PHYSICOCHEMICAL STUDY OF POLY(ISOPRENE:STYRENE) BLOCK COPOLYMERS

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SUMMARY

PHYSICO CHEMICAL STUDY OF POLY(ISOPRENE:STYRENE) BLOCK COPOLYMERS

Anionic polymerization using the 'living' polymer method founded by Szwarc was employed to synthesize a series of A-B block copolymers of polyisoprene and polystyrene. By meticulous care in purging all glassware, solvents, monomers and initiator a technique of synthesis was achieved which enabled 'tailoring' of these copolymers to the required specifications. Polymerization was carried out in benzene, initiated by n-butyllithium. A series of ten block copolymers were prepared: five of them having a constant molecular weight of 100,000 and a composition range of 11-78% by weight of polystyrene, three others with a molecular weight of 250,000 and a composition range of 11-50% by weight of polystyrene and two others of molecular weight 500,000 and composition of 25% and 50% by weight of polystyrene.

The microstructure of the polyisoprene sequence was investigated by using nuclear magnetic resonance spectroscopy (NMR). Unfortunately the aliphatic protons of the polystyrene sequence absorbed in the same region as the polyisoprene. This made the estimation of the microstructure for the high polystyrene blocks difficult. However, it was found that an arbitrary correction could be applied to allow for this background signal. The microstructure of the polyisoprene sequence was virtually the same for all the blocks and

corresponded to the microstructure of the polyisoprene homopolymers. The composition of the block copolymers was determined by using ultra-violet spectroscopy.

Gel permeation chromatography (GPC) proved the absence of any homopolymer in the blocks and enabled the calculation of a complete molecular weight distribution curve from which the values of $\bar{M}w$, $\bar{M}n$ and $\bar{M}w/\bar{M}n$ could be obtained. These values were compared with those obtained from the classical light scattering and osmometric methods. Also, a GPC 'universal' calibration curve was constructed for the copolymers based on the hydrodynamic volume as the universal size-parameter.

Configurational and thermodynamic parameters were determined from viscosity, light scattering and osmometry data. These parameters were studied as a function of the nature of the solvent, the molecular weight and the composition of the block copolymers. Three intrinsically different solvents were employed. Toluene - a good solvent for both parent homopolymers, cyclohexane - a good solvent for polyisoprene but poor for polystyrene; and methyl isobutyl ketone - a poor solvent for both parent homopolymers. Measurements under theta conditions were also made. The results in solvents equally good or equally poor for both parent homopolymers suggested that the distribution of segments is similar to that of normal homopolymers. This means that in non-preferential solvents the copolymer chain can be considered as a random distribution of segments. For this reason solution theories developed for homopolymers and based on this type of distribution, are also applicable to the copolymer systems. In preferential solvents, such as cyclohexane, a different behaviour was indicated. The results could be best explained by assuming that some degree of intramolecular phase separation was occurring.

Intrinsic viscosity against temperature plots for the block copolymers in cyclohexane, methyl cyclohexane and decalin confirmed the general behaviour of the copolymers in preferential solvents. The results were explained by assuming that a phenomenon of intramolecular phase transition was occurring at a characteristic temperature T_p.

The results of the hydrodynamic studies provided support for the validity of two-parameter semi-empirical theories, developed originally for flexible homopolymers. Such theories were applicable even in preferential solvents provided the operational temperature was above the transition temperature T_p.

The morphology of solvent cast films of the copolymers was studied by measuring the glass transition temperature using a differential scanning calorimeter (DSC). In all cases multiple glass transitions were observed. Depending on the casting conditions, the multiple transitions were assigned either to the pure homopolymer phase, or to a mixed phase.

The mixed phase transition was found to be a function of composition. The results suggested domain formation in the bulk copolymer.

This thesis contains no material previously submitted for a degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.

<u>Mario Girolamo</u>

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Chapter 1

INTRODUCTION.

Although the dilute solution properties of polymers have been studied extensively for many years, some of these investigations have involved materials having ill-defined distributions in molecular weight. Since most theories of dilute polymer solutions assume the use of 'monodisperse' samples,[1] it is evident that conclusions based on such results could be misleading. This applies even more so to copolymers whose heterogeneity in molecular weight is usually higher than the corresponding homopolymer, with the added disadvantage of possessing a possible heterogeneity in composition. Previously, so called 'monodisperse' polymers could only be obtained by the classical fractionation technique. This of course is laborious, time-consuming and requiring large amounts of polymer, with no guarantee of the homogeneity of the fractions obtained. This is even more complicated for copolymers, which strictly should be fractionated both in terms of molecular weight and composition - a problem which presents practical difficulties.[2] It is not hard to see that fractionation of these copolymers could possibly lead to a more heterogeneous product than the starting material. For this reason earlier work on solution properties of systems, employing this technique of obtaining homogeneous polymers, should be treated with caution.

The advent of recent techniques in aniomic polymerization, employing the 'living' polymer method firstly discovered by Szwarc,[3-7] has opened the road to the possible synthesis of narrow molecular weight distribution polymers and also narrow composition in the case of copolymers. Under favourable conditions, this technique can lead to polymers which are more appropriate for dilute solution studies, without further working.

Recent theoretical developments,[8] concerning the dilute solution properties of linear macromolecules, have generated renewed interest in this area of study. Knowledge of the statistics of polymer chains, their thermodynamic and configurational properties has been considerably augmented in the past few years. At the present time there is a well documented body of theories which allow explanation of the majority of known phenomena when applied to homopolymers. Unfortunately the same cannot be said for the case of copolymers. At this stage the only theories applicable to copolymers are merely extensions of theories originally derived for flexible homopolymers. Such extensions and generalizations are far from satisfactory and must always be treated with reservations. Where they are satisfactory, the theories are simply used as they stand. In situations where the theories are inadequate to explain the solution behaviour of these copolymers, extra parameters must be introduced which are characteristic of the copolymer. Such parameters would be the composition and extra interaction parameter, needed to express the effects of the interactions between the unlike monomer units in the composite system. However, the proper objective of any physicochemical investigation of copolymers in solution, is to try and explain the properties of the composite system in terms of those of the components, with the introduction of a minimum number of new parameters.

Another important consideration when dealing with copolymers, is the configuration of the polymer chain. This is important both from the point of view of determining their properties and in determining whether certain theories, based on a Gaussian distribution law of chain elements, are applicable to systems which, because of their nature, may possess deviations from such configurations (both in the solution and solid state). Until recently the application of such theories to solutions of copolymers has not been pursued to any extent and progress in this field has been slow, due to the complexity of the subject. Thus investigations of copolymer solution properties is relatively only in the initial stages. Because of the wealth of information which can be obtained from such solution studies and because it is the copolymers which are likely to supply the increased diversification in properties being demanded by modern technology, it is important that such studies be pursued. The optimistic view must be, that eventually a body of theories will be developed which can account for the various phenomena occuring in such composite systems as copolymers.

For the purpose of this project, it was decided to prepare a series of block copolymers having varying molecular weight with constant composition and varying composition with constant molecular weight, as well as possessing uniform molecular weight and composition distribution. In short, the aim was to 'tailor-make' a series of block copolymers having predetermined specifications, which would be suitable for an extensive physicochemical study. The purpose of the study was to determine the effect of various parameters, such as molecular weight, composition and nature of the solvent on the dilute solution properties, as well as testing the applicability of certain solution theories originally derived for flexible homopolymers. In this respect the study presented is believed to be more comprehensive than any previously reported.[9,10] Previous studies of solution properties of block copolymers have been almost entirely devoted to polystyrene-polymethylmethacrylate in various solvents.

The parent homopolymers of the block copolymers were chosen to be polystyrene and polyisoprene, because these two homopolymers have been reasonably well characterized in terms of their solution behaviour in various solvents. The method of preparation also governed the choice of possible monomers. Even more important, styrene and isoprene were chosen because of their widely diverging physical properties. At normal temperatures polystyrene is hard and brittle whereas high cis-1,4 polyisoprene is a rubber, similar in properties to natural rubber. The joining together of two such different homopolymers to form a block copolymer should result in some interesting physical properties of the bulk material (as has recently been recognized[11,12]) as well as some interesting and possibly unusual solution behaviour. Also, homopolymer solution theories, would be more rigorously tested when applied to copolymers made up of such differing homopolymer constituents, than when applied to copolymers containing very similar homopolymer segments.

To achieve the aim of the synthesis, the method of anionic termination-free polymerization, firstly realized by Szwarc[3-7] was employed. This method is generally referred to as 'living' polymerization. The system used in this work was the butyllithium initiator in benzene solvent. This has a number of advantages. Firstly, the initiator is monofunctional and produces an active polymer with only one 'living' end, which allows the production of two sequence A-B type block copolymers. This is in contrast to the three sequence A-B-A type block copolymer produced by difunctional initiators, such as sodium naphthalene in tetrahydrofuran solution.[13] Secondly, it produces the polyisoprene sequence having a high cis-1,4 content[14] and the polystyrene being highly syndiotactic, when the system is pure.[15] Thirdly, the reaction is sufficiently slow to allow the batch technique, in which monomer and initiator are mixed in a single operation, to be used.

Although the literature is replete[16,17] with various methods for the synthesis of block copolymers by both free radical and ionic mechanisms, virtually none of the procedures are accompanied by comprehensive characterization data. This is unfortunate, as polymer characterization must be carried out if some insight into the efficiency and efficacy of the synthesis procedure is to be obtained. This is apart from the wealth of information on the properties of the polymer which can be obtained from such a study.

The first attempt at the dilute solution behaviour of copolymers, both from a theoretical and experimental approach, was made by Stockmayer and coworkers.[18] Following this several other authors[19-21] have attempted to predict some of the solution and fractionation behaviour of block copolymers. Lautout-Magat[21] has applied the Guggenheim[22] semi-chemical method to the study of the thermodynamic properties of block copolymers. The findings suggest that the approximations obtained by the Guggenheim method are no better than the more simple calculations based on the mean value of the solubility parameters of the constituent homopolymers. This approach was initially used by Scott[23] in his discussion of the self-compatibility of copolymers. Kilb and Bueche[19] have used the Flory-Huggins[24] lattice model and find that the solubility of a block copolymer should be critically dependent on the heat of interaction of the various polymer segments with the solvent and be independent of the distribution of these segments along the polymer chain. Evidence both in support[25,26] of and in contradiction[13] to this theory have been reported. The only possible conclusions from these works is that the solubility of a block copolymer should lie somewhere between that of the corresponding homopolymers. These workers made no attempt to consider the effect of the nature of the monomers and the solvent on the properties measured.

More recently reported studies on the solution properties of block copolymers have been almost entirely devoted to polystyrene-polymethylmethacrylate (SM), in various solvents. The results are often contradictory. While some authors[27,28] found that the intrinsic viscosities $[\eta]$ and chain dimensions of block copolymers are larger than those of either homopolymers, of equal degree of polymerization, others[29-31] made the opposite observation. Inagaki[32] tried to explain this apparent contradiction by grouping the data into two classes, the first for samples containing 46-62% of polystyrene and the second for all other compositions. A regular change of properties with change of molecular weight within these classes is then observed. However, his observations are restricted to the (SM) block system in one solvent (toluene) and therefore cannot be generally valid. Also when applied to limiting low contents of one of the parent polymers, it gives wrong results. Nevertheless, this observation probably brings out one important point, i.e., that the composition is an important parameter in determining the solution properties of block copolymers and should not be neglected as some authors have done.

There is also little agreement as to the configuration a block copolymer molecule may assume in solution. It is now well known that the incompatibility of two different polymers in the presence, as well as in the absence, of diluent is a general rule rather than an exception.[33-35] This fact has led some authors to postulate that a block copolymer composed of an incompatible homopolymer pair would always exhibit a phenomenon of intramolecular (or intrachain) phase separation, irrespective of the nature of the solvent.[27-30] This idea initially originated from the analogy with a ternary system, containing a mixture of two polymers and the solvent and which can exhibit intermolecular phase separation.[27] From a qualitative consideration of this analogy, some authors[36,37] arrived at the conclusion that intramolecular phase separation could not take place at all, unless the parent homopolymers in the given solvent have extremely poor compatibility. There is no general agreement as to whether this phenomenon is always present in block copolymer solutions, or as to the conditions leading to it. Nevertheless many authors have attempted to interpret certain anomalies found in such solutions as the result of this effect. There is much evidence now that this same phenomenon becomes apparent for certain block copolymers in bulk phase.[38,39] However, in view of the solubilizing effect of the solvent in a ternary system involving two incompatible polymers,[34] there is doubt whether the phenomenon would always take place in block copolymer chains in infinite dilution. Optimistically, one might expect that the phenomenon should be influenced by molecular weight, composition, architecture of the block copolymer, the extent of dilution and also the nature of the solvent. If one is to gain insight into this effect then a careful study considering all these parameters should be undertaken.

