the volume fraction at the initial precipitation point and $c$ the concentration of polymer remaining unprecipitated at any point during titration. However, $\gamma^*$ is linear in $\log f(M)$ for polymethyl methacrylate but, whereas $\gamma^*$ is linear in $\log f(M)$ for small values of $M$ in the case of polyvinyl pyrrolidone, it is more nearly proportional to $1/M$ for a large range of molecular weight. On the other hand, Scholtan (1957), in a very detailed study, finds proportionality to $1/M^{0 \cdot 8}$ for the same system. For polystyrene in the system butanone–isopropanol, Urwin *et al.* (1964) find the relation

$$\gamma_p = X + YM^{-\frac{1}{2}} \tag{17}$$

to give a good fit. Plots of $\gamma_p$ against $M^{-\frac{1}{2}}$ for various values of log $c_0$ are shown in Fig. 1. $X$ is the intercept and the value of $Y$ can be determined by plotting the slopes of the various $c_0$ lines against log $c_0$ (see Fig. 2). For this particular system the final equation becomes

$$\gamma_p = 0 \cdot 108 + \left( \frac{218 \cdot 13 - 57 \cdot 85 \log C_0}{M^{\frac{1}{2}}} \right) \tag{18}$$

and thus a knowledge of the stage of the precipitation $\gamma$ and the initial concentration $c_0$ allows the determination of the molecular weight precipitating. When compared with the final form of the relationship of Mathieson, the similarity is striking. It is necessary to establish experimentally the solubility–

molecular weight relationship for each polymer in the particular solvent–precipitant system used. There is no short cut to establishing these relations, however, when this is achieved, it is done, once and for all.

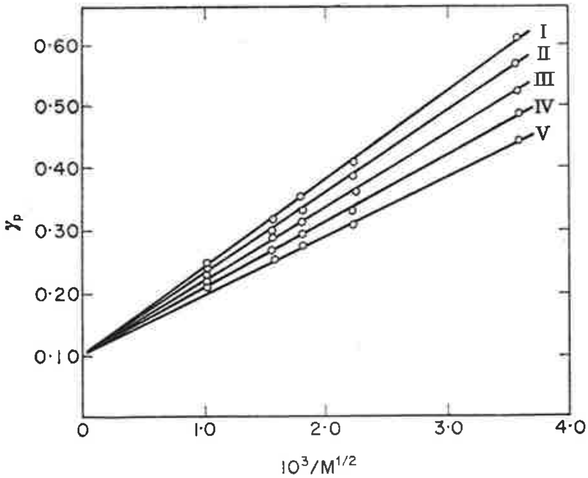

**Figure 1.** Plot of volume fraction of precipitant as a function of molecular weight for the following values of log ($c_0 \cdot 10^5$)I I, 1·4; II, 1·6; III, 1·8; IV, 2·0; V, 2·2. $c_0$ expressed in g/100 ml (Urwin *et al.* (1964)).

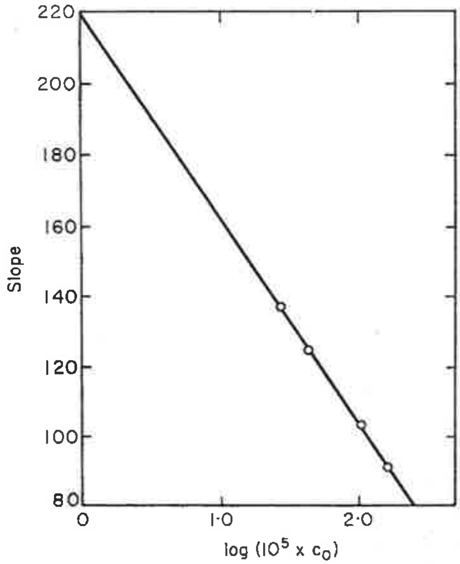

**Figure 2.** Plot of the slopes of lines in Fig. 1 against log ($c_0 \cdot 10^5$) (Urwin *et al.* (1964)).

## V Molecular Weight Distribution from T.T. Data

### A PRESENTATION OF DATA

A polydisperse polymer may be characterized by the integral weight distribution

$$W_r = \sum_{r=0}^{r} w_r$$

where $w_r$ is the weight fraction of "$r$ mer", i.e. polymer of chain length $r$. For continuous distributions the summation is replaced by the integral

$$W_r = \int_0^r w_r \, dr$$

from which the name integral weight distribution is derived. By contrast $w_r$ is generally referred to as the differential weight distribution.

There are a number of ways of presenting and using molecular weight distributions, all of which may be satisfactory under certain circumstances. The simplest approach is to examine and compare, by visual inspection, the integral distribution curves obtained from well characterized, narrow fractions with curves obtained from the polymer under examination. Unimodal and bimodal distributions are easily recognized and by the comparison of the two integral curves, one can state qualitatively whether the breadth of distribution is similar or otherwise. This purely qualitative approach leaves much to be desired, but it can nevertheless, be very useful, particularly for the rapid examination of mixtures of polymers such as is found in block and graft copolymers where homopolymer is often produced along with the main product. The method is sensitive to changes in the distribution and this can often be effectively utilized in kinetic studies.

The log normal distribution is commonly found to fit much fractionation data satisfactorily and exponential functions and other similar functions have been found to fit fractionation data in other instances. Some authors have chosen to start with the assumption that a particular distribution is in fact obeyed. Generally, the information from turbidimetric titration is displayed graphically and often in linear form. For example, the log normal distribution is plotted on probability graph paper and from the graph, the usual averages $\overline{M}_w$ and $\overline{M}_n$ are calculated. The ratio $\overline{M}_w/\overline{M}_n$ is often quoted as a measure of the heterogeneity. Claesson has obtained the differential curve by employing a grid based on solubility curves. An improved version by Gooberman is also worth consideration as a method of obtaining the differential molecular weight distribution. Finally, the integral curve may be differentiated graphically and the averages $\overline{M}_w$ and $\overline{M}_n$ calculated directly.

The reliability of these distribution curves should be tested against full scale fractionation but, because this is a tedious process, it is often neglected.

In this connection, there is a definite advantage in calculating the usual averages, since comparison can be made with values from light scattering and osmometry, thereby providing a valuable and quick check on the method. Whatever technique is employed to display the results, the practical method of obtaining them falls into two categories. (i) Those which require calibration with known samples, i.e. the empirical methods and (ii) the method proposed by Beattie, where it is applicable, which is "absolute" in that no calibration is required.

## B EMPIRICAL METHODS

In their search for a simpler or more rapid method of obtaining the chain length distribution function Morey and Tamblyn (1945) first determined the solubility law which relates the point of solution saturation to molecular weight and concentration of a dissolved polymer. They then proceeded to show that the molecular weight distribution, in a heterogeneous sample, could be obtained by a suitable operation on a curve relating the mass of polymer precipitated to the amount of precipitant added. The fraction of polymer precipitated was measured by the intensity of light scattered from the suspended polymer. The original method of Morey and Tamblyn was, in fact, based on the observation that the curve of turbidity against percentage precipitant added, closely resembles the cumulative weight distribution curve. The development of turbidity was followed either with the drop in transmission or with an increase in the scattering at right angles the photocell output being recorded on a galvanometer type recorder. The trace yielded a curve relating the intensity of transmitted or scattered light as a function of the amount of precipitant added.

The specific value of the solvent–precipitant composition $\gamma'$ at which the precipitate appears was found to depend on five factors (i) the molecular weights $M_i$ present in solution (ii) the concentration of each species of molecular weight in solution $c_i$ at the time of precipitation (iii) the type of polymer (iv) the temperature of the system and (v) the solvent–precipitant system used. Experimentally, the last three are controlled so that we may simply write $\gamma' = f(M,c)$ at saturation. This function has to be determined by employing homogeneous fractions of known molecular weight at known concentrations. The effect of concentrations on the saturation limit is then studied using different starting concentrations and noting the percentage of precipitant at which precipitation starts. Since the exact value of saturation and corresponding $\gamma'$ value depend upon the sensitivity of the turbidity measuring device, when this point is defined as the point at which precipitation first appears, it is more convenient to adopt another arbitrary point such as when 1 per cent of maximum turbidity develops.

From the optical data a graph of the function $Z = G(\gamma')$ can be drawn in which $Z$ is the percentage of dissolved polymer precipitated and the corresponding increments of $\Delta Z = G'(\gamma')\Delta\gamma'$ may be read off the graph. It was recognized from the outset that $\Delta Z$ does not correspond to a single molecular weight species but rather contains a distribution around some probable value, just as relatively homogeneous, but never perfect fractions, can be separated from a heterogeneous mixture. Nevertheless, each $\Delta Z$ can be assigned some representative value and it is assumed that all of the $\Delta Z$ is of this single value only.

Supposing that the species $M_i$ is present in an amount such that the solution becomes saturated for this species at a value of $\gamma' = \gamma_i'$, then if $\gamma'$ is increased by $\Delta\gamma'$, a percentage $(\Delta Z)^\gamma$ of the total comes out of solution. In terms of concentrations ($c_i^0$ and $c_T^0$ being the initial concentrations of the species $i$ and of all species respectively), the percentage of the total quantity precipitated becomes:

$$100\left(\frac{c_i^0}{c_T^0}\right) = \frac{(\Delta Z)_i^\gamma}{1-10^{\Delta\gamma/K}\left(\dfrac{100-\gamma_i'}{100-\gamma_i'-\Delta\gamma_i'}\right)} \tag{19}$$

in which the right hand side can be evaluated completely. To do this $\Delta\gamma'$ is kept small and constant at, say, 0·5 and a nomogram is constructed for the denominator of eqn. (19) plotted as ordinate against $\gamma'$ as abscissa with the appropriate value of the constant $K$. The correct value for the ratio $c_i^0/c_T^0$ is read off the nomogram along the vertical line representing the proper $\gamma'$ for the value of $(\Delta Z)^\gamma$. To assign the actual value of the molecular weight $M$, each value of the ratio $c_i^0/c_T^0$ and its corresponding $\gamma'$ value are inserted in the relation

$$\frac{c_i^0}{c_T^0}\left(1-\frac{\gamma'}{100}\right) = \frac{1}{c_T^0}\cdot 10^{\gamma'/D}\cdot 10^{-f(M)/G} \tag{20}$$

In practice, the function $f(M)$ is determined experimentally on fractions of known number average molecular weight and a second nomogram is constructed, based on the saturation law

$$\gamma' = -K\log c^r + f(M)$$

in which $K$ is the same constant as that appearing in eqn. (19). A series of curves for various values of the fraction $c_i^0/c_T^0$ with $M$ as ordinate and $\gamma'$ as abscissa must be constructed and, upon selection of the correct distribution ratio, the intersection with the proper values of $\gamma'$ yields the correct value for $M$. A plot of percentage weight against $M$ over suitable class intervals of say $\Delta M = 10\,000$ forms the required distribution curve. Some modification is required to apply this to polymers other than that investigated by Morey and Tamblyn because the saturation laws may be quite different, cf. Table 2.

These authors found that a mixture of two polymer fractions could be readily identified by this method. The procedure requires cosiderable initial labour but, according to the authors, it is capable of yielding accurate results.

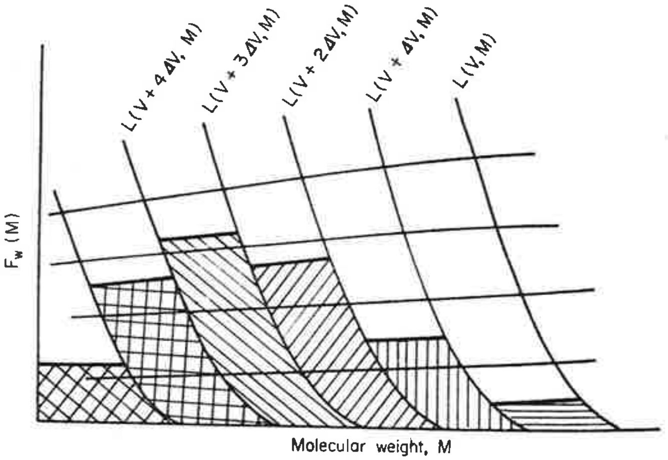

**Figure 3.** Solubility curves of Claesson obtained from an initial calibration (vertical curves). Intersecting lines constructed to give areas of equal polymer weight (Channen, 1959).

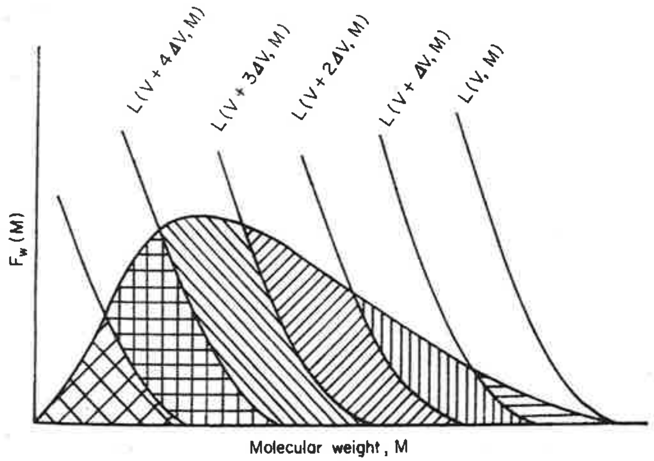

**Figure 4.** Curvilinear histograms representing the distribution of the original polymer constructed from the areas shown in Fig. 3 which represent the weight of polymer in each fraction (Channen, 1959).

An alternative procedure to that proposed by Morey and Tamblyn has been propounded by Claesson (1955). In this method, a histogram is constructed in curvilinear co-ordinates, similar to that shown diagrammatically in Fig. 3. (Channen, 1959). The shaded areas appearing in the figure are proportional to the weights of the various fractions precipitated. According to Claesson, the shaded areas bounded by the solubility frequency curves $L(\alpha,M)$; $L(\alpha_1,M)$; $L(\alpha_2,M)$ etc. or alternatively $L(V,M)$; $L(V+\Delta v,M)$; etc. and the molecular weight frequency distribution $c_0 . F_w(M)$ for an initial concentration of polymer in solution $C_0$ (g/ml) [cf. Fig. 4], represent the distribution of the fractions which are precipitated on decreasing the temperature by $\alpha^\circ$ or by addition of successive volumes of the precipitant $\Delta v$. The function $F_w(M)$ is the normalized weight frequency distribution so that the concentration of molecules in the molecular weight interval $M$ to $M+\mathrm{d}M$ becomes $c_0F_w(M)$ when the initial concentration in solution is $C_0$.

The hatched areas represent the amount of polymer precipitated between any two increments of precipitant, for example $\Delta A_2 = A(V+2\Delta v)-A(V+\Delta v)$ represents the amount of polymer precipitated between the addition of volumes $V+\Delta v$ and $V+2\Delta v$, cf. Fig. 3 where $V$ is the volume of precipitant necessary to induce incipient precipitation. The fraction of polymer precipitated is measured by turbidimetric titration, that is the turbidity is assumed to be a direct measure of the amount precipitated. Experimentally, this procedure is best carried out by constructing lines which enclose areas corresponding to definite values of $\Delta A(\alpha)$ or $\Delta A(v)$, that is areas representing a unit of polymer weight. Such a construction is shown by the horizontal lines in Fig. 3. Normalization is achieved by keeping $c_0$ constant in all experiments. The weights precipitated by each addition of precipitant may then be marked off as shown in Fig. 3. Smooth curves may be drawn through the histogram if desired, thus producing a distribution curve as shown in Fig. 4. The result is based on the somewhat doubtful assumption that the solubility frequency distribution is independent of the molecular weight distribution. This assumption is certainly untrue in concentrated solutions, but at the low concentrations generally used in turbidimetric titrations it may be considered less unreasonable.

The determination of the curves $L(V,M)$ is achieved by dissolving a reasonably narrow fraction of weight average molecular weight $M$ at different total concentrations and determining the volume of precipitant required to precipitate one half of the polymer. The solubility [or value of $L(V,M)$] is one half of the concentration for the pair of values $V+\Delta v_i$ and $M$, that is after addition of the $i$th increment. By a series of such experiments with fractions of different $M$ the whole set of curves $L(V,M)$ is obtainable. Claesson has drawn attention to the fact that the method requires a reasonable separation of multiple distributions if the curves are to be resolved, which means in effect that the solubility curves must be a system of non-intersecting curves. The actual success of the method will depend to a large extent upon the proper choice of a solvent–precipitant system for the particular polymer to be examined.