Another problem (related to the above) is to what extent the shape, which the block copolymer molecule assumes in solution, affects the segmental distribution, i.e., the deviation from a normal Gaussian distribution. As most dilute solution theories are based on a Gaussian distribution of segments about the centre of mass, this is an important consideration. Froelich[31] firstly suggested that a completely segregated chain model (in which no overlapping of the domains of chemically different blocks is permitted) of a two sequence type block copolymer, would have the mean-square radius of gyration larger by about 15 percent from that of a corresponding random flight chain. It is hard to judge whether a deviation of this magnitude would cause a measurable anomaly in the solution properties measured. Recent experimental evidence seems to suggest that even block copolymer chains may assume random coil configuration, similar to homopolymer chains; at least in such solvents which have similar solubility towards both homopolymer constituents.[40] In solvents which have different solubility towards each parent homopolymer the problem is even more complicated. Some authors have suggested that in such solvents block copolymers would form peculiar configurations, or even form aggregates,[36,37] while others have concluded that even in such solvents sufficient interpenetration of the chemically different domains might occur, giving the appearance of normal behaviour.[41]

The most important parameter which governs the solution properties of a block copolymer is the polymer 1 - polymer 2 interaction, i.e., the interaction parameter due to heterocontacts (χ_{12} or β_{12}). Here again opinions vary. While some authors[41,42] have obtained a positive value for this parameter, a negative value[31] as well as a zero value[43] have recently been reported.

There are a number of factors responsible for these conflicting observations and conclusions. Polymer solution theories can only be applied effectively to polymer molecules which are linear and homogeneous with respect to molecular weight and for the case of block copolymers composition as well. Therefore this consideration is an important prerequisite for any solution studies on block copolymers. A copolymer molecule is also characterized by its molecular weight, composition, size and architecture of the blocks (and for the purpose of solution studies the nature of the solvent must play an important role). From the practical point of view it is very difficult to prepare a large series of samples in which one of these parameters will be constant. The only hope to achieve this is by judicious choice of the synthesis method and meticulous care in carrying it out. Moreover, the only theory[42] of block copolymer solutions is a generalization of homopolymer theory.[44] The validity of such extensions must first be established before any useful conclusions regarding the solution behaviour of a given system can be made.

The reason for starting this investigation was to comprehensively study the physicochemical properties of the poly(isoprene:styrene) block system. By careful planning of the project, both in the synthesis and in carrying out the experiments, it was hoped that some light might be thrown on the various problems confronting solution studies on block copolymers, as discussed above.

With the recent recognition of the technological usefulness of block polymers and related heterophase elastomers,[45,46] great effort has gone into the synthesis of these types of materials. Experimentally, solution methods provide the simplest means of determining certain block copolymer parameters such as molecular weight, homogeneity and structure. However, if this is to be used as an effective method of control of industrial products then relations valid for such systems must be first established. Because of the complex nature of such systems the size and shape of the macromolecule is going to be a function of molecular structure, composition and the distribution of segments along the chain, so that a combination of the various characterization techniques is often required in order to adequately characterize a block copolymer. Used in concert with one another, the various techniques can yield much useful information pertaining not only to the polymer itself but also to the method of preparation.

In this work a series of block copolymers were synthesized to predetermined specifications. The technique of gel permeation chromatography (GPC) was used to determine the molecular weight distribution of the copolymers and to give the various molecular weight averages by the use of a universal calibration curve. The microstructure of the polyisoprene sequence was determined by nuclear magnetic resonance (NMR). Light scattering and viscosity studies were used to determine the dimensions and configurational parameters in various solvents. Osmometry was used to determine the thermodynamic parameters. The use of the viscosity technique was extended to give some indication of the shape of the copolymer molecule in solution. Differential scanning calorimetry (DSC) was used to probe into the morphology of the bulk copolymer having a known thermal history.

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Chapter 2

SYNTHESIS

INTRODUCTION

Most theories of polymer solutions are based on ideal polymer-solvent systems. The effect of molecular weight and structural heterogeneity on the various parameters are not fully understood, particularly when applied to the more heterogeneous copolymers.[1] Previously it was assumed that fractionation would give a sufficiently ideal system adequate for solution study. When applied to copolymers certain difficulties are encountered. A copolymer, which is generally more heterogeneous than a similar homopolymer, is fractionated according to both molecular weight and composition. This can lead to more heterogeneous fractions than the starting material, unless a suitable solvent non-solvent system is employed.[2] The alternative to fractionation is a synthesis which will produce a model block copolymer. The need to have homogeneous block copolymers is not only desirable for solution studies but also to give the desired physical properties and technological importance of these systems - a factor which has only recently been recognized.[3,4]

The possibility of employing block copolymers as materials that might possess desirable and interesting properties was originally considered by Mark.[5] Since that time most of the effort directed towards the synthesis of block (as well as graft) polymers has been focused in the realm of radical polymerization systems.[6-10] Simultaneously the investigation of ionic polymerization systems languished. This was unfortunate, since it is the homogeneous anionic systems which have recently proved the more fruitful in producing well-defined block copolymers, having unusual and interesting properties.[11,12] The special feature of these homogeneous anionic systems is that spontaneous termination is avoidable through judicious choice of experimental conditions -- a fact which Szwarc[13,14] was the first to comprehend and appreciate fully. As a consequence, these termination-free systems have been given the name 'living' polymerizations. A potent feature of this characteristic is the fact that these 'living' polymer-carbanions can be reacted at the discretion and 'leisure' of the experimenter, with additional monomer selected to meet a particular need. In effect the method has opened a path to the synthesis of 'tailor-made' macromolecules, i.e., it permits the synthesis of well-defined macromolecules of novel architecture, e.g., branched polymers of various shapes and block polymers. The preparation of these block polymers is made possible by the absence of a termination step in the polymerization. This feature is of considerable importance from the standpoint of polymer synthesis. In the first place, when all the chains are initiated more or less simultaneously they will possess a narrow molecular weight distribution (Poisson distribution), as forecast by Flory.[15] Secondly, the sequential addition of various monomers can lead to the formation of linear block copolymers containing segments of controlled molecular weight with differing properties. Thirdly, the molecular weight is governed by the ratio of monomer to initiator. Thus for the case of an initiator which generates a chain with one active end, the number average molecular weight is given by

$$\bar{M}n = \frac{\text{grams of monomer}}{\text{moles of initiator}}$$

whereas for an initiator capable of initiating a chain with two active ends (e.g. sodium naphthalene) the relationship becomes

$$\bar{M}n = \frac{\text{grams of monomer}}{0.5\ \text{moles of initiator}}$$

This affords a method of controlling the molecular weight.

Two classes of initiators are generally employed to achieve this termination-free polymerization. These include; a) alkali-metal complexes[14,16] such as sodium naphthalene and, b) organo-alkali compounds such as the isomers of butyllithium.[17]

The first class of initiators include both alkali-metals and alkali-metal complexes in ether solvents, e.g., lithium metal,[18,19] sodium naphthalene,[20-22] sodium biphenyl[23,24] and more recently the promising dilithium initiators.[25] The initiation is by electron transfer from initiator to monomer, as originally suggested by Szwarc.[13,14,26] The feature of these type of initiators is that they are difunctional, i.e., have two growing ends. For this reason they cannot be used for the synthesis of two sequence A-B type block copolymers, but only for the three sequence A-B-A type blocks. Also they have a disadvantage for the synthesis of block copolymers involving a polydiene (polyisoprene or polybutadiene) in that they are soluble only in ether, or similar solvents, which leads to a low -1,4 content in the polydiene, i.e., a non-rubbery polymer.

The second class of initiators, i.e., the organoalkali compounds are by far the most versatile for the synthesis of block copolymers. Foremost among these are the isomers of butyllithium. The verstility of these type of initiators comes from the fact that they are soluble in a variety of solvents, including hydrocarbons. This is important if the elastomeric property of the polydiene is to be retained. These organolithiums act by direct anionic attack. They have one growing end, i.e., are monofunctional, thus allowing the synthesis of two sequence A-B type block copolymers, as well as the A-B-A type. Carrying out the synthesis in hydrocarbon solvents (e.g. benzene) and using lithium-based initiators, is a necessary feature if a high cis-1,4 polyisoprene is desired. Structural investigations[27-31] of polyisoprenes have shown that certain ethers, thioethers and amines, alter the microstructure from the about 80% cis-1,4 form (obtained in hydrocarbon solvents), to that of a chain containing 3,4-, 1,2-, and trans-1,4 forms. A parallel effect is encountered when alkali metal counterions other than lithium are used. At the same time it is interesting that changing reaction conditions, such as the temperature, appears to have little effect on the microstructure.[27,29]

The question of microstructure is an important one, both from the point of view of solution studies (dimensions) and the bulk properties of the polymer chain. Unfortunately there is poor agreement between the microstructure analysis reported by different authors for a particular initiator and solvent; particularly with the polar solvents. Infra-red spectroscopy methods[32] have been the standard technique for determination of microstructure, but more recently nuclear magnetic resonance (NMR) methods have been used.[33,34] The standard infra-red techniques are inadequate for polyisoprene. The determination of the relative amounts of cis- and trans-1,4 structures in particular are subject to large errors,[28] since the infra-red bands are virtually coincident and differ only in shape and intensity. The NMR method[33] is more satisfactory, at least for the determination of cis-1,4 and trans-1,4 ratio.

Isotactic polystyrene has been reported to be formed by butyllithium initiation in hydrocarbon solvents at low temperatures.[34,35] However, this has been shown to be due to the presence of lithium hydroxide caused by termination of the initiator.[36]

In highly pure systems, containing no hydroxide, the polystyrene was found to be highly syndiotactic.[37] Other adventitious impurities, such as lithium methoxide and lithium iso-butoxide, do not cause formation of isotactic polymer. It has also been found that the presence of lithium alkoxides inhibit the initiation of styrene[38] (as well as the rate of propagation) while apparently accelerating the rate of initiation of isoprene.[39] From this behaviour it is clear that this type of polymerization reaction, in a medium of low dielectric constant, is highly sensitive to trace amounts of polar substances and adventitious impurities. If a highly stereospecific substance is required, a judicious choice of conditions must be made and precautions against impurities must be taken.

Despite recent efforts, reactions involving organolithium compounds with either styrene, or diene monomers have been only partially deciphered. The problem arises from the fact that such compounds are highly associated in hydrocarbon solvents.[40-45] For example, n-butyllithium[43] exists primarily in the hexameric form in such solvents. The slow initiation reaction of this initiator was originally conceived[31] as resulting from the monomer reacting only with free organolithium, while the associated form was assumed to be unreactive towards monomer. However, this has recently been criticized on energetic grounds[46] and it has been suggested that monomer can react directly with associated organolithium:

at least with dimer and tetramer. A similar problem exists in trying to determine the detailed mechanism of chain growth of these systems. In these anionic polymerization systems the growing chain end can consist of a free-ion, or ion-pair, or both,[47,48] and its structure (and reactivity) can be influenced by the medium because of dielectric effects, or solvation effects. Despite a number of attempts,[49-52] elucidation of the exact structure of many of these anionic chain-ends remains incomplete. For this reason most kinetic data cited describe apparent rates and not absolute rates.

The system synthesized in this study was the poly(isoprene : styrene) diblock copolymers, initiated by n-butyllithium (BuLi) in benzene solvent. From what has been said above, this initiator-solvent system should result in a two sequence block copolymer; both sequences being highly stereospecific, provided sufficient precautions against impurity are taken. Use of a non-polar solvent, such as benzene, offers a further advantage in that propagation is slow. Homogeneous reaction conditions, necessary for narrow distribution polymers, can be obtained easily for slow polymerization by using a simple batch technique. In the case of rapid polymerization only a continuous monomer feed can maintain homogeneous conditions.

In order that precise control be exercised over the molecular weight and molecular weight distribution, the following conditions must be fulfilled;

a) uniformity of reaction conditions with regard to temperature and concentration of reactants;
b) homogeneity during both the initiation and propagation reactions;
c) the absence of depropagation steps and bond interchange reactions;
d) a high ratio of the apparent initiation to propagation rates;
e) rigorous exclusion of substances capable of causing termination or transfer; and
f) accurate dispensing of reactants under vacuum.

Conditions a) - d) may be achieved by having strict control over all the kinetic steps involved in the synthesis. The last two conditions govern the degree of predictability and assume an even greater role in the synthesis of block copolymers, where homopolymer impurities are highly undesirable. These conditions can be achieved by using high vacuum techniques and designing an appropriate synthesis method whereby strict control over the purity of all reactants and apparatus is maintained and which allows the accurate dispensing of reactants under vacuum.

In the synthesis of the A-B blocks, the isoprene monomer was synthesized first, followed by the polystyrene. The reason for this was so that the microstructure of the homopolyisoprenes could be compared directly with that of the polyisoprene sequence in the block - both having been prepared under identical conditions.

In the complete synthesis the following stages may be considered.

1. Initiation of isoprene monomer by butyllithium

   $$\mathrm{BuLi} + \mathrm{I} \xrightarrow{ki} \mathrm{BuILi}$$

2. Propagation of the 'living' polyisoprene chains

   $$\mathrm{BuI_{n-1}Li} + \mathrm{I} \xrightarrow{k_p} \mathrm{BuInLi}$$

3. Cross-initiation of the styrene monomer with the 'living' polyisoprene chains

   $$\mathrm{BuInLi} + \mathrm{S} \xrightarrow{kxi} \mathrm{BuInSLi}$$

4. Propagation of the polystyrene sequence

   $$\mathrm{BuInS_{m-1}Li} + \mathrm{S} \xrightarrow{kxp} \mathrm{BuInSmLi}$$

5. Termination

   $$\mathrm{BuInSmLi} + \mathrm{MeOH} \xrightarrow{kt} \mathrm{BuInSmH} + \mathrm{LiOMe}$$

Because of the association of organolithiums and of the propagating ends of 'living' chains, as discussed previously, the above steps are only a simplified version of the actual processes. Any rates deduced from this scheme will only be apparent rates, based on the total concentration of species (neglecting any variance in the reaction rates of species in different forms of association)

To obtain narrow distribution polymers the ratio of the rate of initiation to propagation must be as large as possible, i.e., $ki/_{kp}$ and $kxi/_{kxp}$ in the above scheme must be large. There are two ways of accelerating the initiation reaction involving n-butyllithium and isoprene. One is by adding trace amounts of ethers, such as tetrahydrofuran, but as discussed above this is undesirable because it leads to a drastic reduction of the cis-1,4 structure of the polyisoprene. However, more recent evidence seems to suggest that trace amounts of the aromatic-ether, anisole, or the aromatic-amine, amiline, will speed up the initiation reaction without any apparent effect on the microstructure of the polyisoprene.[53] The other method is by temperature control. Work in this laboratory[54,55] has shown that a decrease in reaction temperature will lead to a more effective conversion of initiator to isoprenyllithium. Lowering of the temperature causes the rate of propagation to decrease by a greater extent than does that of initiation, thus resulting in a high value for $ki/_{kp}$. The crossover rate constant for the reaction of the isoprenyllithium species with styrene has been determined[57] and the reaction rate found to be fast in comparison to the homopropagation. A large $kxi/_{kxp}$ can be readily obtained. The homopropagation rate for styrene in benzene has been studied by several groups of workers[58,59] and that for isoprene in benzene has also been investigated in this laboratory.[60] There is sufficient data to be able to choose the conditions which will lead to complete conversion.

After consideration of the kinetics there is still an important question left to consider, this is the question of purity of all systems, in order to achieve the aim of the synthesis. This is more important in copolymers which have more production steps than homopolymers, therefore predictability is generally more difficult to achieve due to a greater chance of adventitious termination. This necessitates the use of rigorous conditions in all steps of the synthesis. The method of synthesis and precautions carried out are outlined below.

EXPERIMENTAL

Vacuum System

A schematic diagram of the vacuum system constructed for the use in the synthesis is shown in Fig. 2.1. The set up was as simple as possible, eliminating any unnecessary bends and taps, so that the system was efficient both in its use and in the time required to obtain the desired high vacuum. The pumping system of the assembly consisted of a 'Speedivac' three-stage mercury vapour diffusion pump, backed by an efficient rotary oil pump. The vapour pump was equipped with a stainless steel mercury vapour trap. The suction inlets were reduced to a practical minimum and were arranged in two sections. Manifold (M_1) was used for the handling of solvents, i.e., degassing, distillation and purification and manifold ($M2$) was used for the evacuation of air only. This ensured that the desired reaction vessel could be evacuated to a high vacuum in the minimum of

Fig. 2.1. Vacuum assembly used in the synthesis:

B - oil backing pump

O - oil safety valve

T - liquid N_2 cooled traps

    T_1 - for solvents

    T_2 - for mercury

D - mercury diffusion pump

    1 - electrical heater

    2 - mercury reservoir

    3 - stainless steel mercury trap

I - ionization gauge

M_1 - manifold used for degassing and solvent distillation

M_2 - high vacuum manifold.

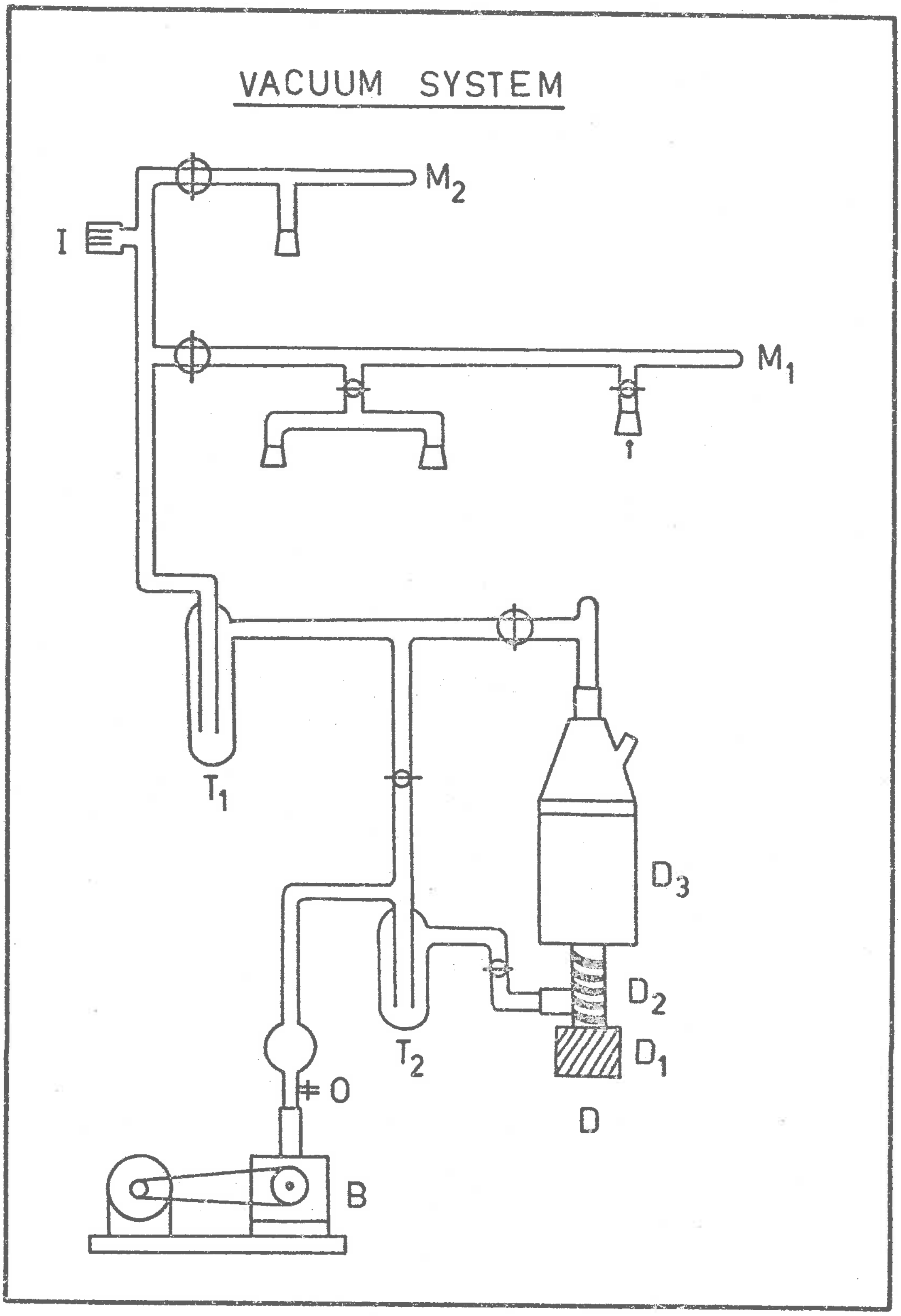


Fig.2.1

time. A Metrovac VC9 ionization gauge attached to the manifold was used to measure the pressure. High vacuum Apilzon T grade grease was used on all stopcocks in the system.

Solvent - Benzene

Univar A.R. grade benzene was refluxed over calcium hydride for about 48 hours, after which it was fractionally distilled through a stainless steel packed column - a 50% centre fraction being collected each time in flasks containing fresh calcium hydride. These fractions, contained in flasks, were degassed on the vacuum line 3-4 times (by freezing in liquid nitrogen, pumping out to a high vacuum, thawing and repeating the cycle). The fractions were then distilled into a stock vessel containing 'living ends' (low molecular weight polystyryllithium under vacuum). When solvent was needed it was taken from this stock solution. The actual solvent used for the various steps of the synthesis was taken from sealed ampoules, equipped with glass break-seals, which contained the solvent over 'living ends'. These ampoules, containing from 120-150 mls. of benzene each, were prepared by distilling the benzene from the stock vessel into a flask containing break-seal ampoules and an ampoule of n-butyllithium; a small quantity of syrene was also distilled into the flask. This vessel (Fig. 2.2a) was then pumped to a high vacuum and cut off at R while still under pumping vacuum. The n-butyllithium was broken in and initiated the polymerization of the styrene contained in the flask. This was evident by the appearance of an immediate bright orange colour. The quantities of styrene and n-butyllithium were such as to ensure low molecular weight polystyryllithium 'living ends' (Mn about 250). Quantities of this solution were sealed off into ampoules and stored in deep freeze (-10 to -15°C) until used. This bright orange solution of polystyryllithium in benzene was used to purge all vessels and monomers and as a source of ultra pure benzene - free of any moisture and any other potential terminating material. The persistence of the orange colour indicated the purity of a particular system as well as the presence of a high vacuum.

Monomers

Preliminary cleaning. Styrene, containing catechol inhibitor, was placed in a flask over calcium hydride and continuously shaken until there was no further effervescence, it was then left over fresh calcium hydride for a further period of 48 hours. This was then transferred into a flask containing freshly ground calcium hydride, placed on the vacuum line and degassed 4-5 times. On the line this was consecutively flash distilled into three different flasks containing fresh calcium hydride, the top and bottom fraction being discarded each time. This was finally distilled into a flask containing side ampoules (Fig. 2.2b), pumped down to a high vacuum and then cut off the line at R. The styrene was distributed into the ampoules and stored in deep freeze in the dark until used.

Isoprene (99,4 Mo 1% - Fluka A.G.) A grade purity was transferred into a flask containing calcium hydride, placed on the vacuum line, degassed 4-5 times and then flash distilled into three consecutive flasks containing fresh calcium hydride; for this only the middle fraction was used each time. Finally it was distilled into a flask containing attached ampoules, pumped to a high vacuum, cut off the line and distributed into the ampoules, which were stored in the freezer in the dark similar to the styrene.

Final purging of monomers before use. The apparatus used for purging of monomers was as shown in Fig. 2.2c. Flask A had attached to it an ampoule of the previously cleaned monomer and an ampoule of purging solution. Flask C had accurately graduated ampoules attached to it and also an ampoule of n-butyllithium in benzene. The apparatus was evacuated to a vacuum of 10^{-6}MM while continuously flaming it out with a yellow gas flame. It was then cut off the line at R1. The n-butyllithium was broken into C and used to purge the whole vessel, especially C with its attached break-seal ampoules and the measuring compartment B. This was done by vigorously shaking and swirling for a period of 3-4 hours. When this was complete the n-butyllithium was tipped into vessel A, at this stage the purge was broken in and the benzene was distilled

Fig. 2.2. Apparatuses used in the preparation of purging solution and for purging of monomers.

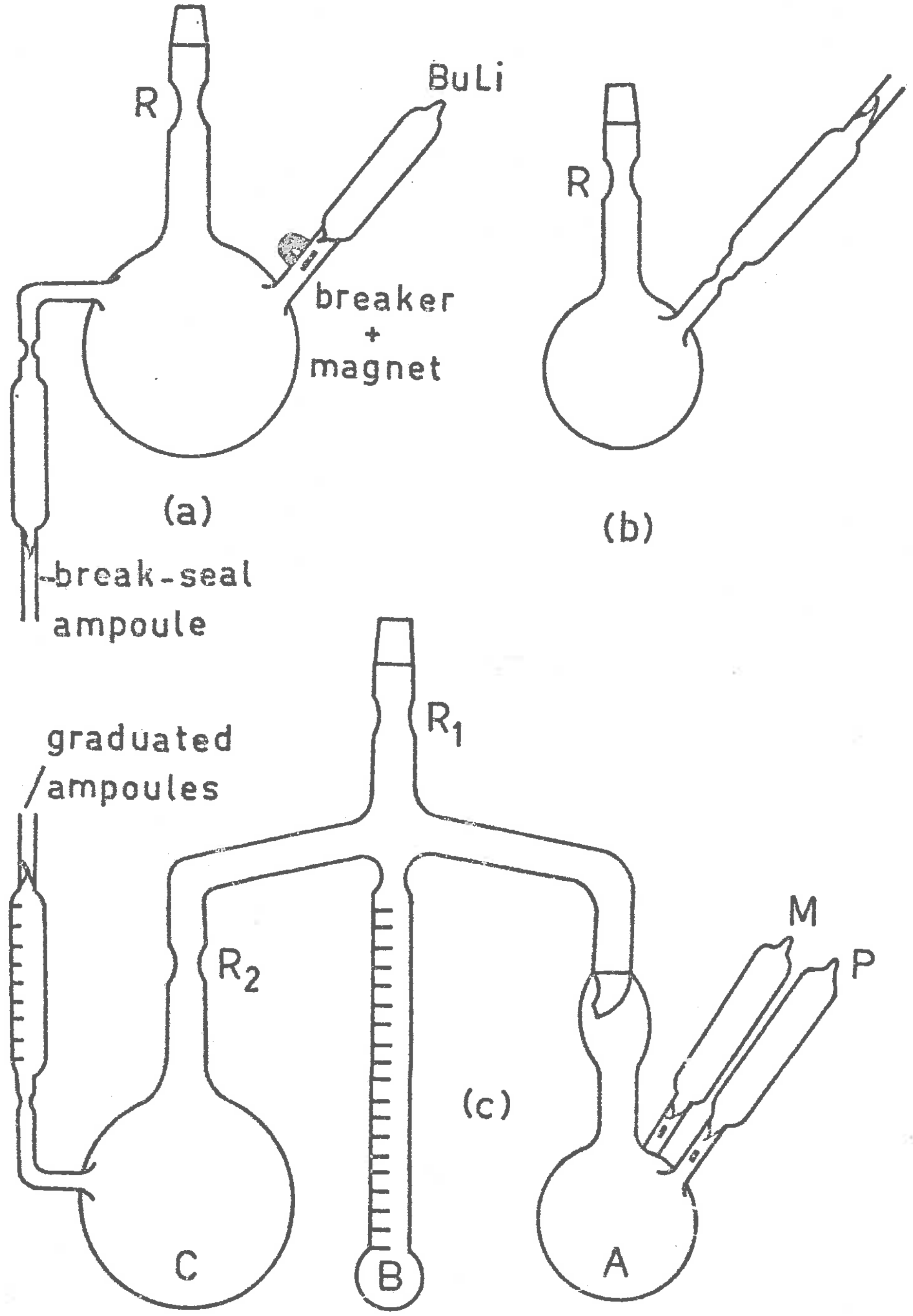

R
BuLi
breaker
+
magnet
(a)
break-seal
ampoule
R
(b)
graduated
ampoules
R_1
R_2
M
P
(c)
C
B
A