Gooberman (1959) proposed the use of an improved grid technique, based on Claesson's method. The grid is constructed by plotting the saturation concentration of the polymer as a function of molecular weight at various values of the volume fraction of precipitant $\gamma$. The differential distribution for a polymer sample is found by the Morey and Tamblyn method. The molecular weight for polymer precipitating between two $\gamma$ values, where $\Delta\gamma$ is small, is known from the titration. The differential distribution is then plotted on the graph by trial and error, such that the polymer precipitating between two adjacent saturation curves has the same average molecular weight as that calculated by the first method. The area bounded by the two saturation curves, the distribution curve and the $\overline{M}_w$ axis, is measured and plotted against the corresponding value of the mass precipitating $\Delta m_n$. The process is repeated

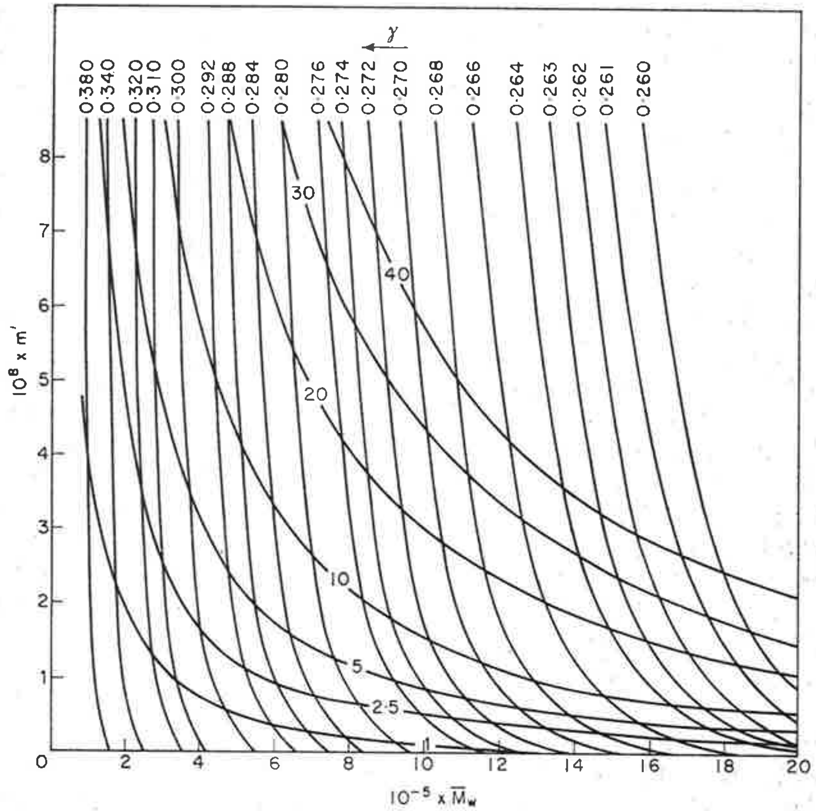

**Figure 5.** Modified Claesson grid: Plots of solubility as a function of molecular weight with $\gamma$ as parameter [the quantity $m'$ is proportional to $c/(1-\gamma)$]. Transverse curves are lines of constant $\Delta m_n/\Delta\gamma$, the indicated values of which refer to an initial polymer concentration of 0.002 per cent (w/v) (Gooberman, 1959).

and the ordinate scale of the differential distribution adjusted until the plot of area *versus* $\Delta m_n$ is linear and passes through the origin. On the basis of the $\Delta m_n$ and area relationship, another set of curves is constructed on the same graph, cf. Fig. 5. With $\Delta m/\Delta \gamma$ as parameter, the area bounded by one of these curves, the $\overline{M}_w$ axis and two saturation curves such that the values of $\gamma$ differ by $\Delta \gamma$, is equal to $\Delta m_n$. The molecular weight distribution for a given sample is derived by choosing two values for $\gamma$ which are close together and which correspond to two of the saturation curves. From the titration data the value corresponding to $\Delta m_n/\Delta \gamma$ is calculated. That section of the $\Delta m_n/\Delta \gamma$ curve lying between the appropriate saturation curves gives one part of the differential distribution. To complete the distribution curve, the process is repeated over the entire titration.

Scholtan (1957), using an empirical approach similar to that described, examined the system aqueous polyvinyl pyrrolidone precipitated by aqueous sodium sulphate. The dependence of the initial precipitation point on concentration and molecular weight was found and the T.T. data converted to the integral molecular weight distribution curve. Scholtan compared curves obtained by the methods of (1) Morey and Tamblyn, (2) Claesson and (3) fractionation with his own method. It is claimed that the Morey and Tamblyn method gives results which are too low, whereas the Claesson method yields values which are too high; that is assuming the normal fractionation procedure to yield the correct results. Gooberman concluded that his modified Claesson grid method yields better results than the Morey Tamblyn technique relative to conventional fractionation.

The representation of the distribution by frequency distribution or cumulative distribution curve is not the only method of displaying the data as has already been stated and perhaps the most instructive device is that which represents the cumulative curve as a straight line, e.g. the probability graph. Whilst several distributions have been suggested as suitable for displaying the data such as the exponential and the binomial distribution, we shall consider only the log-normal distribution

$$W(M) = \left[\frac{1}{\sigma\sqrt{2\pi}} \cdot \frac{1}{M}\right] \exp\left\{-\frac{1}{\sigma^2} \ln^2 (M/M^0)\right\} \tag{21}$$

where $\sigma$ is the standard deviation and $M^0$ the geometric mean molecular weight. The cumulative curve is displayed on the probability graph with a logarithmic abscissa axis. $\overline{M}_w$ and $\overline{M}_n$ may be calculated from the relations:

$$\overline{M}_w = M^0 \exp(\sigma^2/2) \tag{22}$$

$$\overline{M}_n = M^0 \exp(-\sigma^2/2) \tag{23}$$

Once the graph is constructed on the probability grid, the mean molecular weight is read off from the 50 per cent point on the cumulative curve and the standard deviation calculated from the difference between the mid-point and the 16 or 84 per cent values.

Generally the ratio $\overline{M}_w/\overline{M}_n$ is obtained as a measure of the heterogeneity. Actually, the value $U = \overline{M}_w/\overline{M}_n - 1$ is the measure of the polydispersity derived from the squared coefficient of variation which shows that $U$† is not an absolute measure of polydispersity but is relative to the average molecular weight (Herdan, 1960). Figure 6 shows a probability plot for a series of commercial polypropylenes A, B, and two samples C, D, synthesized using $AlEt_2Cl—TiCl_3$ initiator. Values of the intrinsic viscosity ([$\eta$]) which is a function of $M$ have been plotted on a log scale on the $X$ axis in place of molecular weight. The good linear plots obtained show that the log normal distribution function is obeyed, at least over the range 5–90 per cent of the distribution.

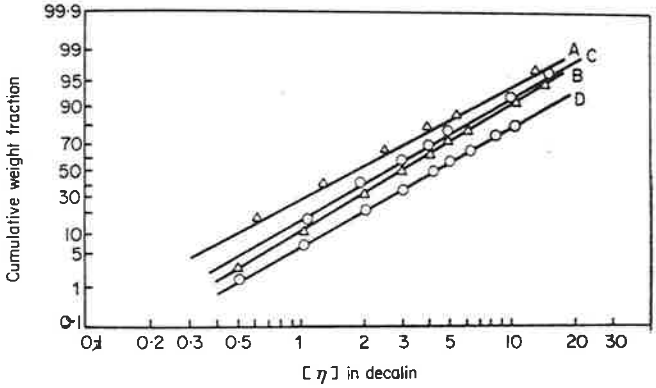

**Figure 6.** Cumulative weight fraction against [$\eta$] plotted on logarithmic probability scale (Tanaka *et al.* 1965).

The classical method of graphical differentiation has also been used on samples of polystyrene in the system butanone/isopropanol. From the weight values and molecular weights calculated from eqn. (18), at equal intervals of $V$, the integral molecular weight distribution curve was constructed. The differential molecular weight distribution was obtained from this curve by graphical differentiation. To calculate the weight mean molecular weight a plot of the product $WM$ against $M$ was constructed. The area which was determined by planimeter, was divided by the area of the $W$ against $M$ curve, to give the weight mean molecular weight.

Recognizing that most distributions will be skewed, the assumption that the mid-point of the precipitation curve corresponds to the weight average

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† [The polydispersity index denoted by $h'$ in Chapter 14 is simply the reciprocal of this quantity U.]

molecular weight is therefore likely to be in error. It was assumed that for moderately skewed curves the relation

$$(\text{mean}-\text{mode}) = 3(\text{mean}-\text{median})$$

holds. The mode is the maximum in the curve and refers to the greatest weight of material having a particular molecular weight. The median corresponds to that point at which one half of the material has molecular weights in excess of that value; that is the area on one side of the median is equal to the area on the other. These points may be found by inspection and the mean calculated.

The number average distribution curve may be constructed first by dividing the curve for the differential weight distribution function $W(M)$ by molecular weight. The number mean molecular weight is then found from the relation

$$M_n = \frac{\int_0^\infty NM \, \mathrm{d}M}{\int_0^\infty N \, \mathrm{d}M} \tag{24}$$

where $N = W(M)/M$ is the differential molecular weight distribution. Values of $M_w$ found by this method were within 10 per cent of the value obtained by viscosity measurements. However, the difficulties involved in estimating the probable error are great and it is not clear just how a rigorous test of accuracy could be devised.

Taylor and Tung (1962) have utilized the change in slope of the turbidity against temperature curve with molecular weight distribution to evaluate the breadth of the distribution ($\beta$) occurring in the Wesslau distribution from a calibration curve of the slope parameter with $\beta$. The Wesslau integral distribution function, I($M$), given by

$$I(M) = \frac{1}{\beta\sqrt{\pi}} \int_{-\infty}^{\ln M} \exp\left[-\frac{1}{\beta^2} \ln^2 (M/M^0)\right] \mathrm{d} \ln M \tag{25}$$

has been found satisfactory in the case of linear polyethylenes, as a method of describing fractionation data and was therefore applied to T.T. data on the same system. $M^0$ is in this case obtained from limiting viscosity and $\beta$ is related to molecular weight averages by

$$\overline{M}_w/\overline{M}_n = \exp(\beta^2/2) \tag{26}$$

and

$$\overline{M}_w = M^0 \exp(\beta^2/4) \tag{27}$$

Knowing $M^0$ and $\beta$ the distribution curve can be constructed. The slope is obtained rather arbitrarily from the points corresponding to 20 and 50 per cent precipitation. Taylor and Graham (1964) have employed a different slope parameter, the slope index S.I., determined by dividing the height of the curve at 120° and 180°C (temperatures were chosen for linear polyethylene) by the total height of the curve. It is claimed by these authors that this device normalizes the effect of molecular weight on turbidity.

### C ABSOLUTE METHOD

All of the methods so far discussed require an empirical calibration. A direct calculation of the amount of polymer precipitating can only be made when the size of the particle, or more correctly the size distribution, is known at each stage of the titration and that the parameter $\tilde{n}_r$ can be determined reliably. Until recently, only the empirical methods appeared to be feasible. An "absolute" method, not requiring calibration, has been proposed (Beattie, 1965) based on the observation that the scattering function $K/\zeta$ is found to be almost constant with respect to $\zeta$ over a small range of $\tilde{n}_r$ at the turbidity first maximum which occurs at $\zeta \cong 3{\cdot}0$ (Meehan and Beattie, 1961).

The relationship between turbidity $\tau = (2{\cdot}3)l \log I_0/i$ and the concentration of precipitated phase $c_p$ takes the form

$$\tau/c_p = [3\pi\tilde{n}_1(\tilde{n}_r-1)/\rho'\lambda_0]\overline{(K_s/\zeta)}_w \tag{28}$$

where $\rho'$ is the density of particles of polymer rich phase, $\overline{(K_s/\zeta)}_w$ is the weight average of $K_s/\zeta$ and the other terms have their usual meaning. Introduction of the Gladstone and Dale mixing rule

$$(\tilde{n}_r-1)\tilde{n}_1 = \Delta\tilde{n}\phi \tag{29}$$

where $\Delta\tilde{n} = \tilde{n}_2-\tilde{n}_1$ and $\phi$ is the volume fraction of polymer in the particulate phase, into eqn. (1) and on substituting $c/\rho = \phi c_p/\rho'$ we have

$$c = \rho\lambda_0\tau/[3\pi\overline{(K_s/\zeta)}_w\Delta\mu] \tag{30}$$

$K_s/\zeta$ is found to be almost independent of $\tilde{n}_r$ in the region $\zeta<5$ which means, in turn, that turbidity is almost independent of $\tilde{n}_r$ and the difficult determination of this quantity is made unnecessary.

Experimentally, a series of precipitations is made using different volume fractions of non-solvent. The usual method of incremental or continuous addition cannot be used here because, at the beginning of the titration, the particles are highly swollen causing $\tilde{n}_r$ to be low, and to attain maximum turbidity the particle size must be large. At the end of the titration the opposite must hold; $\tilde{n}_r$ is high and particles should be small. Obviously, this situation will not occur with the usual titration methods.

The condition $\zeta \cong 3$ may be attained in principle by particle growth and or adjustment of the wave length, although this may not always be experimentally possible. The maximum $\overline{(K_s/\zeta)}_w$ depends on both $\tilde{n}_r$ and the width of the particle size distribution. Narrow distributions will have little effect on the value obtained and, in this case, variations in particle size are not important. In the case of broader distributions, a log normal distribution may be assumed and, by a curve fitting procedure, the breadth of the distribution $\beta$ may be obtained, the maximum in $\overline{(K_s/\zeta)}_w$ is then found corrected to the $\tilde{n}_r$ of the particles. For broad distributions which do not conform to log normal behaviour the method fails. In the case of broad log normal distributions $\tilde{n}_r$ must be calculated and a correction, which is usually less than 10 per cent, must be applied. Approximate volume fractions of polymer may be calculated from weights of precipitated phase, density of pure polymer, estimated density of the mixture of solvent and precipitant in the polymer rich phase and estimated density of the precipitated phase.

Finally, the concentration of precipitated polymer is plotted as a function of the volume fraction of precipitant and the resulting curve is a solubility distribution. The curve may be converted to a molecular weight distribution provided that a relationship between solubility and molecular weight is known. The time to reach maximum turbidity is found to vary with concentration, amount of precipitant added and wave length but not with stirring rates, rate of addition or method of addition. Thus the usual precautions of T.T. are unnecessary using this method.

Beattie and Jung (1968) have examined light scattering at the first maximum as an alternative method to transmittance measurement for T.T. They chose to use vertically polarized light, which has been shown to extend the range of validity of the Rayleigh–Gans theory. The Rayleigh ratio is then given by

$$R_{\theta v} = 4nV^2\pi^2(\tilde{n}_r - 1)^2 P(\theta)/\lambda_0^4 \qquad (31)$$

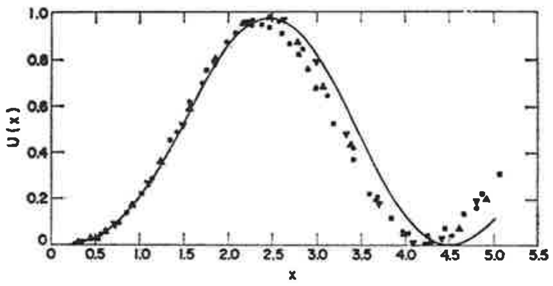

**Figure 7.** Plot of the function U(X) against X. The continuous line calculated for Rayleigh–Gans scattering for $\tilde{n}_r = 1{\cdot}1$. Points calculated from Mie scattering. ■, 30°; ▲, 45°; ●, 90°; ◆, 135° (Beattie and Jung, 1968).