Fig.2.2

off and used to wash the apparatus free of n-butyllithium. Extreme care was taken to ensure that no butyllithium remained in the tips of the break-seals attached to C. These washings were repeated several times until compartments B and C were considered free of butyllithium. After this all the benzene solvent was distilled from A into the measuring cylinder B, leaving behind a dried film of 'living ends' (with their characteristic orange colour) and butyllithium in vessel A. The benzene in B was allowed to equilibrate to 20°C and the volume noted. At this stage both vessels A and B were cooled to ice temperature and the monomer broken into A. The monomer was left over the mixture of 'living ends' and butyllithium for a period of about 30 minutes, while continuously swirling. After this cylinder B was dipped into a dewar containing liquid nitrogen and the purged styrene was allowed to distil over onto the benzene. When the required dilution ratio was reached any monomer remaining in flask A was allowed to slowly polymerize by gradually raising the temperature of vessel A to room temperature. The temperature of vessel B was then allowed to equilibrate to 20°C and the total volume of benzene plus monomer noted. From the previously noted volume of benzene the exact dilution ratio at 20°C could be deduced. The dilution ratio of monomer to benzene was usually about one to five; this was desirable both to reduce errors during dispensing of volume and to reduce risk of self polymerization of the monomer (especially styrene.)

The isoprene was purged in exactly the same manner as styrene, except, because of the slower polymerization of this monomer, it could be purged at room temperature (with only an occasional dip in the ice bath). Also, cylinder B needed only to be cooled in an acetone-ice-salt bath to obtain a controllable rate of distillation.

The mixture of benzene and monomer was tipped from B into C and sealed off at S2. From the dilution ratio and the density of the monomer at 20°C, the diluted monomer could be distributed into the accurately graduated ampoules in quantities required for polymerization. These ampoules were sealed off, wrapped in aluminium foil and kept in the freezer until used. A practice was made to prepare this purged monomer just before use, to eliminate letting it stand for an unnecessary period of time.

Initiator

Preparation of stock solution. The vessel used for the preparation of the n-butyllithium initiator is shown in Fig. 2.3a. The flask was flushed out with dry argon via A. While flushing, high purity lithium chips (99.8%, Koch-Light) were cut up and washed in dry benzene to dissolve the layer of paraffin (in which they were stored). These were introduced into the flask through B; the handling was done under an inert atmosphere of nitrogen. Freshly cut surfaces of lithium retained their shine in this atmosphere and showed no signs of tarnish. When this was completed the flask was stoppered at B, attached to the vacuum line via A and quickly evacuated (at this stage the shiney surfaces of lithium still remained). When a good vacuum was attained benzene solvent was distilled in off the 'living ends' contained in the stock reservoir on the line. The required amount of purged butyl chloride was also distilled in. The flask was pumped to a high vacuum while at liquid nitrogen temperature. After this it was maintained at 0°C for a day (while still attached to the vacuum line) and then gradually allowed to warm up to room temperature. At this stage there was no chance of a violent reaction and the mixture was allowed to stand under vacuum for three days, while continuously being stirred with a magnetic stirrer. When the reaction was complete a blue precipitate formed and the excess lithium chips floated to the surface (this excess lithium ensured that all the butyl chloride was consumed). At this stage the mixture was degassed thoroughly 3-4 times, pumped to a high vacuum and cut off the line at R while frozen. The n-butyllithium in benzene was then filtered through the porosity G3 filter into the attached break-seal ampoule. This gave a pure stock of n-butyllithium of about 2M concentration.

Dilution to initiator strength. If predictability of molecular weight is desired, care must be taken in determining the exact concentration of initiator, as well as preventing any of it being accidentally destroyed. To achieve this, a

Fig. 2.3. Apparatus for the preparation and dispensing of initiator (BuLi).

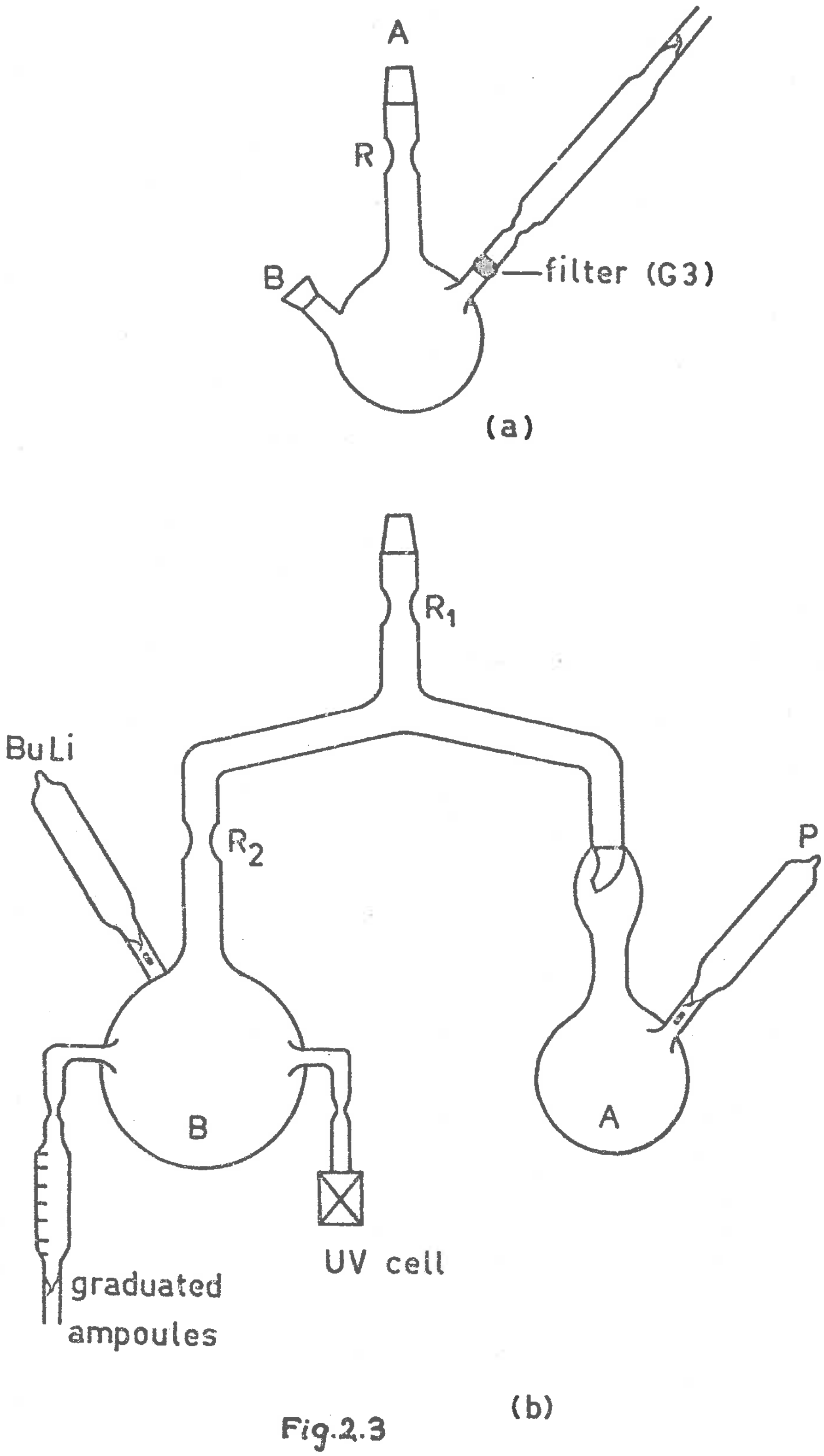


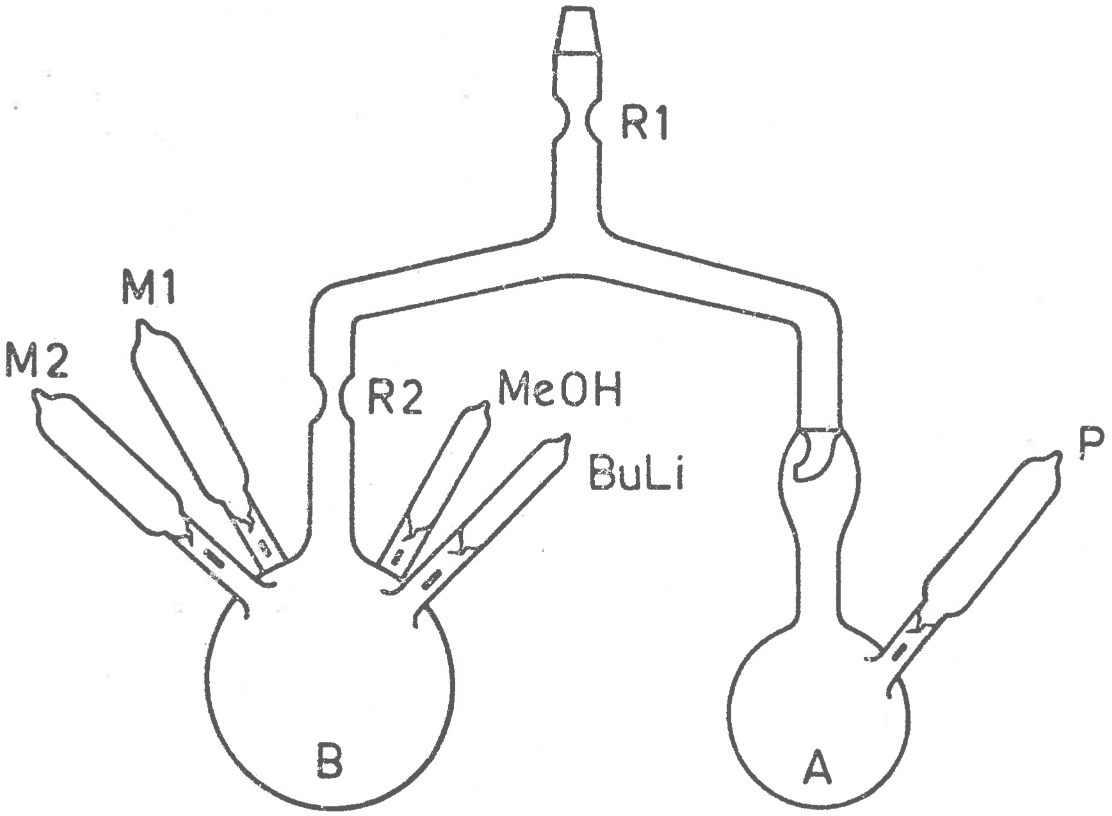
Fig.2.3

technique of dispensing under vacuum with a minimum of steps and using prepurged vessels was developed. Ultraviolet spectroscopy was used to determine the concentration of the n-butyllithium. The apparatus constructed for this purpose is shown in Fig. 2.3b. This allowed the dilution, dispensing and determination of the exact concentration of initiator to be carried out in one operation. The assembled apparatus was evacuated to 10^{-6}mm (while continuously flaming it) then cut off at R1. Purging solution was broken into A and used to purge the whole vessel for 2-3 hours, after which all the 'living ends' were poured back into A through several washings. The n-butyllithium was then broken into B and diluted with benzene from vessel A. To B were attached two one centimetre silica cells by means of a graded seal. An approximate concentration of n-butyllithium was obtained by sealing off one of the cells and measuring the optical density (at 285 nm), using a Beckmann spectrophotometer equipped with a digital read out. This preliminary result enabled the concentration to be readjusted by either distilling in more benzene from A or taking some off. When the required dilution was attained vessel B was sealed off at R2, the contents thoroughly mixed and the accurate concentration of n-butyllithium determined by using the second UV cell. The n-butyllithium was then distributed into the graduated break-seal ampoules in quantities needed for the synthesis; the ampoules were sealed off and stored in the freezer.

Polymer Synthesis

The vessel used in the synthesis is shown in Fig. 2.4. Purging solution, containing sufficient solvent to give a 3-4% polymerization mixture, was attached to flask A. Flask B had attached ampoules of the two monomers, initiator and methanol as terminator. The vessel, which was perfectly cleaned and dried before hand, was placed on the vacuum line and pumped down to a vacuum of 10^{-6}mm (while continuously flaming out with a yellow gas flame). The required vacuum was reached within two hours. After this, the vessel was cut off the line at R1 and the purge broken in. The whole vessel was thoroughly purged for 4-5 hours, after which all the 'living ends' were poured back into A by repeated washings. At this stage all the benzene was distilled from A into B and vessel B sealed off from the rest at constriction R2. The vessel was then placed in a 6°C water bath, allowed to equilibrate at this temperature and the first monomer (isoprene) broken in, followed by the initiator. The initiation was allowed to proceed for six hours, after which the temperature was raised to 25°C and propagation allowed to continue for a further 12 hours. After the propagation of the isoprene was considered complete the vessel was again cooled to 6°C. The second monomer (styrene) was broken in and cross propagation

Fig. 2.4. Assembled vessel used in the synthesis of the block copolymers.



Synthesis Vessel

Fig.2.4

allowed to continue at this temperature for about six hours. The temperature was then raised to 25°C and the propagation allowed to go to completion (about eight hours). At this stage the methanol was broken in and the reaction terminated (the solution changing colour immediately from the orange of the polystyryllithium 'living ends' to the colourless terminated polymer). This terminated polymer was diluted by the addition of more benzene (to about 1% solution) and precipitated in a large amount of cold methanol with rapid stirring, using a magnetic stirrer. The precipitation was carried out by the slow addition (using a specially constructed burette type delivery column packed with glass wool at the bottom) of the diluted polymer solution to a large volume of stirred cold methanol. All precipitating solvents used were filtered through a G4 filter. The precipitated polymer was recovered, dried under vacuum and stored under vacuum and in the dark at 20°C. This procedure gave a pure polymer, free of any dust, or other contaminants.

Polymer Characterization

Microstructure. Table 2.1 shows the different structural isomers possible for polyisoprene and the NMR resonance frequencies associated with each isomer. The peak assignments being those due to Chen. The area under each peak indicated, is proportional to the number of protons present. If a = 1,2 isomer concentration, b = 3,4- and c = 1,4-, then a number of simultaneous equations may be deduced, e.g.,

$$\text{area peak 4} = b + 4c$$

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

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

By solving these equations the relative concentrations of the isomers present in the sample may be obtained. To separate the cis- and trans-1,4 structures the ratio of the area under peak 5a to that under peak 5b is used, since this is the ratio of the cis-1,4 to the trans-1,4 plus 3,4 structures. Thus the percentage of cis-1,4 in the sample is given by,

$$\frac{\text{area 5a}}{\text{area 5}} \times 100$$

All the block copolymers and two samples of polyisoprene, synthesized under identical conditions, were analysed using NMR spectroscopy. A Varian D.P.60 NMR spectrometer equipped with an H.A.60 probe at 30°C was used. About a five percent solution of the polymers in benzene as solvent was found to give optimum resolution and was employed throughout the analyses. Benzene was used as the internal lock for the instrument. The area of the relevant peaks was determined by using the integrator on the spectrometer.

The NMR spectra of two copolymers and one polyisoprene are shown in Fig. 2.5. All the copolymer samples, as well as the

Fig. 2.5. The NMR spectrum of a polyisoprene sample (a) and two block copolymers in the region of interest.

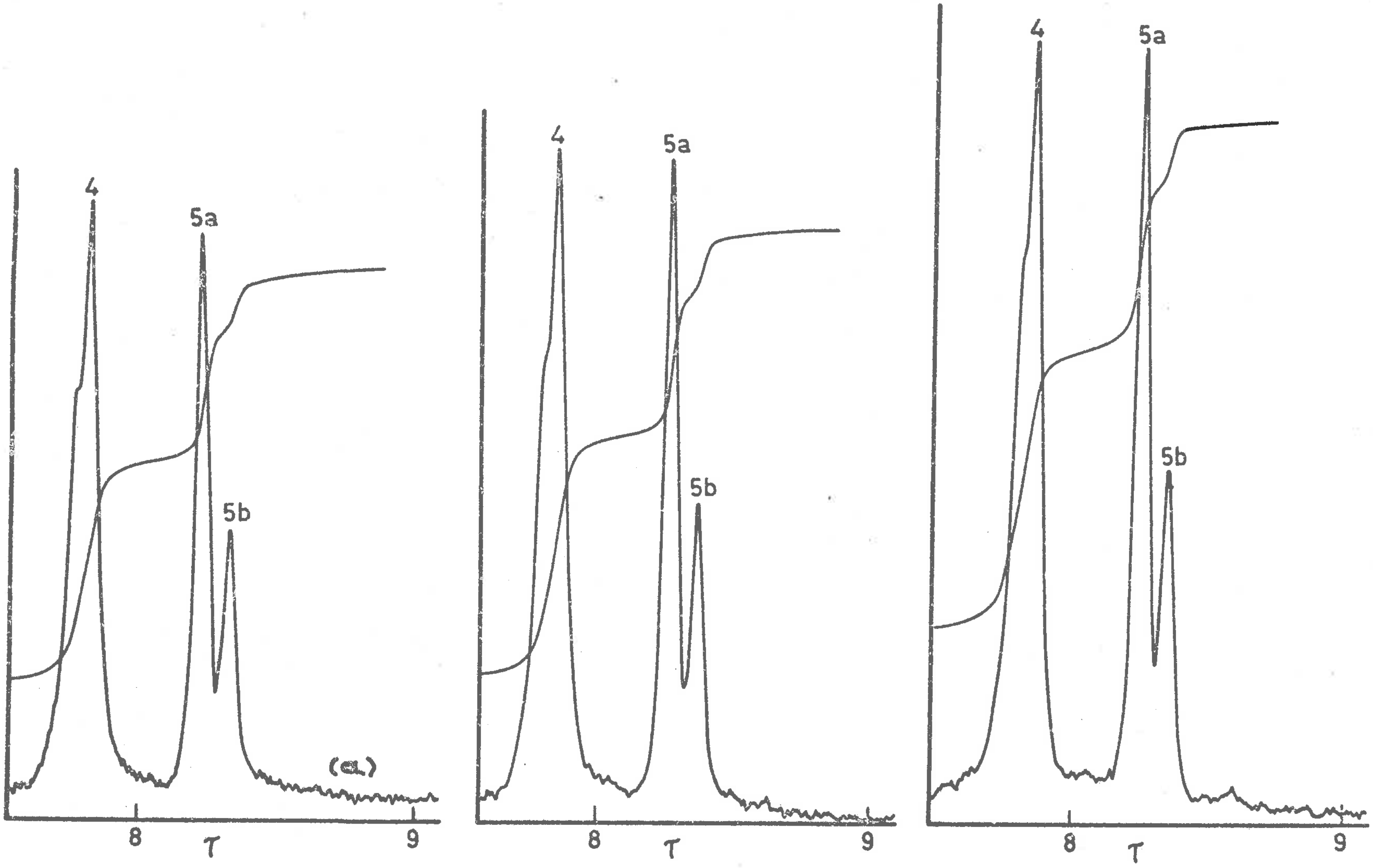
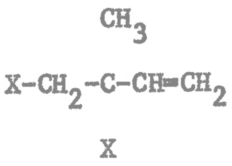


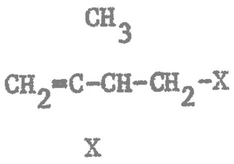
Fig.2.5

Table 2.1. Structural Isomers of Polyisoprene and the Associated NMR Resonance Frequencies According to Chen.[33]



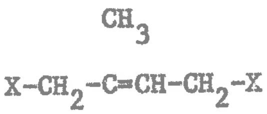
$X-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle X}{C}}-CH=CH_2$

1,2 Isomer



$CH_2=\overset{\displaystyle CH_3}{C}-\underset{\displaystyle X}{CH}-CH_2-X$

3,4 Isomer



$X-CH_2-\overset{\displaystyle CH_3}{C}=CH-CH_2-X$

1,4 Isomer

Peak No.	CPS	τ	Type of Protons	Origin
1	318	4.70	$-CH=C$	1,2
2	302	4.97	$-C=CH_2$	1,2
3	279	5.35	$CH_2=C-$	3,4
4	119	8.02	$-CH-C=$	1,4 and 3,4
5a	100	8.33	$CH_3-C=$	cis 1,4
5b	94	8.41	$CH_3-C=$	trans 1,4 and 3,4
6	76	8.74	$CH-C-$	1,2 and 3,4
7	55	9.08	CH_3-C	1,2

polyisoprenes, showed no peak due to the 1,2 structure; thus it was concluded that such an isomer is not formed under the method of synthesis used. Analysis of the polyisoprenes gave an average isomeric composition as; 82% cis-1,4, 14% trans-1,4, 4% 3,4 and 0% 1,2. Because of the identical method and conditions of synthesis of both the copolymers and the polyisoprenes, the above isomeric composition can also be taken as the one existing in the polyisoprene sequence of the copolymers. Direct determination of the absolute amounts of the various isomers in the copolymers is difficult, because the polystyrene sequence has a broad absorption occurring in the same region as the polyisoprene. For the copolymers containing a low percentage of polystyrene, the estimated isomeric composition was close to that found in the polyisoprenes (within 4%). However, copolymers with a higher percentage of polystyrene gave apparent values for the cis-1,4 content which were up to 20% too low. This difference was constant for different copolymers, provided the composition remained the same. This shows that this method of isomeric analysis is only useful for the low polystyrene copolymers. From a study of the NMR spectra of various solutions of polystyrene, an arbitary correction was attempted to allow for the polystyrene absorption. After applying this correction the percentage cis-1,4 is given by,

$$\frac{A5a}{A5(1-0.6w)} \times 100$$

where A5a and A5 is the area under peak 5a and 5 respectively and w is the weight fraction of polystyrene in the block copolymer. Applying this correction to the copolymers gave a cis-1,4 content equal to (81 ± 2%) for all the copolymers - in very good agreement with the polyisoprene samples.

Composition. The composition analysis of the copolymers was carried out using ultraviolet spectroscopy. The specific extinction coefficient, K, of the block copolymers at a given wavelength can be expressed as

$$K = wK_s + (1-w)K_I$$

where Ks and K_I are the specific extinction coefficients of polystyrene and polyisoprene respectively and w the weight fraction of polystyrene. The extinction coefficient of several peaks of the UV spectrum of polystyrene has been reported.[61,62] The two major peaks at 262 nm and 269 nm were used in this study. The specific extinction coefficient for the copolymers was determined from the equation

$$K\nu = \frac{\text{optical density at } \nu}{\text{cell length (cm.) X Concentration (g/l)}}$$

Chloroform (spectroscopic grade) was used as the solvent and the optical density readings were made with a Beckmann D.U. spectrophotometer, equipped with a digital read out. The instrument was calibrated using optical density standards. One centimetre matched cells were used. The results, together with the predicted compositions, are shown in Table 2.2.

Table 2.2. Calculated and Predicted Composition of the Copolymers in Weight Percent Polystyrene

Polymer	Calculated Wt. % PS (w)	Predicted Wt. % PS (w_k)
IS1	13.5	11.8
IS2	24.7	25.0
IS3	28.2	28.6
IS4	52.2	50.0
IS5	78.2	77.8
IS6	11.8	11.8
IS7	25.5	25.0
IS8	48.5	50.0
IS9	25.1	25.0
IS10	48.7	50.0

Molecular weight. The number average molecular weights ($\bar{M}n$), as determined by osmometry (see Chapter 3), are shown in Table 2.3 together with the values predicted from the kinetic relation,

$$M_k = \frac{\text{grams of monomer}}{\text{moles of initiator}}$$

The weight average molecular weights ($\bar{M}w$) and the heterogeneity ratio, $\bar{M}w/\bar{M}n$, are also shown (for details see Chapter 3).

Table 2.3. Predicted and Measured Molecular Weight Averages and Calculated Distribution of the Copolymers

Polymer	Predicted Mk x 10^{-5}	Measured $\bar{M}n \times 10^{-5}$	$\bar{M}w \times 10^{-5}$	$\bar{M}w/\bar{M}n$
IS1	1.00	1.02	1.06	1.04
IS2	1.00	1.02	1.07	1.05
IS3	1.00	1.01	1.03	1.02
IS4	1.00	1.04	1.07	1.03
IS5	1.00	1.03	1.08	1.05
IS6	2.50	2.53	2.68	1.06
IS7	2.50	2.52	2.62	1.04
IS8	2.50	2.54	2.62	1.03
IS9	5.00	4.99	5.34	1.07
IS10	5.00	5.10	5.41	1.08

DISCUSSION

The microstructure analysis reveals that the polyisoprenes have an isomeric composition in very good agreement with that reported by Worsfold and Bywater.[31] Lithium impurities, such as lithium hydroxide and lithium butoxide, have been reported[31] to cause an increase in the trans-1,4 structure at the expense of the cis-1,4. For this reason the highest grade lithium metal available was used to prepare the n-butyllithium initiator. Also rigorous precausions were employed in its preparation to minimize the chances of such adventitious impurities being present. These precautions are justified by the microstructure results obtained - in comparison to an earlier report.[55] The results also show that the best approach to the microstructure analysis of these block copolymers is to take their isomeric composition as being the same as homopolyisoprenes, synthesized under the same conditions. Copolymers having a low polystyrene content gave an isomeric composition in good agreement with that obtained for the polyisoprene samples. However, copolymers with a high percentage of polystyrene only gave apparent values, which were found to be a function of the amount of polystyrene present in the copolymer. By applying an arbitary correction, which was found to be a simple function of the copolymer composition, the microstructure of all the copolymers agreed with each other and with that of homopolyisoprene. The isomeric composition was found as, 82% cis-1,4, 14% trans-1,4 and 4% 3,4. In all cases there was no 1,2 isomer present.