Eliminating $n$ between eqn. (31) and the concentration of the particulate phase $c_p = nV\rho'$ where $\rho'$ is the density of the precipitate, substituting $V = 4\pi a^1/3$ and replacing $c_p/\rho'$ through the volume fraction $\phi$ via the relationship $c/\rho = \phi c_p/\rho'$ where $c$ is the concentration of polymer in gm/ml and $\rho$ the density of pure polymer and finally introducing the Gladstone–Dale mixing rule [eqn. (29)] yields:

$$R_{\theta v}/c = \frac{16\pi^3 a^3(\tilde{n}_r - 1)\Delta\tilde{n}}{3\lambda_0^4 \rho \tilde{n}_1} P(\theta) \qquad (32)$$

Since $P(\theta)$ is a function of $X = 4\pi a/\lambda_0 \sin(\theta/2)$ rather than $\theta$ and since $a/\lambda_0$ is also a function of $X$, the two functions may be combined into a single one for spherical particles

$$U(X) = \frac{X^3 P(\theta)}{4} = \frac{9}{4X^3}(\sin X - X\cos X)^2 \tag{33}$$

A plot of eqn. (33) in the form $U(X)$ against $X$ shows that $U(X)$ has the value zero at $X = 0$ and rises to a maximum at $U(X) = 0{\cdot}974$, cf. Fig. 7. This occurs at $X = 2{\cdot}5$ and it can also be shown that $U(X)$ varies by less than 10 per cent over the range of $X$ from 2·1–2·8. A limited degree of polydispersity will not, therefore, appreciably alter the intensity of scattering. The practically useful equation for the concentration of precipitate becomes

$$c = \frac{2{\cdot}92\sigma}{\Delta\tilde{n}(\tilde{n}_r - 1)}[R_{\vartheta_v}\lambda_0 \sin^3(\theta/2)]_{\max} \tag{34}$$

The condition of the maximum may be attained in either of two ways. (1) The angle of scattering, the wave length or both may be varied until the product $R_{\theta_v}\lambda_0 \sin^3(\theta/2)$ is maximized. This is satisfactory if the particle size is not changing. (2) The intensity of scattering can be measured over a period of time, at a single angle and wavelength, whilst coalescence takes place. Stirring or agitation may be used to speed the process. When scattering is at a maximum the function $U(X)$ is also at a maximum. Calculations on non-spherical particles (prolate and oblate spheroids of revolution) for the function $U(X)$ have shown that there is an insignificant change in shape of the curves with less than 10 per cent decrease in intensity below that for spheres. The accuracy of the Rayleigh–Gans approximation in this region was checked against calculations based on the Mie theory over a range of $\theta$. For values of $\tilde{n}_r$ up to 1·10 the agreement is quite satisfactory, but above this, the value of $U(X)$ must be calculated from Mie theory for the particular value of $\tilde{n}_r$ and $\theta$. The value of $\tilde{n}_r$ may be calculated by using the Gladstone and Dale equation and refractive indices calculated indirectly from measurements of the composition of the precipitated phase in a separate experiment.

The simple relation eqn. (31) can only be used where $\tilde{n}_r$ is small and known. The method may be extended to higher $\tilde{n}_r$ provided the Mie theory is used. The most important advantage offered by this method over the earlier techniques is that a direct relationship between scattering and concentration is established and the solubility distribution can be determined without recourse to calibration. Apart from observing good light scattering practice, making the appropriate corrections for refraction and observing correct instrument calibration procedure, the main difficulty is in the choice of iso-refractive solvent–precipitant systems. However, several lists of iso-refractive pairs have now been collected (see, for example, Chapter 2) and these should be valuable in making a selection. The necessity to use Mie theory under certain conditions makes the method less attractive. Many workers would not consider such a complicated procedure a viable analytical technique.

## VI Experimental

### A INSTRUMENTATION

The basic equipment required for T.T. measurement is either a light scattering instrument or a good spectrophotometer. In either case, some modification to the equipment is necessary to adapt it to Turbidimetric Titration. Due to the larger physical dimensions of the T.T. cell it is more difficult to accommodate than the conventional light scattering cell. Some light scattering instruments and spectrophotometers are more easily converted than others but, generally, any well designed instrument may be used. It is interesting to note in passing that a spectrophotometer has been adapted to light scattering use, with certain advantages such as the use of a prism in place of the filter which is generally employed in light scattering apparatus (Beattie and Gallaway, 1965). As a rule, commercial spectrophotometers do not make any provision for the stopping down of the incident beam which is important in T.T. analysis and therefore some modification would be necessary here too.

The general specifications for good light scattering equipment are described elsewhere in this book and will not be considered in any detail here. Briefly, well designed optics and geometry are essential if the method is to give satisfactory results. However, a well defined narrow incident beam with provision for isolating a particular wave length and polarization is achieved in all the well known commercial light scattering photometers of the present day. Provision for the measurement of transmission (trans) as well as scattered (sca) light in certain instruments allows the measurement of the ratio $i_{sca}/I_{trans}$ simultaneously without the need for further modification and therefore may be the more logical choice. Tanaka *et al.* (1965) used an instrument, designed specifically for T.T. work, which measures light scattered in three directions (45°, 90° and 135°) as well as transmitted light, manufactured by Shimazu Factories Ltd., Japan.†

Several authors have published details of cells for adapting existing photometers as well as equipment designed specifically for T.T. (Beattie, 1965; Gamble *et al.* 1965; Giesekus, 1958; Guzeev *et al.* 1959; Stearne and Urwin, 1962; Taylor and Graham, 1964).

A brief outline of three instruments is given to illustrate the kind of equipment that has been employed. In the author's experience, it would be

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† The Dual Photomultiplier Photometer, model 2000D, Brice Phoenix Instrument Co., Philadelphia, Pa., U.S.A. allows for simultaneous measurement of scattered light at 90° and transmission. Alternatively dissymmetry at 45° and 135° may be measured.

advisable to begin with a suitable light scattering photometer or spectrophotometer. The construction of such equipment requires skills not usually found in, or associated with, most laboratories. The isothermal precipitation turbidimeter of Stearne and Urwin (1962) allows the continuous measurement of scattering at 45°, 90° and 135° together with transmission. The construction is shown diagrammatically in Fig. 8. The light scattered at the three angles falls on the same photomultiplier by means of suitably positioned mirrors and stops. Solenoids open shutters in a sequence so that a six point recorder gives a "continuous" trace for each angle and for transmission. The variation in volume "seen" at each angle was obtained by rotating the goniometer so that the receiver for each angle was placed in the 90° position and a correction factor obtained. In this instrument, the dissymmetry change during titration may be continuously observed. The measured ratio $(i_{90}/I_t)$ where $i_{90}$ and $I_t$ are the light scattered at 90° and transmitted light respectively, is equivalent to $(i^*_{90}/I^*_0)$ where $i^*_{90}$ is the light scattered from the volume illuminated by incident light $I^*_0$ and corrects for attenuation through the turbid solution.

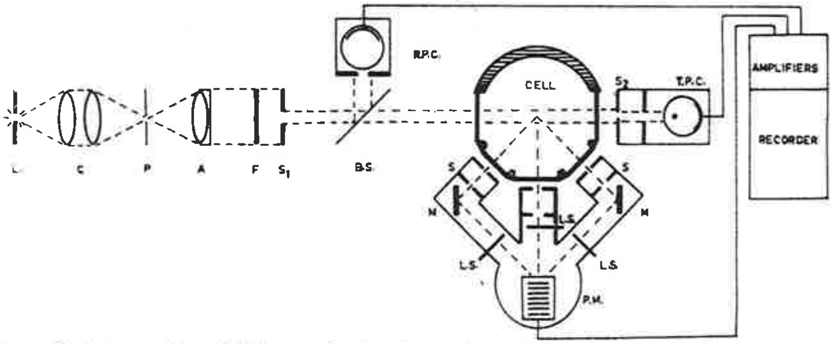

Figure 8. Automatic turbidimeter for isothermal precipitation. Diagrammatic layout of the instrument. L, light source; C, condenser lens; P, pinhole; A, achromat lens; F, Zeiss monochromatic filter; S, $S_1$, $S_2$, slits; B.S., beamsplitter; R.P.C., reference photocell; T.P.C., transmission photocell; M, mirrors for deflecting the scattered light at 45 and 135° to photomultiplier; P.M., photomultiplier (11 stage E.M.I. 6097B); L.S., electrically operated light stops (Stearne and Urwin, 1962).

This correction may be small when very dilute solutions are employed but it should be checked before discarding it. When the quantity $(i_{90}/I_t)_{\mathrm{meas}}$ was corrected for dissymmetry change, the FRESNEL reflections, the volume factor for each receiver and the scattering from the solution was subtracted, it was shown to be directly proportional to the concentration of polymer precipitated over a tenfold range of concentration. However, it must be remembered that this has only been tested on the system polystyrene/butanone/isopropanol. A check over a much wider field would be required to establish its general application. No corrections for refractive index were necessary here since the solvent precipitant mixture is isorefractive.

A thermal gradient turbidimeter has been described by Gamble *et al.* (1965). The instrument consists of an all metal cell, described in the next section, a light source, stirrer, diaphragms and photosensitive element combined with a temperature programmer and X–Y recorder. Temperature control is maintained by a set of electrical heating elements and water cooling system. Temperature and turbidity are recorded on the X–Y recorder with appropriate sensitivity adjustment. The rate of cooling is adjustable from 0·5 to 3°C per minute. The Taylor–Tung method of slopes was adopted for calculating the distribution which is based on the experimental observation that the precipitation curve between 20 and 50 per cent precipitation is essentially linear in the systems investigated. The choice is quite arbitrary and would presumably have to be adjusted for a particular system after inspection of a series of curves of different concentrations and molecular weights. A calibration curve is constructed by plotting the slope function $S$ against the Wesslau parameter $\beta$ obtained from fractionation data separately. Good reproducibility is claimed by the authors.

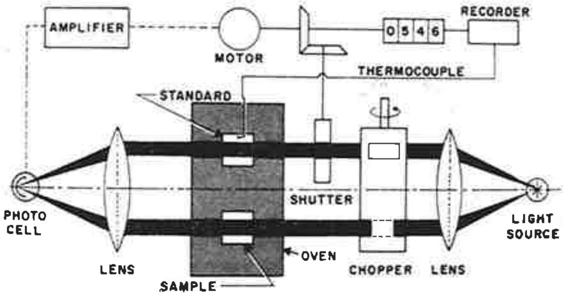

**Figure 9.** Dual beam turbidimeter for thermal gradient precipitation (Taylor and Graham, 1964).

Taylor and Graham (1964) have constructed a dual beam instrument for the same purpose as Gamble *et al.* but which the authors claim is more reliable, cf. Fig. 9. The electrically heated–air cooled oven is programmed to an accurate 1°C per minute drop over a range 170–30°. The instrument has the usual advantages of a dual beam instrument. Measurement of turbidity is made by adjusting a shutter driven by the amplified difference in response between the light intensity from the two beams. A chopper allows each beam to fall on the same photocell separately and alternatively. The movement of the shutter is fed to the X–Y recorder against cell temperature to give the desired turbidity–temperature curve. In this system the slope index S.I., obtained by dividing curve height on the turbidity axis between 120 and 80°C by the total height of the curve or maximum turbidity, is claimed to be independent of molecular weight.

### B Design of T.T. Cells

A number of designs for different types of cell, suitable for T.T. analysis, have appeared in the literature. In the case of isothermal precipitation provision must be made for the addition of precipitant at the same temperature as the rest of the cell, stirring is required to ensure adequate mixing, windows in fixed positions or a circular cell must be provided and adequate provision for overall thermostatting must be made. Probably electrical heating would be the most satisfactory for the latter and magnetic stirring has been shown to be both convenient and satisfactory. The lead-in for the precipitant from an electrically driven pipette or micropump must be preheated by a circulating water jacket, or alternatively, electrically heated as in the case of the main body of the cell. Two types of cells for I.P. have been used (i) the open cell and (ii) the constant volume cell. Both have certain disadvantages; the total volume becomes unwieldly in the former and polymer is ejected in the latter. This results in dilution and makes a complicated continuous correction necessary. Nevertheless, the smaller volume of the constant volume cell makes it more convenient from the practical viewpoint.

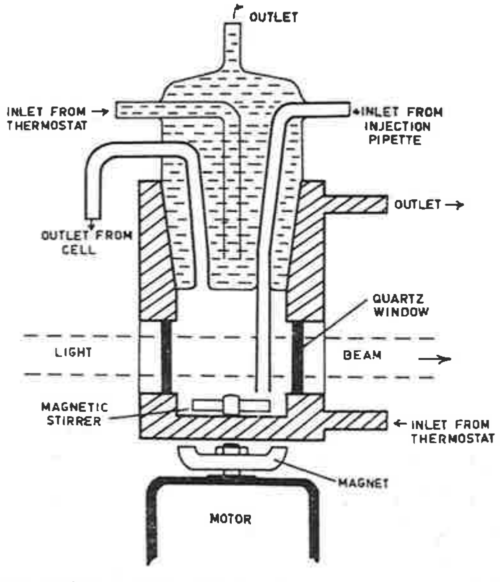

**Figure 10.** Constant volume T.T. cell for isothermal precipitation (Stearne and Urwin, 1962).

A constant volume cell, used by the author (Stearne and Urwin, 1962), was constructed of brass for rapid heat transfer, cf. Fig. 10, with windows of quartz, set in Woods metal and in which the internal surfaces were treated to give a matt black anti-reflective surface. The "stopper" was made from a standard Quickfit joint and incorporates the preheating jacket for the precipitant inlet tube. Accurate location of the cell was achieved by two locating pins underneath the cell, which fit into matching holes in the base plate.

The thermal gradient cell of Gamble *et al.* (1965) is shown in Fig. 11. The unit includes the optics as an integral part of the design. The cell is all metal except for windows of quartz and teflon gaskets. A stainless steel insert in the main copper block forms the wall of the cell. A motor driven stirrer is included but is not used during the cooling cycle. Coagulation of the polymer was reported below 45°C and this effect was more pronounced at higher concentrations. No provision was made for stopping to eliminate forward scattering in this design.

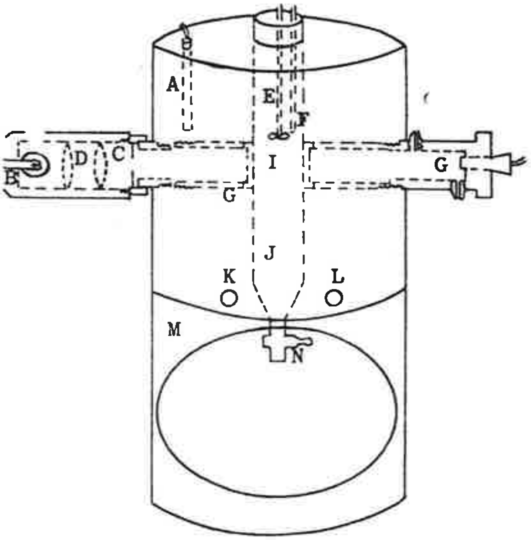

**Figure 11.** Turbidimeter cell for thermal gradient precipitation. (A) Temperature sensing element, (B) light, (C) iris diaphragm, (D) lenses, (E) stirrer, (F) cell thermocouple, (G) photosensitive element, (H) gaskets, (I) quartz windows, (J) cell, (K,L) water outlet and inlet, (M) block support, (N) drain valve (Gamble *et al.* 1965).

### C Corrections and Calibration

The corrections which should be applied to T.T. scattering data are similar to those necessary for light scattering. These are treated comprehensively in Chapter 4 and therefore the discussion will not be repeated here. It will suffice to mention only the important corrections. The usual angular corrections for volume are not important for measurement of T.T. at a single angle, although of course they must be made when comparing scattering at different angles. The corrections for divergence of the beam on leaving the cell due to different refractive indices (Kerker *et al.* 1964) and corrections for back reflectance must be calculated from the known reflectances of glass-air and glass–solution interfaces (Stearne and Urwin, 1962). It should be noted in this connection that some difficulty can arise from the use of double walled cells in which a circulating water jacket has been included in the overall design because the beam passes through two cylindrical walls at the entrance and exit causing divergence of the beam (Beattie, 1965). In this case, resort to an empirical correction must be made.

The constant volume cell suffers from one disadvantage peculiar to this type of cell in that polymer is ejected with solution at each addition of precipitant and that the weight of precipitate observed at any instant is not the cumulative weight required for the interpretation of the molecular weight distribution. To obtain the correct cumulative weight, a correction in the form of an addition for the loss of polymer during titration must be applied. It has been shown that the weight of polymer lost, $(W_p)_L$, at any stage of the titration is given by (Urwin *et al.* 1964)

$$(W_p)_L \cong \Delta\gamma \sum_{n=0}^{n=i} (W_p)_n$$

where $\Delta\gamma$ represents one of $n$ equal parts of the total range of the volume fraction, over which the titration was carried out and $(W_p)_n$ is the total weight precipitated at the $n$th increment.