The results of the number average molecular weight and the composition are in excellent agreement with the predicted values; showing that the method of synthesis employed and the rigorous precautions taken are justified. The aim of the synthesis: to produce well characterized model block copolymers, suitable for a physicochemical study, has been achieved. The molecular weight distribution is narrow, as shown by the heterogeneity ratio $\bar{M}w/\bar{M}n$. Also, gel permeation chromatography (see Chapter 3) showed the absence of any homopolymer impurities and confirmed the narrow distribution of the copolymers.

SYNTHESIS: Chapter 2

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Chapter 3

MOLECULAR WEIGHT DISTRIBUTION

INTRODUCTION

Earlier methods of obtaining information on the molecular weight distribution (MWD) of a polymer sample have invariably involved some form of fractionation.[1] However, such methods are laborious, requiring large amounts of material and normally yield fractions which are not especially narrow in molecular weight, or composition distribution. In the case of copolymer fractionation, using a solvent non-solvent, the problems are even greater.[2] Usually experimenters avoid the determination of the distribution and simply report any two molecular weight averages from $\bar{M}n$, $\bar{M}w$ and $\bar{M}z$, representing the first, second and third moments of the distribution respectively. The ratio of any two, e.g., $\bar{M}w/\bar{M}n$ gives a measure of the width of the distribution. This ratio of $\bar{M}w/\bar{M}n$, normally known as the heterogeneity ratio, may be obtained from light scattering and osmometric measurements. The accuracy is never better than about 10%, even under optimum conditions. The greatest error is in the determination of $\bar{M}w$ from light scattering, employing the usual Zimm method.[3] The accuracy is even less for block copolymers where readings in at least three different solvents must be made in order to calculate $\bar{M}w$.[4] Of course this ratio of $\bar{M}w/\bar{M}n$, although useful as a measure of the width of the distribution, gives no indication of the presence of more than one species in the polymer sample. Knowledge of this nature is desirable in the study of copolymers where there is always the possibility of homopolymer being present.

The introduction of the relatively new technique of gel permeation chromatography (GPC),[5] has given new impetus to attempts in obtaining molecular weight distributions. This technique has provided the researcher with a rapid and generally quantitative method for determining the size distribution of polymer molecules. With the appropriate calibration, one might hope that this technique will not only give the MWD, but will also supply the normal molecular weight averages such as $\bar{M}w$ and $\bar{M}n$. These may then be compared directly to the values obtained by the classical methods of light scattering and osmometry. GPC also provides a quick and sensitive check on the number of species present in the sample - a very important consideration when studying block copolymers.

OSMOMETRY

Osmometry is a widely used technique for measuring the chain length of a polymer. The method gives the number average molecular weight $\bar{M}n$. The method is applicable to copolymers equally as well as to homopolymers.[2] In the case of copolymers a true number average molecular weight $\bar{M}n = \Sigma NiMi/\Sigma Ni$ is obtained, as for the case of homopolymers. The theory and experimental set up for osmometry is described in Chapter 4. The number average molecular weight was determined for all the copolymers in three different solvents, toluene, cyclohexane and methyl isobutyl ketone (MIBK), at 30°C. The determination was made according to the equation[6]

$$(\pi/cRT)^{1/2} = (1/\bar{M}n)^{1/2}[1 + (A_2\bar{M}n/2)c] \qquad 3.1$$

where π is the osmotic pressure, c the polymer concentration, A_2 the osmotic second virial coefficient and R and T the gas constant and absolute temperature respectively. The plots of $(\pi/cRT)^{1/2}$ versus C were straight lines for all solvents used. The extrapolation of such a plot to zero concentration gives $\bar{M}n$.

Results and Discussion

Typical plots according to equation 3.1 are shown in Fig. 3.1. As can be seen $\bar{M}n$ is independent of the nature of the solvent employed. Values obtained in three solvents, toluene, cyclohexane and MIBK are shown in Table 3.1. The predicted kinetic values calculated from the relation

$$Mk = \frac{\text{grams of monomer}}{\text{moles of initiator}} \qquad 3.2$$

are also shown.

Table 3.1. Measured and Predicted Number Average Molecular Weights

	Measured $\bar{M}n \times 10^{-5}$			
Polymer	TOL	C-HEX	MIBK	Mk x 10^{-5}
IS1	1.02	1.04	1.02	1.00
IS2	1.03	1.05	1.00	1.00
IS3	1.02	1.00	1.01	1.00
IS4	1.03	1.03	1.05	1.00
IS5	1.03	1.03	1.04	1.00
IS6	2.57	2.50	2.54	2.50
IS7	2.51	2.56	2.49	2.50
IS8	2.53	2.60	2.48	2.50
IS9	4.99	5.01	4.97	5.00
IS10	4.98	5.04	4.97	5.00

The results show excellent agreement between measured and predicted $\bar{M}n$'s, showing that predictability of molecular weight has been achieved in the synthesis of these block copolymers. This, coupled with the good agreement between predicted and measured composition (Chapter 2), qualitatively shows that these materials must be expected to have a reasonably narrow distribution in both molecular weight and composition.

Fig. 3.1. Typical plots of reduced osmotic pressure against concentration for copolymer (IS4) in toluene, cyclohexane and MIBK.

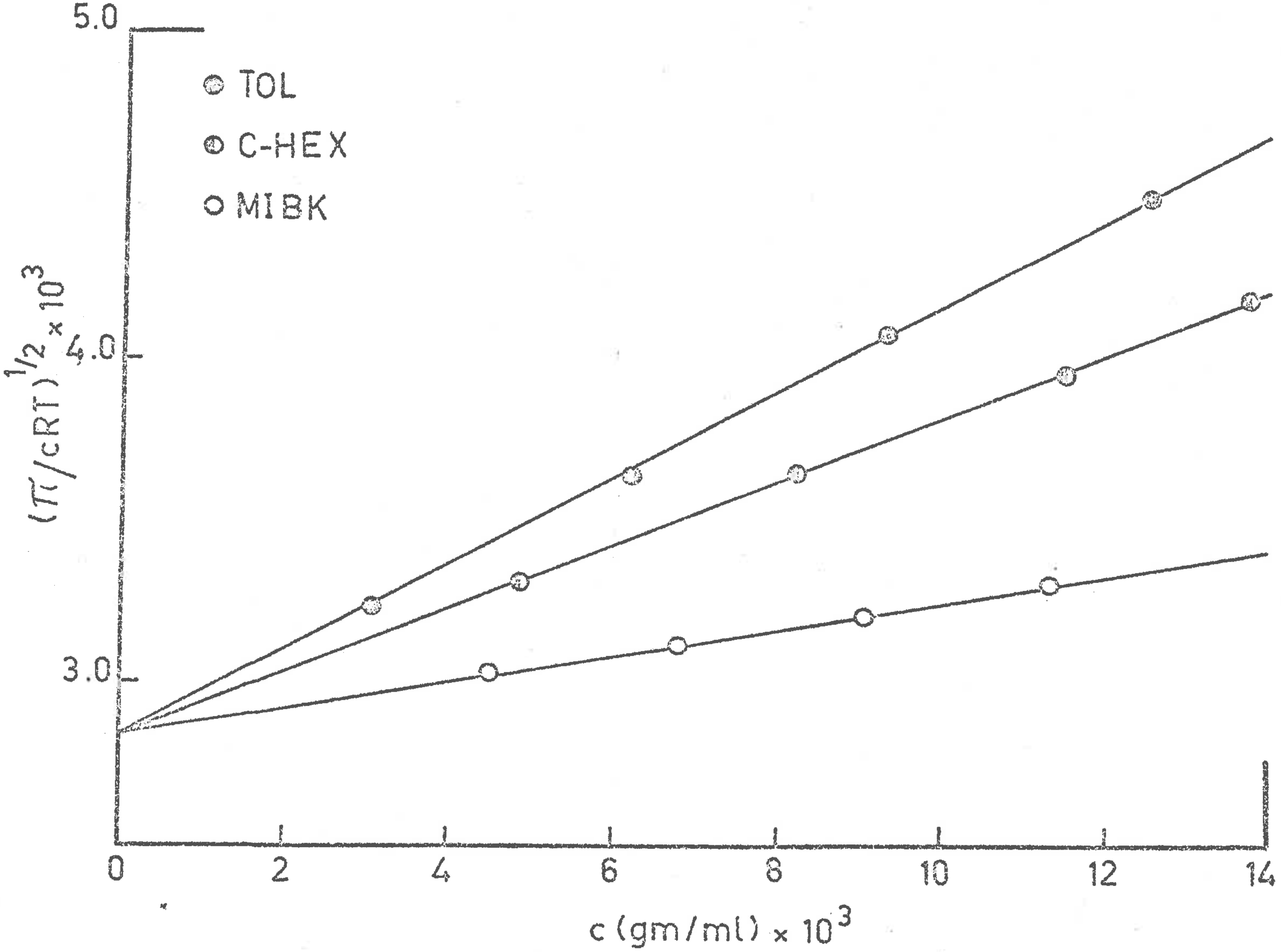

5.0
4.0
3.0
TOL
C-HEX
MIBK
$(\pi/cRT)^{1/2} \times 10^3$
0
2
4
6
8
10
12
14
c (gm/ml) × 10^3

Fig. 3.1

LIGHT SCATTERING

Introduction

Ever since Debye[7] showed that the intensity of light scattered by a polymer solution is related to the mass of the polymer molecule, light scattering technique has developed into a standard procedure for the determination of molecular weight of homopolymers. However, extension to copolymers is a more recent consideration.[4,8-12] The first attempt was made by Tremblay and coworkers[9] using a butadiene-styrene copolymer. Their work suggested that the intensity of light scattered by the copolymer depended not only on the molecular weight but also on the heterogeneity of composition of the various polymer segments in the chain. From this observation it was first suggested that light scattering might offer a method of assaying the nonuniformity of composition in copolymers. This suggestion was later confirmed by Krause[10] while working with a series of copolymer fractions. Stockmayer and coworkers[4] were able to derive an expression demonstrating how the intensity of the light scattered by a copolymer varied with the molecular weight and composition of the sample. This expression has since been confirmed by Bushuk and Benoit.[8]

In a homopolymer there is only one type of scattering element, however in a copolymer there may be two or more different types, depending on the number of different monomers present in the copolymer.

In their derivation Stockmayer and coworkers[4] assumed that the refractivity of a copolymer is a simple sum of the refractivities of the component homopolymers. According to this the refractive index of a copolymer ($\nu = dn/dc$) can be given by

$$\nu = \sum_i w_i \nu_i \qquad 3.3$$

where ν_i is the refractive index of the pure component i and w_i is its weight fraction in the copolymer. They pointed out that this should be particularly true for block copolymers and probably would not introduce a very large error when applied to random copolymers as well. Using this approximation the following expression was derived,[4]

$$[I\theta/K^1C]_{\theta=0}^{c=0} = \nu^2\bar{M}w + 2b\nu P + b^2Q \qquad 3.4$$

where Iθ is the ratio of the intensity of scattered light, measured at an angle θ and at a fixed distance from the scattering volume, to the intensity of the incident light; c is the concentration of the polymer solution and ν is the refractive index increment of the copolymer-solvent system; $K^1 = 2\pi^2 no^2 K/\lambda_o^4 N_A$ where no is the refractive index of the solvent for light of wavelength λ_o in vacuo, N_A is Avogadro's number and K is a function of θ, which includes the instrument calibration constant. The function b is related to the difference in refractive index increment between the polymer segments comprising the copolymer chain, such that

$$b = \nu_A - \nu_B \qquad 3.5$$

where the subscripts A and B refer to the two homopolymers of a binary copolymer chain. Equation 3.4 also contains two parameters, P and Q, which are related to the composition distribution of the copolymer such that

$$P = \sum_i \gamma i \ \ Mi\ (x_i - x) \qquad 3.6$$

$$Q = \sum_i \gamma i \ \ Mi\ (x_i - x)^2 \qquad 3.7$$

where γi is the weight fraction of component i, whose molecular weight is Mi and composition x_i and x is the average composition of the copolymer sample. Here the parameters P and Q represent the heterogeneity in composition: P relates to the composition variation with molecular weight and Q to its broadness.

The determination of the molecular weight of a copolymer in a single solvent, will therefore only yield an apparent value (Map), in accordance with the equation

$$[Io/K^1C] = Map\ \nu^2 \qquad 3.8$$

From this, equation 3.4 may be rewritten as

$$Map = \bar{M}w + 2P(b/\nu) + Q(b/\nu)^2 \qquad 3.9$$

The true molecular weight ($\bar{M}w$) may only be obtained by performing measurements in at least three solvents, having different refractive indices, in order to determine the three unknown values of $\bar{M}w$, P and Q in equation 3.9. The results can be illustrated graphically by plotting Map against (b/ν) which varies with the refractive index of the solvent. The points should describe a parabola from which the values of the parameters $\bar{M}w$, P and Q could be estimated. The parameters P and Q which are related to the heterogeneity in composition of the sample by equations 3.6-3.7, can vary between the following limits:

$$-x\bar{M}w < P < (1 - x)\bar{M}w \qquad 3.10$$

$$0 < Q < [1 - x\ (1-x)]\bar{M}w \qquad 3.11$$

If the copolymer is monodisperse in mass, or if the distribution of chain composition is independent of molecular weight, equations 3.10 and 3.11 simplify further, since under such conditions $P = 0$ and $0 < Q < x(1-x)\bar{M}w$. The maximum value of Q can only be realized with a mixture of two homopolymers.