Calibration of different instruments has been carried out in different ways according to the experience of the experimenter, including the use of special opal glass standards, perspex blocks, colloidal silica solutions, solutions of fluorescein and solutions of polymer of known molecular weight. Perhaps the most widely used method to check on the asymmetry of the instrument is the use of the fluorescence from solutions of fluorescein combined with a yellow filter placed in the light path of the photomultiplier to eliminate scattering. However, the use of a standard glass is simple and effective, since it is based on scattering from the glass relative to the scattering from some liquid such as benzene, which can be easily checked from time to time. Calibration procedures should be carried out very carefully according to the recommendations of the manufacturer of the instrument and a comprehensive treatment of the subject should be consulted, cf. Chapter 4, before embarking on a programme of work.

## D AUXILIARY EQUIPMENT

A number of ways of delivering precipitant to the titration cell have been suggested including various motor driven pipettes and micropumps. The volume delivered is usually measured by monitoring the number of rotations of the motor. Reduction gearing is necessary between the motor and the slowly revolving lead screw which pushes the plunger of the pipette. The micropump is well worth investigating since accurate and variable delivery rates are now obtainable and the volume delivered may be recorded on a time base scale and finally converted to volumes.

Many suggestions have been proposed for thermostatting and controlled cooling. The wide use of thermistors and solid state devices nowadays has encouraged a more sophisticated approach to these problems in recent years and the reader is advised to consult a suitable text on the application of electronics to laboratory equipment or to discuss the problem with someone well versed in electronics before making decisions on the design of thermostats.

## VII Conclusions

### A ALTERNATIVES

At this point one should have established whether or not a molecular weight distribution is required or whether an average molecular weight $\overline{M}_w$ or $\overline{M}_n$ by light scattering or osmometry or even whether the ratio $\overline{M}_w/\overline{M}_n$ representative of the breadth of distribution will suffice. If it is established that the molecular weight distribution is really required then one is faced with making a choice among the several alternatives (Schneider, 1965). These are the traditional method of Fractional Precipitation (F.P.), Turbidimetric Titration (T.T.) and Gel Permeation Chromatography (G.P.C.). If one has to examine a single polymer, say, then F.P. seems the most obvious choice on the grounds of cost since the method requires little in the way of apparatus. However, if the number of samples is large, F.P. is eliminated because of the time factor and the choice is reduced to T.T. or G.P.C. Some of the points that should be considered are:

(1) The cost of G.P.C. (*ca.* £7,000) is high compared with T.T.
(2) G.P.C. cannot be used for secondary roles such as exploring solvent-precipitant systems for fractionation, c.e.d. values and the determination of $\Theta$ points.
(3) On the other hand, G.P.C. can be used preparatively, i.e. for isolating fractions for further examination.
(4) G.P.C. also yields the distribution curve directly and is probably simpler and quicker. (The method of analysis by refractometry is much simpler than light scattering.)
(5) Calibration problems are about the same in both methods.

The relative costs, particularly where the basic equipment, i.e. a light scattering instrument or spectrophotometer is already on hand, would swing the choice in favour of T.T. However, if the cost is not prohibitive or one has to purchase the basic equipment, then G.P.C. would seem to be the more logical choice.

### B CHOICE OF METHOD

If the choice is limited to one of the T.T. methods, the availability of a light scattering photometer or spectrophotometer may decide the issue. One has then to make a decision between I.P. and T.G.P. among the empirical methods or between transmission (turbidity) as against scattering in the case of the "absolute" method. The latter is soundly based theoretically and is attractive practically. It deserves serious consideration as a method and this is particularly so, where a light scattering photometer is already available in the laboratory and a suitable isorefractive solvent–precipitant pair can be selected. On the other hand, if a good spectrophotometer is available, one might consider its conversion for scattering measurements. Alternatively, after making provision for proper stopping to eliminate the contribution from forward scattering, the "absolute" method of Beattie or the much simpler T.G.P. method of Taylor and Tung may be well worth investigation as a means of determining molecular weight distributions. Whatever the choice, the time spent weighing the advantages and disadvantages of the various alternatives will be time very well spent in the long run.

## REFERENCES

Allen, P. E. M., Downer, J. M., Hastings, G. W., Melville, H. W., Molyneux, P. and Urwin, J. R. (1956). *Nature* **177,** 910–912.

Bawn, C. E. H. (1948). *Research* **1,** 343–352.

Beattie, W. H. (1965). *J. Polymer Sci.* **3,** 527–549.

Beattie, W. H. and Gallaway, W. S. (1965). *J. Appl. Optics* **4,** 1607–1615.

Beattie, W. H. and Jung, H. C. (1968). *J. Colloid and Interface Sci.* **27,** 581–590.

Bishoff, J. and Desreux, W. (1951). *Bull. Soc. chim. Belges* **60,** 137–155.

Boyer, R. F. (1952). *J. Polymer Sci.* **9,** 216. 197–218.

Brönstead, J. N. (1938). *Compt. rend. trav. lab. Carlsberg, Ser. chim.* **22,** 99–108 (reported by Mathieson).

Campbell, H., Kane, P. O. and Ottewill, I. G. (1954). *J. Polymer Sci.* **12,** 611–620.

Casassa, E. F. (1960). *Polymer* **1,** 169–177.

Channen, E. W. (1959). *Reviews of Pure and Applied Chem.* **9,** 225–255.

Claesson, S. (1955). *J. Polymer Sci.* **16,** 193–199.

Cornet, C. F. and Ballegooijen, H. (1966). *Polymer* **7,** 293–301.

Cotton, G. R. and Schneider, W. C. (1963). *J. Appl. Polymer Sci.* **7,** 1243–1255.

Dunn, A. S., Stead, B. D. and Melville, H. W. (1954). *Trans. Faraday Soc.* **50,** 279–290.

Elias, H. G. (1959). *Makromol. Chem.* **33,** 140–165.

Elias, H. G. and Gruber, U. (1964). *Makromol. Chem.* **78,** 72–99.

Flory, P. J. (1953). "Principles of Polymer Chemistry." Cornell University Press, Ithaca, New York. Chapts. IX, X, XIII.

Gamble, L. W., Wipke, W. T. and Lane, T. (1965). *J. Appl. Polymer Sci.* **9,** 1503–1513.

Giesekus, H. (1958). *Kolloid Z. u. Z. Polymere* **158,** 35–39.

Gooberman, G. (1959). *J. Polymer Sci.* **40,** 469–486.

Gucker, F. T. and Egan, J. J. (1961). *J. Colloid Sci.* **16,** 68–84.

Guzeev, V. V., Morozov, V. I., Shtarkman, B. P. and Rytov, E. E. (1959). *Vysokomol. Soedin.* **1,** 1840–1843.
Harris, I. and Miller, R. G. (1951). *J. Polymer Sci.* **7,** 377–392.
Hastings, G. W. and Peaker, F. W. (1959). *J. Polymer Sci.* **36,** 351–360.
Heller, W. (1965). *J. Polymer Sci. Pt. A* **3,** 3313–3329.
Heller, W. and Pangonis, W. J. (1957). *J. Chem. Phys.* **26,** 498–506.
Hengstenburg, J. (1956). *Z. Elektrochem.* **60,** 236–245.
Herdan, G. (1960). "Small particle statistics." Butterworths, London. Chapter 15.
Howard, G. J. (1963). *J. Polymer Sci. Pt. A* **1,** 2667–2678.
Kerker, M., Kratohvil, J. P. and Matijevic, E. (1964). *J. Polymer Sci. A* **2,** 303–311.
Kratohvil, J. P. (1964). *Anal. Chem.* **36,** 458–472.
Krozer, S., Vainryb, M. and Silina, L. (1960). *Vysokomol. soedin.* **2,** 1876–1881.

S cap.

Mathieson, A. R. (1960). *J. Colloid Sci.* **15,** 387–401.
Meehan, E. J. and Beattie, W. H. (1961). *Anal. Chem.* **33,** 632–635.
Melville, H. W. and Stead, B. D. (1955). *J. Polymer Sci.* **16,** 505–515.
Molyneux, P. (1960). *Makromol. Chem.* **43,** 31–60.
Morey, D. R. and Tamblyn, J. W. (1945). *J. Appl. Phys.* **16,** 419–424.
Morey, D. R., Taylor, E. W. and Waugh, G. P. (1951). *J. Colloid Sci.* **6,** 470–480.
Oth, A. (1949). *Bull. soc. chim. Belges* **58,** 285–300.
Oth, A. and Desreux, V. (1951). *Bull. soc. chim. Belges* **63,** 261–284.
Schneider, N. S. (1965). *J. Polymer Sci. Pt. C* **8,** 179–204.
Scholtan, W. (1957). *Makromol. Chem.* **24,** 104–132.
Schulz, G. V. (1937). *Z. Physik. Chem.* **A179,** 321–355.
Shen, K. P. and Eirich, F. R. (1961). *J. Polymer Sci.* **53,** 81–85.
Stearne, J. M. and Urwin, J. R. (1962). *Makromol. Chem.* **56,** 76–87.
Suh, K. W. and Clark, D. H. (1967). *J. Polymer Sci. Pt. A1* **5,** 1671–1681.
Tabibian, R. M., Heller, W. and Epel, J. N. (1956). *J. Colloid Sci.* **11,** 195–213.
Tanaka, S., Nakamura, A. and Morikawa, H. (1965). *Makromol. Chem.* **85,** 164–172.
Taylor, W. C. and Graham, J. P. (1964). *Polymer Letters* **2,** 169–172.
Taylor, W. C. and Tung, L. H. (1962). *Soc. Plastics Engineers Transactions* **2,** 1–3.
Tompa, H. (1956). "Polymer Solutions." Butterworths, London. Chapter 7.
Urwin, J. R., Stearne, J. M., Jordan, D. O. and Mills, R. A. (1964). *Makromol. Chem.* **72,** 53–67.
Van der Hulst (1957). "Light Scattering by Small Particles." Wiley, New York.

of sodium (1·5 g.) in dry methanol (20 c.c.), with stirring and cooling, at such a rate that the temperature did not rise above 0° (5 mins.). The solution was set aside at room temperature for 16 hours and then boiled under reflux for ½ hour. Water (4 c.c.) was added, and the solution boiled for a further ½ hour. Methanol was then distilled off, water being gradually added so that the final volume was *ca.* 50 c.c. On being cooled, the solution deposited long needles of a sparingly soluble sodium salt; this was collected, suspended in water (30 c.c.), and strongly acidified with hydrochloric acid, to give a solid acid (*A*). Acidification of the filtrate from the sodium salt gave a solid acid (*B*). Recrystallisation of (*A*) from aqueous methanol gave fluffy needles (2·25 g.) of *α-bromo-ββ-diphenylacrylic acid*, m. p. 148—150°, raised by one further crystallisation to 150°: the solvent of crystallisation was not readily removed by drying (Found, in material dried at 56°/0·01 mm.: C, 57·9; H, 4·25; Br. 24·9. Dried at 100°/0·01 mm.: C, 59·3; H, 3·75; Br, 26·2. $C_{15}H_{11}O_2Br$ requires C, 59·4; H, 3·65; Br, 26·4%). Recrystallisation of (*B*) from aqueous methanol gave material, m. p. 125—135°, which was not further examined.

*Stability of the Halogen in α-Bromo-ββ-diphenylacrylic Acid.*—(i) The bromo-acid (0·1 g.) was heated in 3·7N-sodium hydroxide (0·5 c.c.) in a sealed tube at 100° for 2 days. The liberated bromide ion, estimated as previously described, required 0·10 c.c. of 0·101N AgNO$_3$, equiv. to 3% reaction. (ii) The bromo-acid (0·2 g.) and 4N-methanolic sodium methoxide (2 c.c.) were heated for 2 days at 100°; the liberated bromide ion required 0·65 c.c. of 0·101N-AgNO$_3$, equiv. to 10% reaction.

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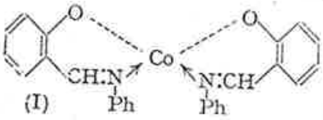
## 922. Studies on Bond Type in Certain Cobalt Complexes. Part III.* The Polarographic Reduction of Some Cobalt Inner-complex Compounds.

By J. R. Urwin and B. West.

The polarographic reduction of some cobalt complexes with various salicylideneanilines has been attempted. Two-step irreversible curves have been obtained in all curves but the mechanism of reduction has not been clarified.

The polarographic reduction of a group of cobaltous compounds of the non-electrolyte, inner complex type has been attempted, the object being to discover whether the method provided a measure of the relative stabilities of these compounds. Eight compounds have been examined, all being of the bis(salicylideneaniline)cobalt type (I), with various substituents in the aniline ring. It had been hoped to carry out these investigations in aqueous pyridine in order to facilitate comparisons with the work of Bailes and Calvin (*J. Amer. Chem. Soc.*, 1946, 68, 949) and the exchange work being carried out by West (Part I, *J.*, 1952, 3115), but this proved impossible since pyridine is reduced at a potential lower than any of the complexes examined.


(I)

After considerable trial, the reductions were finally carried out in 80% ethylene glycol–water solution with potassium chloride or lithium chloride as the supporting electrolyte. For each compound, when the chloride-ion concentration was greater than 0·01N, two-step waves were obtained on reduction, their definition increasing with increasing chloride-ion content. Since comparative results were required, all substances were examined in solutions containing 0·1N-chloride ion. The figure shows some examples of curve obtained.

The reductions all appear to be irreversible, the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for the lower curves being shown in the table. These values are all much greater than should correspond to a two-electron step, *viz.*, −0·029v, but in several cases values close to −0·059v, the value for a one-electron step, have been obtained. This may imply that the first step in the

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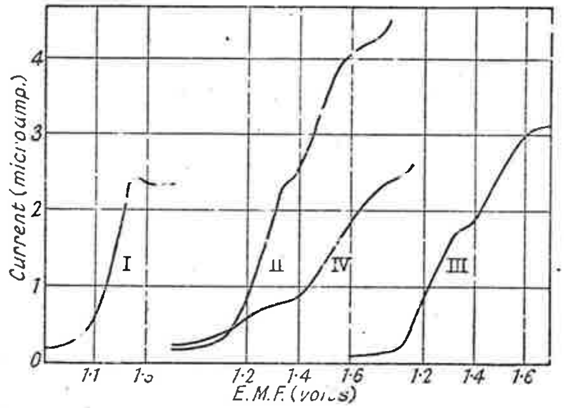
* Part II, *J.*, 1952, 3123.

*Polarographic reduction of cobalt chelate complexes at 25°.*

| R in complex $Co(NR{:}CH{\cdot}C_6H_4{\cdot}OH\text{-}o)$ | First wave $E_{\frac{1}{2}}$ (v) | $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ | Second wave $E_{\frac{1}{2}}$ (v) | Supporting electrolyte | p*K* of amine [a] |
|---|---|---|---|---|---|
| ($CoSO_4$) | −1·156 | −0·061 | — | 0·1N-KCl | — |
| *m*-$Cl{\cdot}C_6H_4$ | −1·211 | −0·09 | −1·45 | ,, | 3·52 |
| Ph | −1·238 | −0·10 | −1·49 | ,, | 4·58 |
| ,, | −1·220 | −0·064 | −1·44 | Sat. LiCl | — |
| *m*-$C_6H_4Me$ | −1·225 | −0·11 | −1·47 | 0·1N-KCl | 4·69 |
| *p*-$C_6H_4Me$ | −1·237 | −0·12 | −1·47 | ,, | 5·07 |
| *cyclo*-$C_6H_{11}$ | −1·34 | −0·065 | [b] | ,, | 10·61 |
| *p*-$Cl{\cdot}C_6H_4$ | −1·260 | −0·11 | −1·46 | ,, | 4·00 |
| ,, | −1·190 | −0·070 | −1·43 | Sat. LiCl | — |
| *o*-$C_6H_4{\cdot}OMe$ | −1·280 | −0·14 | −1·48 | 0·1N-KCl | 4·49 |
| ,, | −1·240 | −0·11 | −1·46 | Sat. LiCl | — |
| *p*-$C_6H_4{\cdot}OMe$ | −1·299 | −0·15 | −1·50 | 0·1N-KCl | 5·29 |
| ,, | −1·250 | −0·10 | −1·49 | Sat. LiCl | — |
| (Salicylideneaniline) | −1·58 [c] | −0·15 | — | 0·1N-KCl | — |

[a] Values taken from Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469, determined in aqueous solution. [b] Second wave was very large and its finish was not determined. [c] Wave commences at −1·35 v.

reduction of these compounds is that of the central cobalt ion to the univalent state. Calvin and Bailes (*loc. cit.*) have shown that reduction of the analogous cupric complexes presumably involves a reduction to the cuprous state (first wave) and then (second wave) reduction of a simple cuprous ion, the cuprous complexes apparently dissociating upon formation to liberate free cuprous ions. The reduction of cobaltous ions under similar conditions to the complexes gave only one wave showing a pronounced maximum which could not be completely inhibited by the use of gelatin. This wave appears also to be irreversible as calculated from the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ formula, although the value found, **−0·061v**, is very close to that required for a one-electron step. There appears to be no evidence for the reversible reduction of simple cobalt ions in aqueous solutions; in fact, Brdicka (*Coll. Czech. Chem. Comm.*, 1930, 2, 489, 545; 1931, 3, 396) has shown that large amounts of chloride ions must be present in solution in order to make the normal reduction of cobalt *approach* reversibility. Presumably, it is the chloro-complex ions in aqueous solution which tend to reduce reversibly rather than hydrated cobaltous ions.