If the copolymer molecules are of uniform composition then $\nu_i = \nu$ for all values of i, $(x_i - x) = 0$ and equation 3.9 reduces to $Map = \bar{M}w$. For this case the molecular weight obtained from light scattering data will be independent of the refractive index of the solvent.

Experimental

The light scattering apparatus used was a SOFICA Photogoniodiffusometer model 4200. It was modified by the addition of a Kipp and Zonen 'Microva' multirange microammeter model AL4, to enable light intensity measurements to be made more easily and accurately. The symmetry of the system was checked by measuring the fluorescence from dilute solutions of sodium dichlorofluoresceinate, with a red filter (Ilford 204 Tricolour Red) placed in the photomultiplier compartment to eliminate scattered light. The values of $r(\theta) \sin \theta$, where $r(\theta)$ is the ratio of the photo-currents due to the scattered and incident light at the angle θ, showed negligible dependence on θ in the range 30°-150°. No symmetry correction was required. The volume correction was found to be satisfactory, after allowing for depolarization as discussed by Coumon.[13] The instrument was calibrated using purified dust free benzene. The Rayleigh ratio of benzene (R_B) was taken[13] as 15.8×10^{-6} at a wavelength of 546 nm.

Treatment of solvents and solutions. Solvents used were of A.R. grade. All solvents for light scattering and all other uses (e.g. osmometry and viscometry) were treated in the manner described below. The solvents were dried over calcium hydride, refluxed over freshly ground calcium hydride for 24 hours and then distilled through a 3 foot column of stainless steel wire.

A fractionating head was fitted to the column which allowed the centre fraction to be collected at a 1:10 take off rate. The solvents were then filtered under dry nitrogen pressure through a sintered glass filter porosity G5. The ketones (viz. methyl isobutyl ketone and methyl ethyl ketone) were treated under slightly different conditions. The solvent was dried over anhydrous potassium carbonate, filtered from the dessicant and fractionated through an efficient column packed with glass beads. The purity of all solvents used for light scattering measurements was further checked by measuring the refractive index and by vapour phase chromatography.

Scattering data was obtained for five polymer concentrations, prepared by diluting a concentrated solution to 80, 60, 40 and 20 percent of the original. Concentrations were adjusted so that the smallest scattering was not less than twice the value of the solvent. The dedusting procedure adopted was centrifugation in a Beckmann Model L ultracentrifuge, using a swinging bucket rotor and stainless steel inserts. Solutions and solvents were centrifuged at 30,000G for 3-4 hours after which they were transferred from the centrifuge tubes to the light scattering cells. This transfer must be carried out within 10 minutes of stopping the rotor, otherwise Brownian motion would disturb the dust adhering to the bottom of the centrifuge tubes. Transfer must also be carried out with extreme

Fig. 3.2. Transfer apparatus used in light scattering measurements.

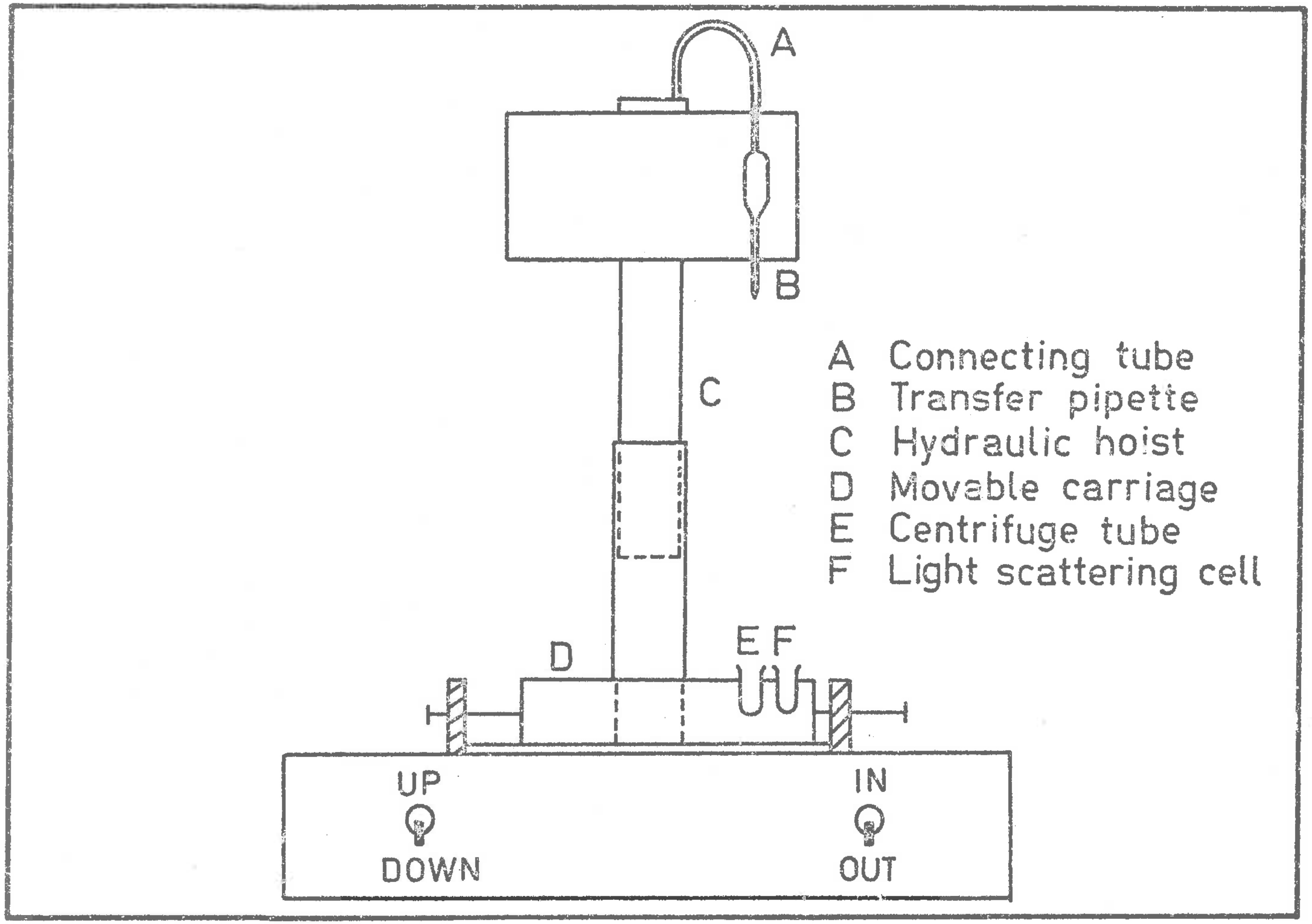

A
B
C
D
E F
UP
DOWN
IN
OUT
A Connecting tube
B Transfer pipette
C Hydraulic hoist
D Movable carriage
E Centrifuge tube
F Light scattering cell

Fig.3.2

caution so as not to disturb the dust particles. For this step a specially constructed transfer apparatus was used (Fig. 3.2). This consisted of a motor driven hydraulic hoist which lowered and raised the transfer pippettes. A motor driven suction apparatus sucked up the sample from the rotor tube and delivered it into the light scattering cell. This enabled the simultaneous transfer of three samples with minimum delay and disturbance. All apparatuses used in the handling of solutions were subjected to a rigorous cleaning procedure before each use. Glass ware was first soaked in a dilute solution of chromic acid, followed by distilled water and finally soaked in the solvent to be used. Rotor tubes, cells and transfer pippettes were cleansed of dust in specially constructed washing towers just prior to use.

Measurement of the specific refractive index increment. Refractive index increments of the copolymers in toluene, cyclohexane and MIBK were determined using a Brice-Phoenix differential refractometer (model BP-2000-V), equipped with a thermostatically controlled cell. The instrument was calibrated using aqueous solutions of potassium chloride (A.R. grade, purified and dried in a vacuum oven at 90°C). The values of the refractive index increments were measured at $\lambda = 546$ nm and were found to be independent of the polymer concentration in the range studied. Where possible the refractive index was measured on the same batch of solution as used for the light scattering measurements. A series of 10 consecutive readings of the micrometer scale, for each polymer solution, were taken and averaged to obtain consistency in the readings. The values obtained for the block copolymers are shown in Table 3.2.

Table 3.2: Specific Refractive Index Increments of the Copolymers in Toluene, cyclohexane and MIBK.

Polymer	ν (546 nm)		
	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)

Table 3.2 (Contd.)

$^+$ Values in brackets calculated from $\nu = w_A\nu_A + (1-w_A)\nu_B$

The specific refractive index increment ν of a binary copolymer may be approximated as a linear function of composition, taken as independent of molecular weight, according to equation 3.3, i.e., $\nu = w_A\nu_A + (1-w_A)\nu_B$. This factor is used by many experimenters to avoid making refractive index measurements directly on the copolymer. However, although this assumption might be justified it nevertheless involves two separate refractive index measurements and a composition measurement in order to calculate ν for the copolymer. This must inevitably lead to a larger error in the calculated ν than the directly measured one. The accuracy of ν is an important consideration as it appears as a squared term in the light scattering equation. In this work the refractive index increments of the copolymers were measured directly. Having measured ν and knowing w_A the slope of a plot of ν versus w_A allows the calculation of $b = \nu_A - \nu_B$ directly from the results of the copolymers. Alternatively it can be calculated from the specific refractive index increments of the homopolymers.

Treatment of data. The light scattering measurements were made using unpolarized light of wavelength $\lambda = 546$ nm. The Rayleigh ratio R_θ, for each polymer-solvent system, was determined at 11 preselected angles from 30° - 150° at five concentrations. The readings obtained were corrected by the factor $\alpha = \sin\theta/(1 + \cos^2\theta)$ 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. This gives a series of values of K^1c/R_θ, where $K^- = 2\pi^2\nu^2/N_A\lambda_o^4R_B$, ν is the specific refractive index increment, R_B is the Rayleigh ratio of pure benzene and c is the concentration in g/ml. It should be noted that the refractive index of the solvent (N_o), which usually appears in this equation, is eliminated by the refraction correction for the instrument.[14]

The dependence of K^1c/R_θ on concentration and angle is given by

$$\lim_{\theta = 0} (K^1c/R_\theta) = \bar{M}w^{-1} + 2A_2C + 3A_3C^2 + \cdots \qquad 3.12$$

$$\lim_{c = 0} (K^1c/R_\theta) = \bar{M}w^{-1}\, P(\theta)^{-1} \qquad 3.13$$

in which the particle scattering factor $P(\theta)$ is given by

$$P(\theta)^{-1} = 1 + u/3$$

$$u = 16\pi^2N_1^2\lambda_o^{-2} <S^2> \sin^2(\theta/2) \qquad 3.14$$

The quantities Mw, A_2 and $<S^2>$ representing the weight average molecular weight, second virial coefficient and mean-square radius of gyration respectively must be changed to the apparent values, Map, (A_2)ap and $<S^2>$ap when dealing with block copolymers; for the reasons discussed above. These parameters are normally determined by a graphical method proposed by Zimm.[15] In a Zimm plot the light scattering data is presented as a plot of (K^1c/R_θ) against $\sin^2(\theta/2) + kC$, where k is an arbitrary constant chosen to give a convenient spread of the experimental data when plotted on a grid like curve. The relevant parameters are obtained by extrapolation to both zero concentration and zero angle. However, such extrapolations are not always simple and are subject to a lot of personal bias in curve fitting. This results in the commonly accepted accuracy[3] of ±8% for the determination of $\bar{M}w$ for homopolymers. The problem for copolymers is even greater, for here at least three separate Map's in three different solvents must be measured in order to estimate $\bar{M}w$. A computer program was written[16] to carry out the computations, with the aim of increasing the accuracy and removing the tedium of manual calculations. The program treats the data statistically and a Zimm grid is not plotted. The raw data from the SOFICA light scattering instrument, i.e., the galvanometer reading of the solvent and each concentration of polymer at each measuring angle is fed directly into a CDC 6400 computer. The print out is arranged so that all the parameters, Map, (A_2)ap, (A_3)ap and

$<S^2>$ap are calculated. An extension to the program (relevant to block copolymers only) considers values of Map in three or more solvents and calculates the three paramters $\bar{M}w$, P and Q of equation 3.9. The extensive testing of the program, both with homopolymers and block copolymers and comparison of these results with those obtained by the classical Zimm method, has also been reported elsewhere.[16]

Features of the computer program are that it prints out the experimental values of (C/R_θ) and also the difference between these and the least squares results. The printed differences allow a readily available critical analysis of the experimental points to be made. A particularly high value for a single entry may indicate a faulty measurement. In this case the relevant data could be omitted from the input and the remaining measurements utilized again on the computer. Any spuriousness in the results due to ineffective dedusting is easily picked up by an inspection of the printed differences. The program also takes into account any curvature in the $\theta = 0$ extrapolation due to the effect of the third virial coefficient A_3 (equation 3.12). This can be quite significant in thermodynamically good solvents (see Chapter 4). In the graphical method curvature due to the effect of A_3 cannot be readily allowed for.

Results and Discussion

The computed apparent molecular weights (Map) of the copolymers in toluene, cyclohexane and MIBK, together with the calculated $\bar{M}w$ are listed in Table 3.3.

Table 3.3: Apparent and Calculated Copolymer Molecular Weights Obtained from Light Scattering Measurements in Three Solvents.