I, $CoSO_4$.
II, *Bis(salicylideneaniline)cobalt.*
III, *Bis(salicylidene-m-toluidine)cobalt.*
IV, *Salicylideneaniline.*

(*All solutions are* 0·001M *in* 20% *aqueous ethylene glycol and contain* 0·1N-KCl *as supporting electrolyte.*)

Chloride-ion concentration appears to play a considerable part in the reductions of the cobalt complexes reported here. It has been stated (p. 4727) that the separation of two waves commenced at 0·01N-potassium chloride or above; below this concentration only one curve could be obtained. Increasing the chloride-ion concentration by using 80% ethylene glycol–water solutions saturated with lithium chloride (*ca.* 1—2N) caused a numerical decrease of about 0·04 unit in the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for several compounds (see table), *i.e.*, the values changed towards the one-electron step value of **−0·058v.**

The second wave present in the reduction curves of the cobalt complexes cannot be reconciled immediately with the reduction of a lower valency state of cobalt, *i.e.*, univalent cobalt. It may be due to the reduction of the CH:N linkage present in all the complexing molecules examined. Salicylideneaniline itself has a reduction potential of $-1{\cdot}35$v, the same as that for the second wave obtained on reduction of bis(salicylideneaniline)cobalt, while the substance prepared by Raney nickel hydrogenation of salicylideneaniline, *i.e.*, containing a $CH_2{\cdot}NH$ linkage, shows no sign of reduction below $-1{\cdot}8$v, at which potential a catalytic hydrogen wave is observed similar to that obtained when doing a "blank" reduction on the solvent plus supporting electrolyte ($0{\cdot}1$N).

Although the work has had to be suspended, the results are believed to imply that elucidation of these mechanisms cannot be accomplished solely by conventional polarographic methods. No solvent has yet been found for the complexes which will also dissolve considerable amounts of a supporting electrolyte and yet not undergo reduction at potentials below that of the complexes being examined. In spite of the foregoing partial failure, an attempt has been made to correlate the half-wave potentials of the first waves obtained with each compound with the p$K$'s of the amines present in the various salicylidene derivatives used in preparing the complexes.

It has been assumed by analogy with Calvin and Bailes's results (*loc. cit.*) that the first wave found is connected with the reduction of the complex molecule probably involving the cobalt ion present in the complex. Therefore the higher the half-wave potential, *i.e.*, the more difficult it is to reduce the complex, the more stable should the complex be. Further, since the p$K$ value of a substituted aniline will be a relative measure of the electron density on the nitrogen atom, it should provide some measure of the "availability" of the unshared electron pair on the nitrogen atom for the formation of a co-ordinate linkage, *i.e.*, some measure of the strength of the Co–N bond. Values of $E_{\frac{1}{2}}$ for the first wave are given in the table together with the appropriate p$K$ values of the amines in water.

The small number of compounds examined has limited the attempted correlation. In view of the marked dependence of half-wave potential upon chloride-ion concentration, it is not at all obvious that all cobalt complexes of this type would form a single stability series dependent upon p$K$.

## EXPERIMENTAL

The polarograph used was a manually operated instrument of conventional design. An H-type cell was used for the reductions, one arm containing the reference electrode (saturated calomel), and the other the dropping cell. The two arms were connected by an agar-saturated potassium chloride bridge, which was separated from the dropping cell by a sintered-glass plate. The complete unit was kept at 25° ± 0·1°. Characteristics of the capillary were: $m^{\frac{2}{3}} \times t^{\frac{1}{6}} = 1{\cdot}77$. Nitrogen, purified by passage through vanadyl sulphate solutions, was bubbled through the solutions to remove oxygen. Corrections for *ir* drop across galvanometer shunts were allowed for on all $E_{\frac{1}{2}}$ values determined.

All solutions used were $0{\cdot}001$M and were prepared by dissolving the required weight of the compound in ethylene glycol, then making the solution up to the requisite volume by addition of aqueous potassium chloride solution and further glycol. The strength of the chloride solution was such as to give a concentration of $0{\cdot}1$N in the final solution. For reductions employing lithium chloride, a stock solution of 20% aqueous glycol previously saturated with lithium chloride by shaking the mixture with solid for 1 hour at 25° was used to dissolve the compound being examined.

Ethylene glycol was purified by vacuum-distillation and gave no evidence of any reducible impurities when "blank" reductions were carried out in the absence of any complex.

Cobalt sulphate heptahydrate was of "AnalaR" grade and was used without further purification. The complexes used were prepared by the method outlined in Part I (*loc. cit.*) for salicylideneaniline-type complexes.

*Hydrogenation of Salicylideneaniline.*—8 G. of the Schiff's base and 3 g. of W.6 Raney nickel in 20 c.c. of absolute ethanol were shaken with hydrogen at 1 atm. until the yellow colour had completely disappeared (6 hours). The solution was then filtered and crystallised. An almost theoretical yield of N-o-*hydroxybenzylaniline* was obtained as colourless needles, m. p. 105° (Found: C, 78·4; H, 6·6; N, 7·3. $C_{13}H_{13}ON$ requires C, 78·4; H, 6·6; N, 7·0%).

The authors are indebted to Dr. S. W. Pennycuick for his interest in this work.

JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE. [*Received, April 16th, 1952.*]

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# THE HYDROLYSIS OF PICOLINAMIDE AND ISONICOTINAMIDE IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS

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*Received March 24, 1953*

The hydrolyses of picolinamide and isonicotinamide were investigated over a range of hydrochloric acid concentrations from 0.1 to 8 *N*. The experimental first-order rate constants do not pass through maxima with increasing hydrochloric acid concentration. The Arrhenius equations at a number of hydrochloric acid concentrations were determined. The energies of activation and the *A* factors increase with hydrochloric acid concentration.

The hydrolysis of amides in concentrated acid solutions was studied by a number of workers.[1] The first-order rate constants pass through maxima in all cases with increasing acid concentrations. Various theories were advanced to account for these maxima; however, none can be considered satisfactory.

Recently, Jellinek and Gordon[2] investigated the hydrolysis of nicotinamide. In contrast to all the other amides, the rate constants for this heterocyclic amide do not pass through a maximum, but increase steadily with the acid concentration.

The present paper extends the work to other heterocyclic amides, such as picolin- and isonicotinamide. It is shown that these amides behave in a similar way to nicotinamide. A study also has been made of the parameters of the Arrhenius equation as functions of the acid concentration. Both the energies of activation and frequency factors, the latter divided by the respective acid concentrations, increase with the acid concentration. In the case of the non-heterocyclic amides, only the energies of activation increase, whereas the frequency factors remain constant.[1]

The differences in the hydrolyses of the three heterocyclic amides are only small, indicating that the position of the amido group on the ring does not exert a significant influence on the reaction.

As in the previous work on nicotinamide,[2] the polarograph was used to analyze the reaction mixtures. The analysis was based on the fact that the polarographic waves of the acids corresponding to the amides disappear at high *p*H values.

## Experimental

**Materials.**—The preparation of picolinamide (m.p. 106.5°) and isonicotinamide (m.p. 156.0°) is described elsewhere.[3] Hydrochloric acid, sodium hydroxide, borax and disodium hydrogen phosphate were Analar reagents.

**Technique.**—The hydrolyses were carried out in sealed glass tubes, immersed in an oil thermostat, kept constant within ±0.5°. The tubes (Hy-sil glass) were cleaned with chromic acid mixture, thoroughly rinsed with distilled water and dried. Tubes were withdrawn from the thermostat at definite time intervals, rapidly cooled and analyzed as described below.

Calibration curves for the polarographic analysis were prepared for picolinamide and isonicotinamide over a range of concentrations from $0.2 \times 10^{-3}$ to $2 \times 10^{-3}$ *M*. These solutions were obtained from stock solutions of the amide in 0.1 *N* hydrochloric acid diluted with 0.1 *N* hydrochloric acid to give a range of amide concentration. Ten-ml. portions of these solutions were made up to 50 ml. with a phosphate buffer. The *p*H values were 11.5 ± 0.1 as determined with a Cambridge *p*H meter in conjunction with an "Alki" glass electrode. The buffer consisted of 100 ml. of *M*/20 $Na_2HPO_4 \cdot 2H_2O$ plus 86.4 ml. of 0.1 *N* sodium hydroxide; this solution made up to 200 ml. with water gave a *p*H value of 12.0.

The diffusion current was found to be a linear function of the amide concentration in the range of concentrations indicated above. It was also ascertained that hydrolysis did not take place in the buffer over several hours at 25°.

The reaction mixtures, after hydrolysis for definite time intervals, were buffered as described above, with the exception of those reaction mixtures which had concentrations of hydrochloric acid of 1 *N* or above. In these instances, the reaction mixtures were first diluted to make them 1 *N* with respect to hydrochloric acid. Ten ml. samples were then almost neutralized with 2 *N* sodium hydroxide and made up to 50 ml. with the phosphate buffer. All final solutions had *p*H values of 11.5 ± 0.2.

## Experimental Results

**(a) Hydrolyses as a Function of the Temperature.**—The hydrolyses in 0.1 *N* hydrochloric acid were carried out over a range of temperatures from 79.5 to 139.3° for picolinamide and from 70 to 130° for isonicotinamide. In both cases the reactions follow a first-order law. Table I gives the initial concentrations of the amides in moles/liter at the various temperatures and the corresponding rate constants in reciprocal seconds. The last column shows these rate constants corrected for thermal expansion of the solutions from room temperature to the respective reaction temperatures. These corrections were made by first calculating the hydrochloric acid concentrations at the respective reaction temperatures. The rate constants were then adjusted linearly to the same hydrochloric acid concentration (*i.e.*, 1/10 *N*) for all reaction

TABLE I

HYDROLYSIS OF PICOLINAMIDE AND ISONICOTINAMIDE IN 0.1 *N* HYDROCHLORIC ACID

| Temp., °C. | Initial concn. of amide, mole/l. (× $10^3$) | Rate constants, sec.$^{-1}$ (× $10^4$) | Cor. rate constants, sec.$^{-1}$ (× $10^4$) |
|---|---|---|---|
| | Picolinamide | | |
| 79.5 | 5.02 | 0.0213 | 0.0216 |
| 90.5 | 5.02 | 0.0807 | 0.0836 |
| 99.5 | 5.02 | 0.155 | 0.161 |
| 119.5 | 4.98 | 0.685 | 0.725 |
| 129.5 | 4.98 | 1.46 | 1.56 |
| 139.5 | 5.05 | 2.53 | 2.73 |
| | Isonicotinamide | | |
| 70.0 | 5.00 | 0.0266 | 0.0271 |
| 79.5 | 5.00 | 0.0576 | 0.0587 |
| 98.3 | 5.03 | 0.238 | 0.248 |
| 120.3 | 4.96 | 1.163 | 1.23 |
| 130.0 | 5.00 | 2.24 | 2.39 |

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[1] B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **20B**, 73 (1942), contain references to earlier work.

[2] H. H. G. Jellinek and A. Gordon, THIS JOURNAL, **53**, 966 (1949).

[3] H. H. G. Jellinek and J. R. Urwin, not yet published.

temperatures. The assumption of linearity is justified for small concentration ranges.

Figure 1 shows the experimental results for picolinamide: isonicotinamide gives very similar straight lines. The first-order law for these amides is obeyed up to about 80% conversion.

Hydrolyses were also investigated in 1, 3 and 8 $N$ hydrochloric acid over a range of temperatures. Table II gives the relevant initial concentrations of amide and rate constants.

TABLE II

HYDROLYSIS OF PICOLINAMIDE AND ISONICOTINAMIDE IN 1, 3 AND 8 $N$ HYDROCHLORIC ACID

| HCl, $N$ | Temp., °C. | Initial concn. of amide, moles/l. (× $10^3$) | Rate constants, sec.$^{-1}$ (× $10^4$) | Cor. rate constants, sec.$^{-1}$ (× $10^4$) |
|---|---|---|---|---|
| | | Picolinamide | | |
| 1.00 | 85.0 | 5.07 | 0.392 | 0.405 |
| 1.00 | 102.0 | 5.07 | 1.56 | 1.63 |
| 1.00 | 113.0 | 5.20 | 3.47 | 3.66 |
| 3.04 | 70.5 | 15.0 | 0.368 | 0.376 |
| 3.04 | 85.0 | 15.0 | 1.43 | 1.48 |
| 3.04 | 100.0 | 15.0 | 4.72 | 4.92 |
| 8.08 | 54.5 | 30.2 | 0.232 | 0.235 |
| 8.08 | 69.5 | 30.4 | 1.095 | 1.12 |
| 8.08 | 85.0 | 30.0 | 5.18 | 5.35 |
| | | Isonicotinamide | | |
| 1.00 | 68.0 | 5.00 | 0.373 | 0.380 |
| 1.00 | 90.5 | 5.05 | 2.21 | 2.23 |
| 1.00 | 100.0 | 5.05 | 4.80 | 5.00 |
| 1.00 | 105.0 | 5.04 | 6.78 | 7.10 |
| 3.04 | 55.5 | 15.10 | 0.375 | 0.380 |
| 3.04 | 68.0 | 14.90 | 1.29 | 1.32 |
| 3.04 | 83.0 | 14.85 | 4.75 | 4.89 |
| 8.08 | 41.0 | 29.3 | 0.294 | 0.296 |
| 8.08 | 55.5 | 29.8 | 1.43 | 1.45 |
| 8.08 | 68.0 | 30.8 | 4.52 | 4.61 |

The Arrhenius equations for the hydrolyses in 0.1, 1, 3 and 8 $N$ hydrochloric acid were derived from plots of the logarithms of the corrected rate constants against the reciprocal of the absolute temperatures:

PICOLINAMIDE

0.1 $N$ HCl $k = 6.5 \times 10^{7} e^{-21500/RT}$ sec.$^{-1}$
1.0 $N$ HCl $k = 7.6 \times 10^{8} e^{-21800/RT}$ sec.$^{-1}$
3.0 $N$ HCl $k = 8.45 \times 10^{9} e^{-22200/RT}$ sec.$^{-1}$
8.0 $N$ HCl $k = 3.80 \times 10^{11} e^{-23500/RT}$ sec.$^{-1}$

ISONICOTINAMIDE

0.1 $N$ HCl $k = 2.7 \times 10^{7} e^{-20500/RT}$ sec.$^{-1}$
1.0 $N$ HCl $k = 9.2 \times 10^{8} e^{-20900/RT}$ sec.$^{-1}$
3.0 $N$ HCl $k = 7.9 \times 10^{9} e^{-21100/RT}$ sec.$^{-1}$
8.0 $N$ HCl $k = 7.4 \times 10^{10} e^{-21700/RT}$ sec.$^{-1}$

**(b) Rate Constants as a Function of the Hydrochloric Acid Concentration.**—Hydrolyses were carried out over a range of hydrochloric acid concentrations from 1.0 to 8 $N$ at 85° for picolinamide and at 68° for isonicotinamide. A first-order law is obeyed for either substance over the whole range of hydrochloric acid concentrations. As can be seen from Table III, the rate constants increase steadily with the hydrochloric acid concentrations. The rate constants for 0.1 $N$ hydrochloric acid were calculated from the corresponding Arrhenius equations.

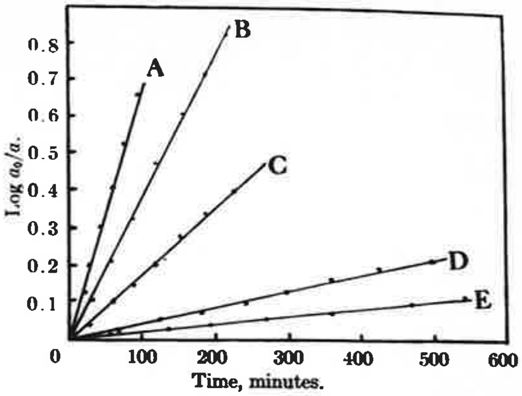

Fig. 1.—Hydrolyses of picolinamide in 0.1 $N$ hydrochloric acid over a range of temperatures: A, 139.5°; B, 129.5°; C, 119.5°; D, 99.5°; E, 90.5°.

TABLE III

RATE CONSTANTS AS FUNCTION OF THE HYDROCHLORIC ACID CONCENTRATION

| HCl, $N$ | Cor. $k_{\text{exptl.}}$ sec.$^{-1}$ × $10^4$ | HCl, $N$ | Cor. $k_{\text{exptl.}}$ sec.$^{-1}$ × $10^4$ |
|---|---|---|---|
| Picolinamide at 85° | | Isonicotinamide at 68° | |
| 0.100 | 0.058 | 0.100 | 0.020 |
| 0.970 | 0.392 | 0.980 | 0.373 |
| 1.94 | 0.875 | 1.96 | 0.775 |
| 2.94 | 1.43 | 2.98 | 1.29 |
| 3.86 | 1.85 | 3.91 | 1.83 |
| 5.73 | 3.28 | 5.02 | 2.56 |
| 6.85 | 4.35 | 5.80 | 3.18 |
| 7.83 | 5.18 | 7.92 | 4.52 |

## Discussion

It is of interest to consider the energies of activation and frequency factors of the Arrhenius equations as functions of the hydrochloric acid concentration for the non-heterocyclic[1] and heterocyclic amides.

Whereas, the energies of activation rise steadily for all amides with increasing acid concentration, the frequency factors divided by the respective acid concentrations, remain practically constant for the non-heterocyclic amides, but rise continuously for the heterocyclic amides. In the latter case, the increase in the energies of activation is just about compensated by the increase in the $A/[\text{HCl}]$ factors. The logarithms of the $A/[\text{HCl}]$ factors plotted against the respective energies of activation give straight lines for picolin- and isonicotinamide, as is shown in Fig. 2.

A satisfactory mechanism has not yet been advanced to account for the maxima in the rate constant *versus* acid curves for non-heterocyclic amides, though a number of suggestions have been made by various authors.[1] The occurrence of these maxima has been ascribed repeatedly to salt or complex formation.[4-6] The reason for the different behavior of the heterocyclic amides is not clear and it would be premature to offer any suggestions at this stage of the work.

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(4) T. W. J. Taylor, *J. Chem. Soc.*, 2741 (1930).

(5) V. K. Krieble and K. A. Holst, *J. Am. Chem. Soc.*, **60**, 2976 (1938).

(6) A. Benrath, *Z. anorg. allgem. Chem.*, **151**, 53 (1926).

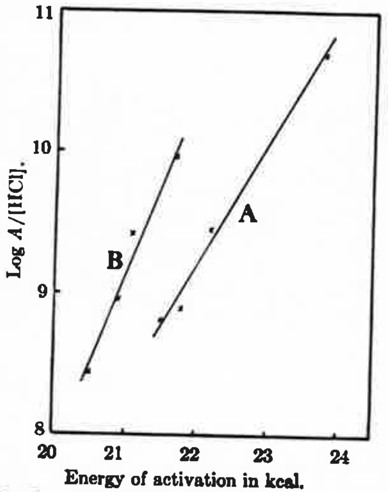

Fig. 2.—Log $A/[\text{HCl}]$ values as a function of corresponding energies of activation for picolinamide (A) and isonicotinamide (B).

A mechanism for the hydrolysis of nicotinamide was presented in a previous paper.[2] However, it is difficult to decide whether such a mechanism is really operative because of medium effects. The experimental results indicate that at low hydrochloric acid concentrations the experimental rate constants are proportional to the first power of the acid concentration and not to the second power as the mechanism, proposed previously, would require. A first power law would be obtained by assuming the following reaction to take place

$$\text{H}^+\text{RCONH}_3^+ + \text{H}_2\text{O} \longrightarrow \text{H}^+\text{RCOOH} + \text{NH}_4^+$$

The experimental rate constants, not considering medium effects, should then be given by

$$k_{\text{exptl}} = k_2[\text{H}_2\text{O}]\frac{K_2[\text{H}_3\text{O}^+]}{1 + K_2[\text{H}_3\text{O}^+]} \qquad (1)$$

If $K_2$ is small, $k_{\text{exptl}}$ is proportional to the first power of the hydrogen ion concentration, which is the case up to about 2 $N$ hydrochloric acid for the three heterocyclic amides. Any deviations can then be ascribed to medium effects. $k_2$ in equation 1 is a rate constant and $K_2$ an equilibrium constant pertaining to the dissociation of the amide.[2,7]

A detailed discussion of mechanisms will be reserved until more data are available for dilute solutions, the main purpose of the present paper being to ascertain the dependence of the experimental rate constants and the parameters of the Arrhenius equation on hydrochloric acid in concentrated solutions.

The three heterocyclic amides do not show very pronounced differences amongst themselves. The energies of activation for picolinamide are higher than those for the other two amides. It may also be mentioned that the energies of activation for the three amides plotted against the logarithms of their experimental rate constants for any one hydrochloric acid concentration do not give straight lines with slopes of magnitude 2.303$RT$, as was the case for other amides.[1]

(7) H. H. G. Jellinek and M. G. Wayne, THIS JOURNAL, 55, 173 (1951).

# POLAROGRAPHY OF PICOLINIC AND ISONICOTINIC ACID AND THEIR AMIDES

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*Received June 30, 1953*

The polarography of picolinic acid, isonicotinic acid and their amides has been studied over a range of *p*H values. In all cases the wave heights decrease rapidly when certain *p*H values are reached. In contrast to the acids, which show only one type of wave each, the amides have two different types of waves. The dependence of the wave heights on *p*H is discussed in terms of a recombination reaction taking place in the electrode interface.

A study of the acid hydrolysis of picolinamide, isonicotinamide and nicotinamide was made previously.[1] The analysis of reaction mixtures containing amide in the presence of its acid was carried out polarographically.

In the present paper, the polarography of pyridine carboxylic acids and their amides has been studied in greater detail. It presents a number of very interesting features, which can now be understood on the basis of theories advanced by Wiesner and Brdicka,[2] Koutecky and Brdicka[3] and Delahay.[4]

The polarography of picolinic and isonicotinic acid was previously studied by Tompkins and Schmidt.[5] However, their data are insufficient just in the range of *p*H values, where a sharp decrease in wave heights takes place. These acids and their amides have been examined here over a range of *p*H values from 1 to 12, and care has been taken to obtain sufficient data of the wave heights as a function of *p*H. The polarography of pyridine, quinoline and its derivatives was investigated more recently by Shchennikova and Korshunov.[5]

## Experimental

(a) **Apparatus.**—The polarograph was a "manual" instrument, constructed on the same lines as the "manual" instrument described by Kolthoff and Lingane.[6] An H-type cell was used consisting of a saturated calomel electrode in one compartment and a dropping mercury electrode in the

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(1) H. H. G. Jellinek and A. Gordon, This Journal, **53**, 996 (1949); H. H. G. Jellinek and J. R. Urwin, *ibid.*, **57**, 900 (1953).

(2) R. Brdicka and K. Wiesner, *Collection Czech. Chem. Communs.*, **12**, 138 (1947).

(3) J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

(4) P. Delahay, *J. Am. Chem. Soc.*, **73**, 4944 (1951).

(5) (a) P. C. Tompkins and C. L. A. Schmidt, *Univ. Calif. Publ. in Physiology*, **8**, No. 16, 229 (1943); (b) M. K. Shchennikova and I. A. Korshunov, *J. Phys. Chem., U.S.S.R.*, **22**, 503 (1948).

(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946

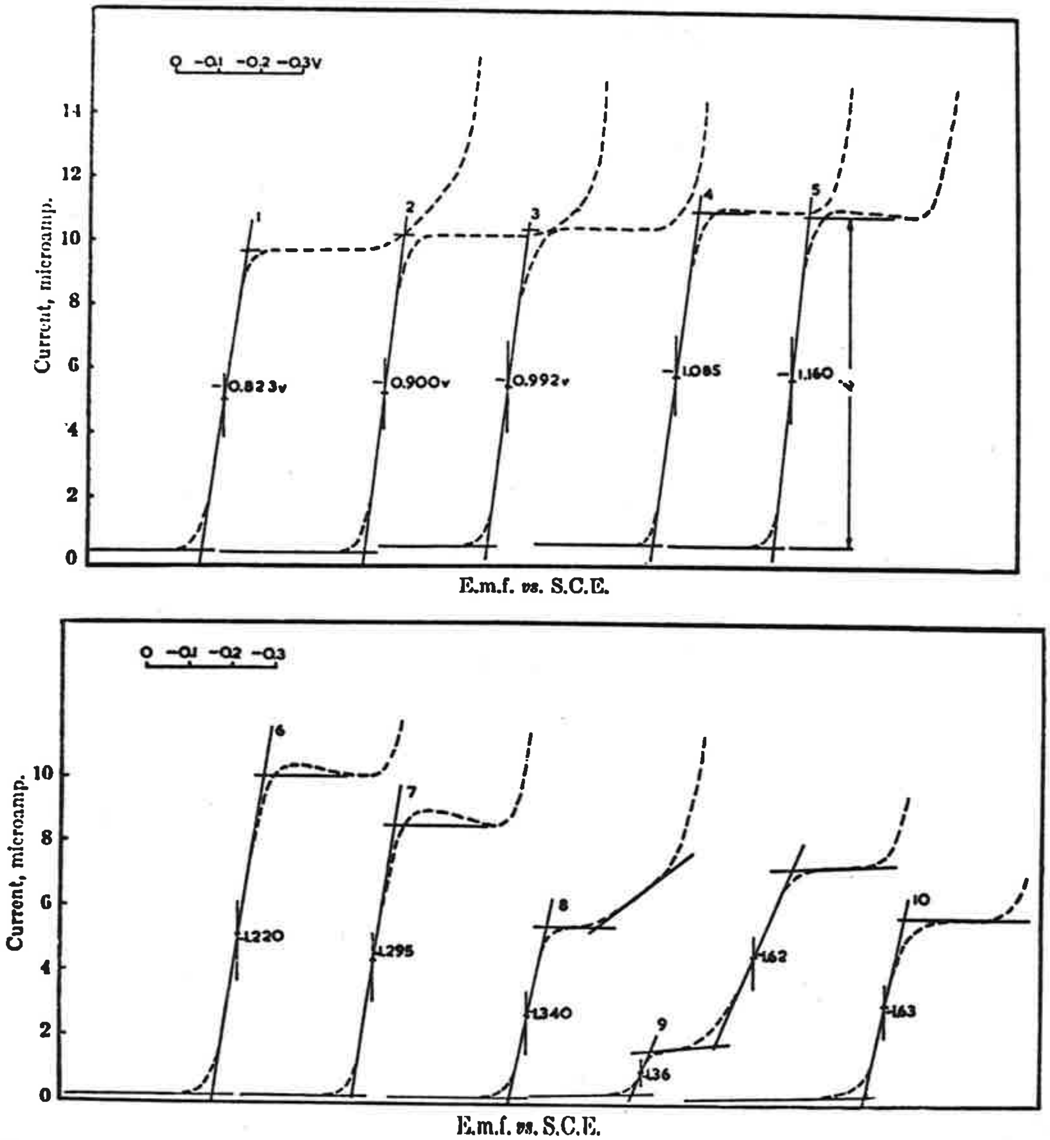

Fig. 1.—Polarographic waves of 1 × $10^{-3}$ *M* picolinamide at various *p*H values: 1 to 10, *p*H: 2.5, 3.45, 4.40, 5.48, 6.36, 7.12, 8.17, 8.93, 9.54 and 11.68, respectively. Ground solutions: 1 to 5, citric acid–phosphate buffer; 6 to 9, sodium barbiturate–HCl; 10, phosphate-caustic soda. Half-wave potentials in volts *vs.* S.C.E.

other, separated by an agar bridge, saturated with potassium chloride. The current measuring circuit consisted of a sensitive galvanometer with a long period (Guthrie type H.S.G. 1; undamped 27 seconds, maximum sensitivity 4 × $10^{-4}$ amp.; internal resistance 3,500 ohms).

Capillaries had internal diameters of 0.03 and 0.05 mm., the drop time was 4 to 6 seconds and the height of the mercury 72 and 64 cm., respectively. The height of the waves was evaluated by drawing straight lines through the residual, limiting currents and along the slope of the wave (see Fig. 1). The vertical distance of the two intersection points was taken as the height of the wave. When a maximum appeared, the value was taken as the height of the minimum. The oscillations were usually small, about 2% of the total wave height.

**(b) Materials.**—All materials were of Analar grade, except picolinic and isonicotinic acids and their amides.

Picolinic acid was prepared by oxidation of *α*-picoline with potassium permanganate according to Singer and McElvain.[7] The picolinic acid obtained in this way was recrystallized several times from an alcohol ether mixture and finally dried over phosphorus pentoxide (m.p. 136°).

Picolinamide was prepared from picolinic acid according to Camps.[8] The amide was recrystallized from an alcohol-benzene mixture and dried over phosphorus pentoxide (m.p. 106.5°).

Isonicotinic acid was obtained from B.D.H. and was recrystallized several times from an alcohol–benzene mixture. Isonicotinamide was obtained from the acid by the same method as that used for picolinamide (m.p. 156°).

## Experimental Results

**(a) Picolinic and Isonicotinic Acids.**—Table I shows wave heights expressed as $i_d^x = i_d/m^{2/3}t^{1/6}$ (where $i_d$ is in microamp., *m* in mg. and *t* in seconds) and corresponding half wave potentials in volts *ver-*

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(7) Singer and McElvain, *Org. Syntheses*, **20**, 70 (1940).

(8) R. Camps, *Archiv. Pharm.*, **240**, 240 (1902).

Table I

| Solution | | Picolinic acid | | | Isonicotinic acid | | | |
|---|---|---|---|---|---|---|---|---|
| | pH | $i_d^x$, μ amp. | $E_{1/2}$ vs. S.C.E., v. | pH | $i_d^x$, μ amp. | | $E_{1/2}$ vs. S.C.E., v. | |
| | | | | | I | II | | |
| McIlvaine's buffer solutions 0.2 M $Na_2HPO_4$ and 0.1 M citric acid | 2.25 | 5.10 | −0.930 | 2.24 | 4.60 | 0.41 | −0.855 | −1.01 |
| | 3.44 | 4.79 | −1.004 | 3.46 | 4.70 | 0.24 | −0.925 | −1.035 |
| | 4.50 | 4.90 | −1.077 | 4.45 | 4.95 | | −0.995 | |
| | 5.46 | 4.64 | −1.160 | 5.45 | 5.20 | | −1.070 | |
| | 6.46 | 4.61 | −1.260 | 6.43 | 4.95 | | −1.150 | |
| | 7.38 | 4.67 | −1.340 | 7.38 | 4.28 | | −1.236 | |
| | 7.84 | 4.61 | −1.382 | 7.83 | 3.61 | | −1.279 | |
| 0.1 M sodium barbitone + 0.1 N HCl Michaelis 1930 | 8.20 | 3.20 | −1.392 | 8.10 | 3.18 | | −1.300 | |
| | 8.60 | 2.32 | −1.415 | 8.48 | 2.56 | | −1.327 | |
| | 8.84 | 1.64 | −1.437 | 8.83 | 2.045 | | −1.357 | |
| | 9.25 | 1.11 | −1.462 | 9.17 | 1.375 | | −1.388 | |
| | 9.60 | 0.84 | −1.46 | 9.30 | 0.905 | | −1.40 | |
| 0.1 M $Na_2CO_3$ + 0.1 N HCl | 10.30 | 0.26 | −1.50 | 10.20 | 0.185 | | −1.44 | |
| 0.01 N HCl | 1.90 | 4.97 | −0.908 | 2.0 | 4.12 | 0.6 | −0.837 | −1.105 |
| M/20 Pot. hydrogen phthalate + 0.1 N HCl | 2.80 | 4.63 | −0.970 | 2.6 | 4.49 | | −0.901 | |
| | 3.75 | 4.84 | −1.040 | 4.0 | 4.85 | | −0.987 | |
| | 4.10 | 4.93 | −1.064 | ... | ... | | ... | |
| M/20 Pot. hyd. phthalate + 0.1 N NaOH | 5.04 | 4.88 | −1.137 | ... | ... | | ... | |
| 0.1 M Phosphate + 0.1 N NaOH | 9.6 | 0.503 | −1.49 | ... | ... | | ... | |
| | 10.9 | Small | −1.6 | ... | ... | | ... | |
| | 11.6 | ... | ... | 11.1 | Small | | −1.45 | |
| 0.1 M Phosphate + 0.1 N HCl | 6.55 | 4.63 | −1.280 | ... | ... | | ... | |
| | 7.46 | 4.63 | −1.340 | ... | ... | | ... | |
| NaOH | 13 | ... | ... | 12.5 | ... | | ... | |
| M/20 Borax + 0.1 N HCl | ... | ... | ... | 8.8 | 2.03 | | −1.376 | |

*sus* the saturated calomel electrode (S.C.E.) for different *p*H values and various buffered and unbuffered mixtures. The half-wave potentials are corrected for the voltage drop across resistances in the circuit. The cell resistance was less than 1000 Ω and no correction was made. It can be seen that the wave heights decrease rapidly in the region of *p*H values from 8 to 9 for picolinic acid and from about 7 to 9 for isonicotinic acid.

Any difference between the $i_d^x$ values found by Tompkins and Schmidt and our values is probably due to different methods of evaluation. The half-wave potentials for either substance increase with increasing *p*H values and agree quite satisfactorily with those found by Tompkins and Schmidt.[5] They can be expressed up to *p*H 9 by the equation

$$E_{1/2} = -0.081pH - 0.711 \text{ v.}$$

The half-wave potentials for isonicotinic acid can be expressed similarly

$$E_{1/2} = -0.080pH - 0.651 \text{ v.}$$

The relationship between wave height and concentration of either picolinic or isonicotinic acid was found to be linear for constant *p*H values.

(b) **Picolinamide and Isonicotinamide.**—The amides show some characteristic differences from the corresponding acids.

Table II shows $i_d^x$ values and corresponding half-wave potentials at various *p*H values in a number of ground solutions.

Table II shows that up to about *p*H 9, the waves for picolinamide show very similar characteristics to those obtained for picolinic acid. However, a second wave appears with a more negative half wave potential at about *p*H 9. The wave heights for this second wave increase as the *p*H is further increased, becoming constant when the *p*H values reach about 9 to 10. The half-wave potentials are independent of *p*H for this second wave. The first wave disappears completely when *p*H values of about 11 are reached. The second wave was used for the analysis of reaction mixtures containing picolinic acid and its amide, when investigating the hydrolysis of picolinamide.[1]

Unlike picolinamide, the wave heights as a function of *p*H do not decrease to zero with increasing *p*H in the case of isonicotinamide, but become constant, when a *p*H value of about 9 is reached. Apparently two waves are also involved in the case of isonicotinamide, but their half-wave potentials are so similar that a separation of the two waves does not take place. At a *p*H of about 9, the first wave has disappeared completely and the second wave, characteristic of the amide, is left.

It was observed by Tompkins and Schmidt,[9] in the case of nicotinamide, that a discontinuity appeared in the half-wave potentials as the *p*H increased. However, these authors did not seem to realize that two different kinds of waves are involved. The first wave is common to the acid and amide, whereas the second is only shown by the amide. Representative polarographic waves of picolinamide and isonicotinic acid over a range of *p*H values, selected from the available experimental data are shown in Figs. 1 and 2.

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(9) Reference 5a, p. 247.

TABLE II

$i_d^x$ = wave height/$m^{2/3}t^{1/6}$

| | Picolinamide | | | | | Isonicotinamide | | |
|---|---|---|---|---|---|---|---|---|
| | pH | $i_d^x$, μ amp. | | $E_{1/2}$ vs S.C.E., v. | | pH | $i_d^x$ μ amp. | $E_{1/2}$ vs. S.C.E., v. |
| McIlvaine's buffer solutions –0.2 *M* $Na_2HPO_4$ and 0.1 *M* citric acid | 2.50 | 6.57 | | −0.818 | | 2.25 | 6.08 | −0.730 |
| | 3.45 | 6.93 | | −0.895 | | 3.46 | 6.98 | −0.812 |
| | 4.40 | 6.93 | | −0.988 | | 4.46 | 7.10 | −0.902 |
| | 5.43 | 7.30 | | −1.080 | | 5.46 | 6.68 | −0.992 |
| | 6.36 | 7.25 | | −1.155 | | 6.44 | 5.98 | −1.066 |
| | 6.40 | 7.13 | | −1.153 | | 7.40 | 4.80 | −1.134 |
| | 7.07 | 6.98 | | −1.220 | | 7.84 | 4.17 | −1.167 |
| | 7.20 | 7.16 | | −1.218 | | ... | .. | ... |
| | 7.42 | 7.08 | | −1.238 | | ... | .. | ... |
| | 7.55 | 6.70 | | −1.258 | | ... | .. | ... |
| | 7.68 | 6.40 | | −1.276 | | ... | .. | ... |
| | 7.92 | 6.20 | | −1.290 | | ... | .. | ... |
| | 8.13 | 5.77 | | −1.305 | | ... | .. | ... |
| 0.1 *M* Sodium Barbitone + 0.1 *N* HCl ref. Michaelis 1930 | 7.12 | 6.83 | | −1.215 | | 8.13 | 3.92 | −1.186 |
| | 8.17 | 5.80 | | −1.295 | | 8.52 | 3.57 | −1.206 |
| | 8.58 | 5.06 | | −1.311 | | 8.88 | 3.38 | −1.222 |
| | 8.93[a] | 3.65[b] | | −1.337[b] | | 9.26 | 3.38 | −1.245 |
| | 9.17[a] | 2.34[b] | | −1.342[b] | | ... | .. | .. |
| | 9.54 | 0.935 | 3.64 | −1.360 | −1.620 | ... | .. | ... |
| 0.1 *M* $Na_2CO_3$ + 0.1 *N* HCl | ... | ... | | ... | | 10.22 | 3.49 | −1.282 |
| | ... | ... | | ... | | 10.98 | 3.34 | −1.300 |
| *M*/20 Pot. hydrogen phthalate + 0.1 *N* HCl | 2.85 | 6.88 | | −0.848 | | ... | .. | ... |
| | 4.12 | 7.34 | | −0.978 | | ... | .. | ... |
| *M*/20 Pot. hydrogen phthalate + 0.1 *N* NaOH | 5.08 | 7.50 | | −1.063 | | ... | .. | ... |
| | 6.58 | 7.10 | | −1.197 | | ... | .. | ... |
| 0.1 *M* $Na_2HPO_4$ + 0.1 *N* HCl | 8.26[a] | 3.24 | 2.17 | −1.317 | −1.613 | ... | .. | ... |
| 0.1 *M* $Na_2HPO_4$ + 0.1 *N* NaOH | 9.78 | 0.68 | 3.38 | −1.36 | −1.617 | 10.1 | 3.43 | −1.32 |
| | 11.04 | ... | 3.38 | ... | −1.617 | 11.6 | 3.43 | −1.33 |
| | 11.68 | ... | 3.42 | ... | −1.627 | ... | .. | ... |
| NaOH | ... | ... | | ... | | 12.4 | 3.12 | −1.36 |

[a] 2nd wave appears, poorly defined. [b] Values uncertain.

The half-wave potentials as a function of *p*H for the first waves of picolinamide can be expressed by the equation

$$E_{1/2} = -0.087pH - 0.597 \text{ v.}$$

The half-wave potentials for isonicotinamide can be expressed by

$$E_{1/2} = -0.083pH - 0.526 \text{ v.}$$

The relationship between wave height and concentration of amide for constant *p*H values was found to be linear.

It was pointed out above that the concentration of the amide can be determined in the presence of its acid polarographically,[1] if the *p*H of the ground solution is high enough (*ca.* *p*H 11.5). The relationship between wave height and concentration at such a *p*H value is linear. Figure 3 gives a typical series of polarograms for picolinamide at definite stages of the hydrolysis. The hydrolysis was carried out in 0.1 *N* HCl at 130°. The solution was diluted five times with phosphate buffer. A ground solution of *p*H 11.5 was thus obtained.

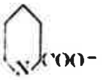
## Discussion

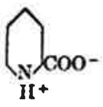
The wave heights as a function of *p*H for picolinic acid show the characteristics of a current composed of a diffusion component and a component due to a recombination reaction. Such cases have been discussed in a simplified way by Wiesner and Brdicka.[2] A strict derivation was given by Koutecky and Brdicka[3] and a somewhat simpler one by Delahay.[4] A paper by Knobloch on catalytic evolution of hydrogen due to nicotinamide is also of interest in this connection.[10]

As the picolinic acid and its amide give similar current *versus* *p*H curves, the reaction current cannot be due to the undissociated carboxyl group, but must be due to a reaction of the nitrogen in the ring with a proton. Thus the reaction taking place in the interface is

$$B + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH^+$$

where

B ~ 

and BH⁺ ~ 

The species ultimately discharged at the electrode is $BH^+$ in this particular case. B can also stand for the respective amide. The rate constants $k_1$ and $k_2$ are interrelated by the dissociation constant $K = k_2/k_1$.

Investigations of the absorption spectra of picolinic acid as a function of *p*H gave a value for the

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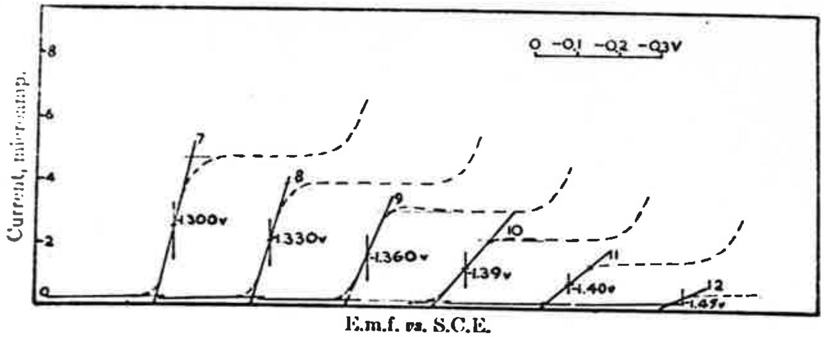
(10) E. Knobloch, *Collection Czech. Chem. Communs.*, **12**, 407 (1947).



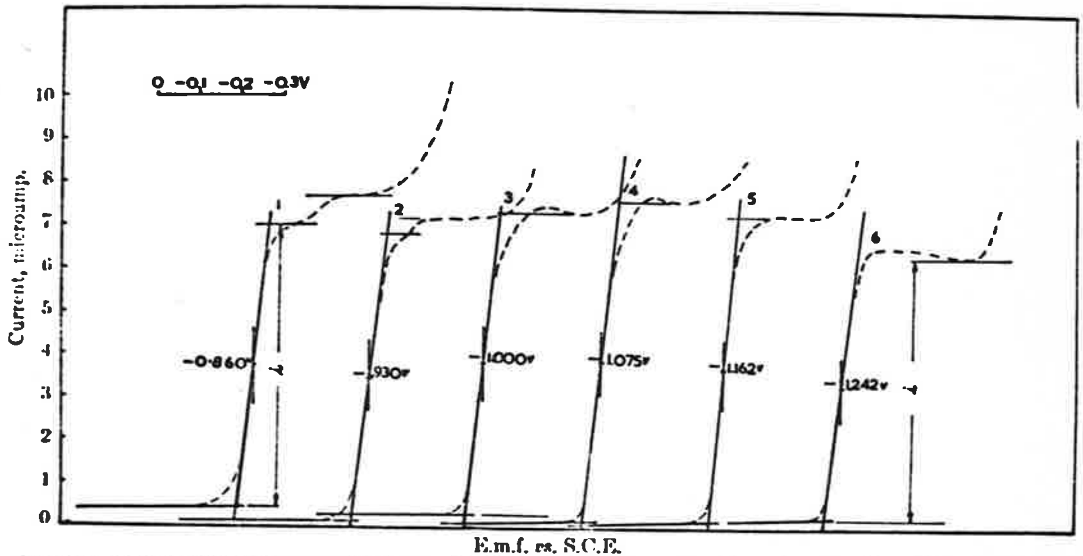


Fig. 2.—Polarographic waves of $1 \times 10^{-3}$ *M* isonicotinic acid at various *p*H values: 1 to 12, *p*H: 1.90, 3.46, 4.45, 5.45, 6.43, 7.38, 8.10, 8.48, 8.83, 9.17, 9.3 and 10.2, respectively. Ground solutions: 1 to 6, citric acid–phosphate; 7 to 11, sodium barbiturate–HCl; 12, sodium carbonate–HCl. Half-wave potentials in volts *vs.* S.C.E.

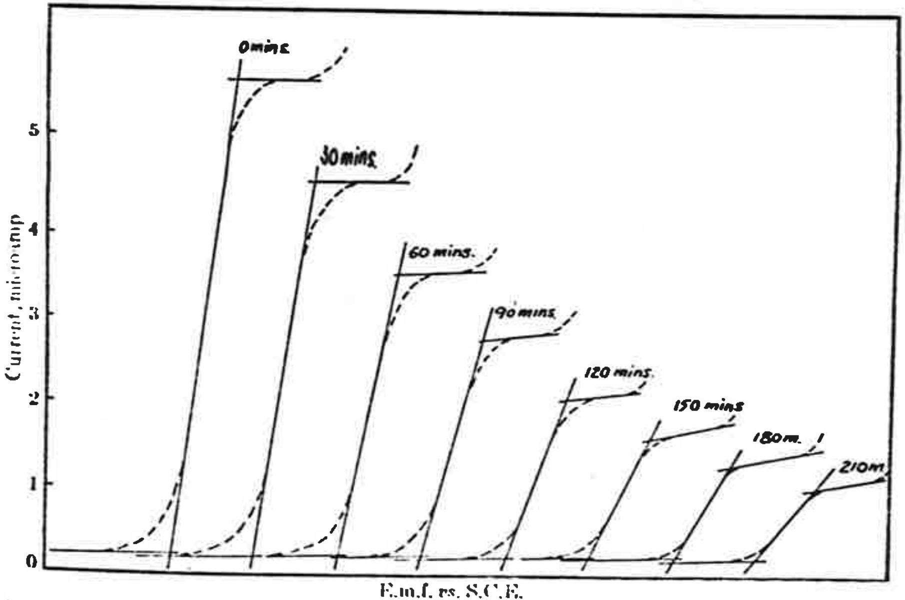


Fig. 3. Polarographic waves for different stages of hydrolysis of picolinamide in 0.1 *N* HCl at 130°; reaction mixtures diluted five times with phosphate buffer; final *p*H 11.5.

dissociation constant $K = 10^{-1.6}$ where $K = ([B]\cdot[H^+]/[BH^+])$.

Koutecky and Brdicka[3] have derived an expression relating the rate constant of recombination $k_1$, the dissociation constant $K$ and the ratio $i/i_\infty$ at definite $p$H values. $i$ is here the wave height at any $p$H, and $i_\infty$ the wave height at a low $p$H, where the current is completely diffusion controlled (100% $BH^+$). For $K \gg [H^+]$, this expression reads as

$$Y_1 = \frac{k_1[H^+]^2 t_1}{K} \qquad (1)$$

where

$$f(Y_1) = \frac{6}{7\sqrt{\pi}Y_1^{7/6}}\int_0^{Y_1} F(Y)\,dY = \frac{i}{i_\infty} \qquad (2)$$

Ruetschi and Trumpler[11] have pointed out that a writing error is inherent in formula (2) as given by Koutecky and Brdicka.[3] Equation 2 above is the form as presented by the Swiss authors. A table of corresponding $Y_1$ and $f(Y_1)$ values was given by the Czech authors.[3]

Equation 1 also can be written in logarithmic form

$$\log k_1 = 2(pH + {}^1/_2 \log Y_1) - pK - \log t_1 \qquad (3)$$

$t_1$ is the mercury drop time.

The theoretical and experimental curves for $i/i_\infty$ as function of $p$H are shown in Fig. 4. The theoretical curve was obtained by calculating $k_1$ for $i/i_\infty = 0.5$, $t_1 = 4.6$ seconds, $k_1 = 10^{14.3}$ sec.$^{-1}$ (mole/l.)$^{-1}$. The theoretical curve shows deviations from the experimental one in the same directions as found by Koutecky and Brdicka for phenylglyoxylic acid[3]) and by Ruetschi and Trumpler for $p$-phenylazobenzoic acid.[11]

The respective rate constants for picolinamide, isonicotinic acid and its amide were calculated in the same way as the rate constants for picolinic acid. The dissociation constants for these compounds were obtained from spectroscopical measurements. The results are summarized in Table III.

TABLE III

RATE CONSTANTS CALCULATED ACCORDING TO THE THEORY OF KOUTECKY AND BRDICKA[3]

| | $p$H$^1/_2$ | $pK$ | log $t_1$ | log $k_1$ |
|---|---|---|---|---|
| Picolinic acid | 8.5 | 1.6 | 0.66 | 14.3 |
| Picolinic amide | 8.9 | 2.1 | .66 | 14.6 |
| Isonicotinic acid | 8.4 | 1.7 | .66 | 14.0 |
| Isonicotinic amide | 7.0 | 3.6 | .66 | 9.8 |

The waves appearing at higher $p$H values, in the case of the amides, are of quite a different nature to those at lower $p$H values. It is clear that these waves do not belong to the dissociation equilibrium considered above; otherwise, the height of these waves should have the same value as that belonging to the first wave at low $p$H values. That this is not the case emerges clearly from the waves belonging to isonicotinamide.

It appears that the second wave has probably the same height over the whole range of $p$H values. Moreover, whereas the half wave potentials of the first waves are a function of $p$H, this does not seem to be the case for the second wave. The second wave of picolinamide has much more negative half wave potentials than the corresponding waves for isonicotinamide. This is the reason why these waves appear only at high $p$H values in the case of picolinamide. As the $p$H decreases, the potential for the discharge of hydrogen becomes more positive and thus the second amide waves are completely masked. The reason why there are no second waves appearing for picolinic and isonicotinic acids is probably that the half wave potentials are more negative than the potentials for the discharge of hydrogen. Thus, the introduction of amido groups facilitates the type of reduction corresponding to the second waves. The number of electrons involved in this reduction can be calculated from the Ilkovic equation and amounts for picolinamide and isonicotinamide to 2.36. (Diffusion coefficient $5.8 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$, this is the value for pyridine.)

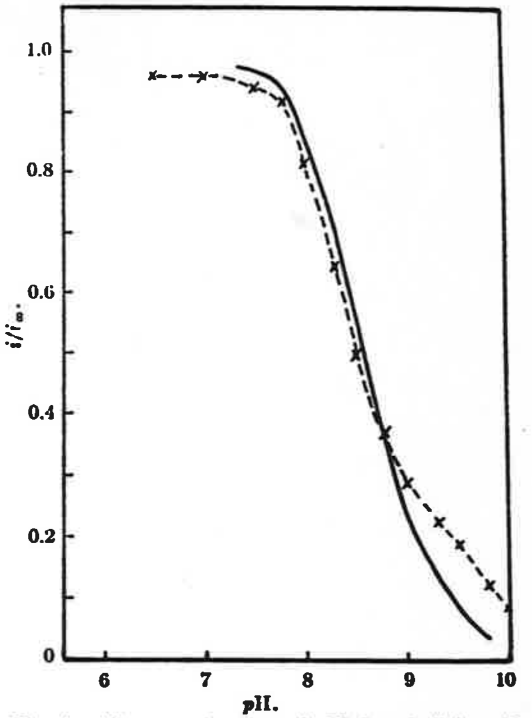


Fig. 4.—$i/i_\infty$ as a function of $p$H for picolinic acid: —x—, experimental; ——, theoretical curve according to equation 3 ($t_1$ = 4.6 sec., $K = 10^{-1.6}$, $p$H$^1/_2$ 8.5).

There is an indication of another small wave in the case of isonicotinic acid at lower $p$H values (see Fig. 2). It is not unlikely that this wave is due to the species B.

Although Tompkins and Schmidt[5,9] advance some suggestions as to the electrode reactions involved in the various reductions, the present authors prefer to refrain from any speculations in this respect.

It is the authors' pleasure to thank Mr. W. G. Jones, Division of Industrial Chemistry, C.S.I.R.O., for the construction of the II-type polarographic cell.

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(11) P. Ruetschi and G. Trumpler, *Helv. Chim. Acta*, **35**, 1957 (1952).

# ULTRAVIOLET ABSORPTION SPECTRA AND DISSOCIATION CONSTANTS OF PICOLINIC, ISONICOTINIC ACIDS AND THEIR AMIDES

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*Received February 20, 1954*

Ultraviolet absorption spectra of nicotinic acid and its amide as a function of *p*H values were presented in two previous communications.[1,2] Dissociation constants were derived from the experimental data. This paper brings an extension of the work to picolinic, isonicotinic acid and their amides. When the work comprising this paper was actually completed, a paper by Evans, Herington and Kynaston[3] was published dealing with the absorption spectra and dissociation constants of the pyridine monocarboxylic acids.

## Experimental

**Materials.**—Isonicotinic acid, picolinic acid, isonicotinamide and picolinamide were the same samples as described in a previous paper.[4] All other chemicals were of Analar grade.

**Apparatus.**—Measurements were made with a Hilger Uvispek spectrophotometer. *p*H values were determined by means of a glass electrode.

**Solutions.**—Solutions were prepared by adding requisite amounts of hydrochloric acid solutions and solutions of the amide or acid to 0.05 *M* sodium acetate and making up the volume to a total of 50 ml. The concentrations of the respective acid or amide ranged from $1 \times 10^{-4}$ to $5 \times 10^{-4}$ *M*. The ionic strength of the solutions down to about *p*H 3.5 had a constant value of 0.01. The measurements were carried out at room temperature, 20 ± 2°.

## Experimental Results and Discussion

The absorption spectra as a function of *p*H values for picolinamide and isonicotinamide are shown in Figs. 1 and 2. The spectra of the respective acids will not be presented, as they have been given by Herington and co-workers[3] and we have found no essential differences. The spectra of picolinic acid show maxima at about 2650 Å. and a shoulder, which shift with the *p*H values in the region of about 2700 Å. At very low *p*H values the maximum absorption shifts to longer wave lengths. There are indications of two pairs of isosbestic points in the region of 2350 and 2750 Å.

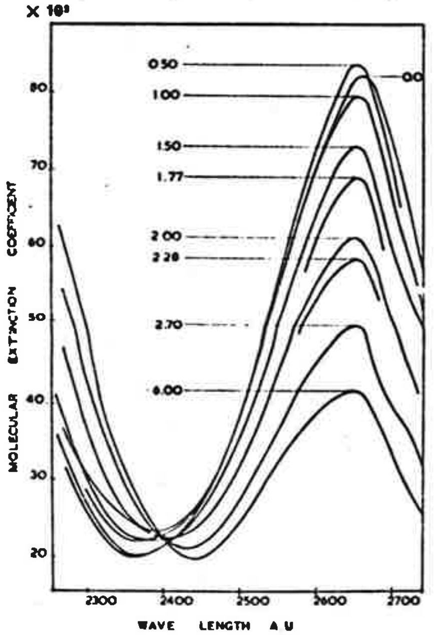

Fig. 1.—Absorption spectra of picolinamide at various *p*H values.

Picolinamide shows absorption maxima at 2655 Å. and a definite isosbestic point at 2400 Å., the absorption curves for *p*H values 0 and lower do not pass through this isosbestic point.

Isonicotinic acid presents a picture of greater complexity. The absorption maxima shift appreciably with *p*H values. The absorption spectra of isonicotinamide, on the other hand, are again simpler. The absorption maxima shift moderately with *p*H values from about 2680 to 2630 Å. There are indications of two isosbestic points at about 2800 and 2340 Å.

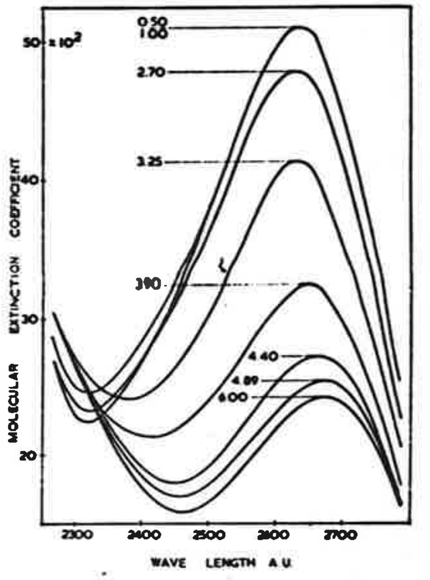

Fig. 2.—Absorption spectra of isonicotinamide at various *p*H values.

It was ascertained that Beer's law was obeyed at constant *p*H values for the ranges of concentrations of acid and amide used in this work.

Molecular extinction coefficients for these compounds as function of *p*H values for constant wave

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(1) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, THIS JOURNAL, 53, 414 (1949).

(2) H. H. G. Jellinek and M. G. Wayne, *ibid.*, 55, 173 (1951).

(3) R. F. Evans, E. F. G. Herington and W. Kynaston, *Trans. Faraday Soc.*, 49, 1284 (1953).

(4) H. H. G. Jellinek and J. R. Urwin, THIS JOURNAL, Vol. 58, 168 (1954).

lengths are shown in Figs. 3 and 4. The theoretical curves are drawn through the experimental points and will be discussed below.

Picolinic acid shows two distinct sections and the points appear to pass through a maximum at low *p*H values. The points for picolinamide also pass through a maximum at low *p*H values.

Isonicotinic acid shows a very distinct maximum at intermediate *p*H values, whereas isonicotinamide passes through a maximum at low *p*H values.

The acids have an acid group and a basic group each, whereas the amides have two basic groups. The respective equilibria can be written as follows

$$^{+}HNRCOOH + H_2O \rightleftharpoons NRCOOH + H_3O^{+}$$

$$NRCOOH + H_2O \rightleftharpoons NRCOO^{-} + H_3O^{+}$$

and

$$^{+}HNRCONH_3^{+} + H_2O \rightleftharpoons H^{+}NRCONH_2 + H_3O^{+}$$

$$^{+}HNRCONH_2 + H_2O \rightleftharpoons NRCONH_2 + H_3O^{+}$$

Calculations were carried out to fit the experimental points in Figs. 3 and 4 by choosing suitable $pK_a$ values and *p*H values for the isoelectric points. The calculations were carried out either according to the first method described in the previous paper on nicotinic acid[1] or that given in the paper on nicotinamide,[2] respectively. The curves drawn through the experimental points in Figs. 3 and 4 were obtained in this way.

Picolinic acid could be fitted by two constants, picolinamide by one constant; the decrease in extinctions at low *p*H values may be an indication of the equilibrium pertaining to the amido group. Isonicotinic acid could be fitted very well by two dissociation constants. The extinction values for the species $^{+}HNRCOOH$ are here smaller than those for NRCOOH for this particular wave length in contrast to nicotinic acid where the reverse was the case.[1] Isonicotinamide could be fitted by one $pK_a$ value and there is an indication of an equilibrium pertaining to the amido group at low *p*H values.

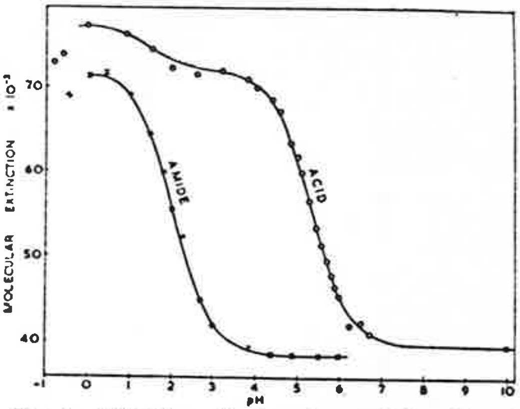

Fig. 3.—Molecular extinctions for picolinic acid and picolinamide as a function of *p*H values. Curves are calculated, points are experimental (λ ~2650 and 2600 Å., respectively).

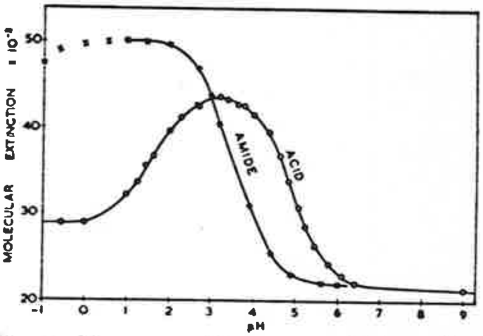

Fig. 4.—Molecular extinctions for isonicotinic acid and isonicotinamide as a function of *p*H values. Curves are calculated, points are experimental (λ ~2600 Å.).

All $pK_a$ values are comprised in Table I. The values marked by asterisks are thermodynamic dissociation constants, where the ionic strength has been taken into account according to the Debye–Hückel theory. Table I contains also values obtained by Herington and co-workers[3] and values for benzoic acid, pyridine and acetamide.

It can be seen that the $K_a$ values belonging to the carboxyl groups are very similar, though somewhat smaller than that for benzoic acid. However, there are some discrepancies in the values for the nitrogen in the ring. The difference between our value and that of Herington, *et al.*,[3] is due to the fact that our solutions contained hydrochloric acid for small *p*H values, whereas Herington, *et al.*, used sulfuric acid. These authors pointed out that the extinctions decreased in HCl solutions with decreasing *p*H, whereas the reverse is true for sulfuric acid solutions. They ascribe this different behavior to the formation of a hydrochloride. The discrepancies found for the nitrogen of nicotinic acid probably are due to the less accurate photographic method used by Hughes, Jellinek and Ambrose, as pointed out by Herington and co-workers.[3]

TABLE I

ISOELECTRIC POINTS AND $pK_a$ VALUES

| Substance | Iso-electric point | Carboxyl group | Nitrogen ring | Amido group | Ref. |
|---|---|---|---|---|---|
| Picolinic acid | 3.48 | 5.40* | 1.60 | ... | This work |
| | 3.21 | 5.40* | 1.08* | ... | 3 |
| Isonicotinic acid | 3.45 | 4.95* | 1.70 | ... | This work |
| | 3.31 | 4.81* | 1.77* | ... | 3 |
| Nicotinic acid | 4.24 | 4.95* | 3.55* | ... | 1 |
| | 3.42 | 4.83* | 2.08* | ... | 3 |
| Picolinamide | ... | ... | 2.10 | <−1.0 | This work |
| Isonicotinamide | ... | ... | 3.61* | <−1.0 | This work |
| Nicotinamide | ... | ... | 3.35* | 0.5 | 2 |
| Pyridine | ... | ... | 5.12* | ... | 5 |
| | | | 5.16* | ... | 7 |
| Benzoic acid | ... | 4.20 | ... | ... | 6 |
| Acetamide | ... | ... | ... | −0.5 | 6 |

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(5) E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, THIS JOURNAL, 53, 410 (1949).

(6) "Handbook of Physics and Chemistry," Chemical Rubber Publishing Company, Cleveland, Ohio.

(7) R. F. G. Herington, *Disc. Faraday Soc.*, No. 9, 26 (1950).

It is possible that the decrease in extinctions for the amides at low *p*H values is due also to hydrochloride formation, though in the present work it has been taken as an indication for the dissociation of the amido group.

The weakest acid is picolinic, where the carboxyl group is in *ortho* position to the nitrogen in the ring. The nitrogen in the ring is a weaker base in the case of isonicotinamide than for isonicotinic acid. It also may be noted that the nitrogen in the ring for the acid shows a similar trend as that for the corresponding picolines.[6] Whereas the methyl groups, being electron-donating, increase the basic strength of the nitrogen, the carboxyl groups act in the opposite way. β-Picoline is the weakest base, whereas nicotinic acid is the strongest. (Thermodynamic dissociation constants for α, β and γ picoline are as follows: $8.77 \times 10^{-9}$, $4.54 \times 10^{-9}$ and $10.62 \times 10^{-9}$, respectively.[7])

The basic strength of the amido groups is smaller than that for acetamide with the exception of nicotinamide, which is appreciably stronger.