	Map X 10^{-5}			
Polymer	TOL	C-HEX	MIBK	$\bar{M}w \times 10^{-5}$
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	1.13	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

The molecular weights calculated for the block copolymers are fairly close to the apparent molecular weights found in the three solvents. This suggests that they must be reasonably homogeneous in composition. The values of Map found in MIBK are especially close to the calculated $\bar{M}w$. This confirms the view held by Bushuk and Benoit[8] and Krause,[10] that measurements on block copolymers in solvents of sufficiently high refractive index will not be greatly in error. In fact MIBK seems a particularly appropriate solvent, for this copolymer system, to use to obtain apparent parameters from light scattering measurements which are very close to the true parameters. The negligible difference in molecular weights can be gauged by the ratio of Map in MIBK to $\bar{M}w$ calculated.

The values of $\bar{M}w$, P and Q calculated from equation 3.9 are shown in Table 3.4 together with the number average molecular weights (from osmometry).

Table 3.4: Weight Average and Number Average Molecular Weights and Heterogeneity Parameters of the Copolymers

Polymer	$10^{-5}\bar{M}w$	$10^{-5}\bar{M}n$	$P/\bar{M}w$	$Q/\bar{M}w$	$\bar{M}w/\bar{M}n$
IS1	1.06	1.02	0.015	0.026	1.04
IS2	1.07	1.02	0.009	0.056	1.05
IS3	1.08	1.01	-0.018	0.232	1.07
IS4	1.07	1.04	0.028	0.116	1.03
IS5	1.08	1.03	0.021	0.163	1.05
IS6	2.68	2.53	-0.002	0.026	1.06
IS7	2.62	2.52	0.036	0.015	1.04
IS8	2.62	2.54	0.023	0.021	1.03
IS9	5.34	4.99	0.014	0.013	1.07
IS10	5.41	5.01	0.034	-0.007	1.08

The results in Table 3.4 show that the block copolymers can be considered as being homogeneous both in composition, as indicated by the P and Q parameters and in molecular weight as indicated by the heterogeneity ratio $\bar{M}w/\bar{M}n$.

GEL PERMEATION CHROMATOGRAPHY

Introduction

Gel permeation chromatography (GPC) is a term first introduced by Moore[5] to describe a form of liquid chromatography which sorts polymer molecules in a gel-packed column according to their size in solution. This relatively new technique has rapidly become a widely used procedure for obtaining size distribution of synthetic macromolecules. The term 'gel permeation' is derived from the method of separation on a column consisting usually of a polystyrene gel that has been crosslinked with divinylbenzene in the presence of diluent (to give the desired permeability). This gel, which can be made with a range of permeabilities, is rigid and possesses sufficient stability for extended use. In general terms separation can be considered to occur on the basis of the permeability of the gel. Molecules larger than the maximum pore size pass through the column in the interstitial volume. Molecules smaller than the maximum pore size enter the gel and are size separated. The smaller molecules require more solvent to elute them through the column.

It is generally agreed that GPC sorts molecules according to their size in solution, but it is not generally agreed as to how this size sorting takes place. This problem has been reviewed by a number of authors.[17-19] Three different mechanisms have evolved: a) restricted diffusion, b) steric exclusion, and c) thermodynamic theories.

The restricted diffusion mechanism for GPC was originally proposed by Ackers.[20] This theory assumes that the time required for a molecule to diffuse in and out of a gel pore is significant relative to the time the molecule spends in the vicinity of that pore. This mechanism has also received backing from other workers.[21,22] On the other hand a number of authors[5,23-25] have stressed the role of steric exclusion of large molecules from small pores as the predominating mechanism of the separation in GPC. Yau[26] has also proposed a theory coupling both these effects. From the good agreement between this coupling theory and his experimental results, he concluded that this provides additional evidence that GPC separation mechanism is due solely to diffusion and exclusion effects. There is also much evidence to support a separation mechanism based on thermodynamic theories.[27-31] Here the evidence is based on the qualitative agreement of the experimental results with the theoretical curves predicted on the basis of thermodynamic considerations.[27] It is beginning to be recognized, however, that a single mechanism is unlikely to prevail universally irrespective of operating conditions and of the nature of solute, solvent and the column material.[22,23]

At this stage it is probably just as useful, and certainly much easier, to consider the mechanism of GPC as exclusively size exclusion and to regard other factors as operating on this simple mechanism.

At present GPC is not an absolute technique: calibration is required to yield accurate or quantitative expressions of molecular weight and molecular weight distribution (MWD) of polymers.[32,33] Ever since its inception, a recurrent theme of study is the search for some general molecular-size parameter that determines the position of any elution peak in a chromatogram. Such a parameter would afford a 'universal' calibration curve independent of polymer type. The most fundamental calibration curve is normally presented as a plot of peak elution volume (Ve) versus log molecular weight.[34] This of course requires a series of narrow MWD polymers of the type in question. Because well characterized standards for most polymers are not available (this is especially true for the case of copolymers), various attempts have been made to circumvent the dependence of the calibration on specific polymer type.[35-40]

Benoit and coworkers[39,40] have recently proposed that elution is governed by the product of intrinsic viscosity (η) and molecular weight for any polymer, linear, or branched.

According to the Einstein viscosity law one can write

$$[\eta] = K(V/M) \qquad 3.15$$

where V is the hydrodynamic volume of the particles, M their molecular weight and K a constant. Therefore a plot of $[\eta]M$ versus elution volume will provide a GPC calibration on the basis of the hydrodynamic volume of the polymer coil. According to Benoit and coworkers,[39,40] when the calibration is established for one polymer, the plot is universal for other polymers, being independent of chemical structure and polymer geometry. This method of calibration has been the subject of much recent investigation.[31,41,42] Another calibration parameter which has recently been suggested[43,44] involves the unperturbed dimensions of a linear polymer molecule; such as the unperturbed root-mean-square radius of gyration ($<S_o^2>^{1/2}$). Writing equation 3.15 in the form proposed by Flory:[6]

$$[\eta] = [<S^2>^{1/2}]^3/M \qquad 3.16$$

shows that this is not really a new calibration parameter, but merely represents a minor variation to the hydrodynamic volume parameter proposed by Benoit and coworkers.[39,40]

Apart from the problem of calibration in GPC there is also the problem of correcting the GPC results for imperfect resolution.[45-49] This lack of infinite resolution and the dependence on certain operational variables, such as flow rate and sample concentration, can cause broadening of the chromatograms obtained. These should be corrected for in order to obtain absolute molecular weight distributions. Various authors have attempted to evaluate the magnitude of these broadening operatives and several computer programs have been written to make the necessary corrections.[45-48] Most of the computer programs are only partly successful and according to a recent review[50] no one method may be exclusively recommended. For the case of block copolymers there may be another factor contributing to chromatogram distortion; that is fluctuations in composition of the copolymer species. Probably the only possible way of assessing the effect of this would be to use two separate detectors[51] - one to follow the distribution in molecular weight and the other the composition.

Despite these problems, GPC is generally accepted as a rapid, reproducible and reasonable quantitative technique for the determination of MWD's. The chromatogram is a composite curve of the Gaussian distribution of its components. It gives a type of differential MWD curve directly. 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 of course is not a problem peculiar to GPC. Studies[52] have shown that optimum working conditions can easily be established. Although resolution is limited, optimum operating conditions may be obtained by the choice of the number and permeability of columns, flow time and concentration of polymer used.

Experimental

Fig. 3.4 shows a schematic diagram of the Waters Associates gel permeation chromatography apparatus used to analyse the block copolymers and constituent homopolymers. The solvent used was tetrahydrofuran (THF). The solvent reservoir contains about 15 litres of solvent. The solvent from this reservoir is degassed, pumped through a filter and split into two streams. The sample control valve is adjusted to give the desired flow through the sample column. The reference flow is adjusted so that the flow through the reference and the flow through the sample column reach the detector in a common front. The reference column is used to provide a suitable pressure drop. When the sample valve is moved the flow will pass through a sample loop, which is normally 2 mls in volume. A solution of the polymer sample (0.25% - 1%) is injected into the sample loop through a heated sample inlet. By timing the depression of the sample valve it is possible to control the amount of sample put on the column. The solvent then picks up the

Fig. 3.3. Schematic diagram of the Waters gel permeation chromatography assembly.

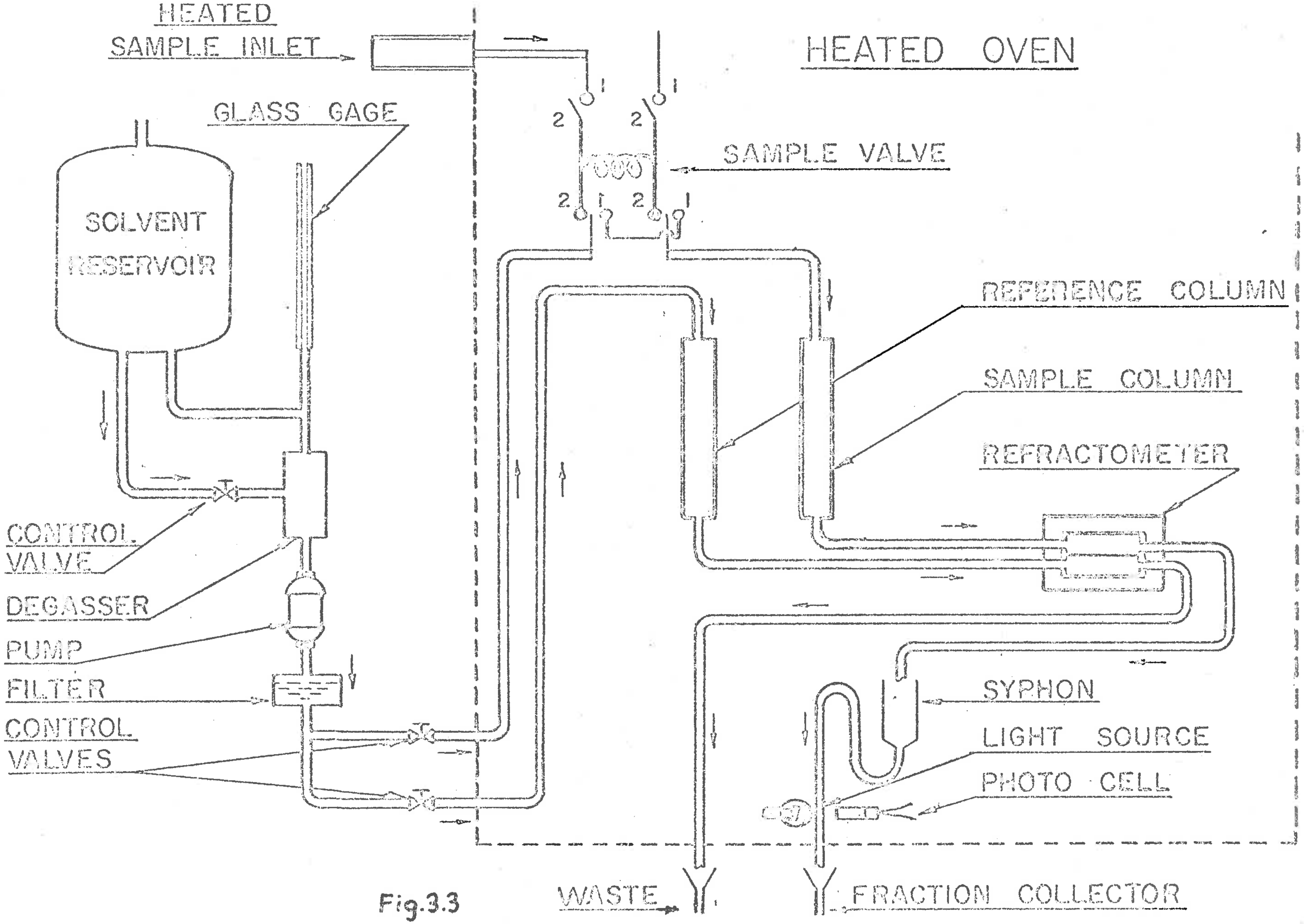

HEATED
SAMPLE INLET
HEATED OVEN
GLASS GAGE
SAMPLE VALVE
1
2
1
2
2
1
2
1
SOLVENT
RESERVOIR
REFERENCE COLUMN
SAMPLE COLUMN
REFRACTOMETER
CONTROL
VALVE
DEGASSER
PUMP
FILTER
CONTROL
VALVES
SYPHON
LIGHT SOURCE
PHOTO CELL
WASTE
FRACTION COLLECTOR

Fig.3.3

sample from the sample loop and carries it onto the sample column. A high sensitivity differential refractometer with a flowing reference cell is used as the detector. A 5 ml. syphon collects the eluent from the sample column and then discharges them to a fraction collector. When a 5 ml. fraction is discharged it passes between a photo-cell and detector. The detector then pulses the recorder at every 5 ml. fraction. Because a given molecular size always comes out with a fixed volume of solvent, these pulses can be used to plot the molecular size scale versus the elution volume.

The GPC curves for the block copolymers and parent homopolymers were obtained on this instrument at 25°C using THF as solvent. The THF was purified by refluxing under an inert atmosphere of nitrogen. Preliminary tests were carried out to ascertain the optimum operating conditions. The GPC curves were determined using a combination of three columns having gel permeabilities of 10^6, 10^5 and 10^4 Å. The flow rate used was 0.5 ml per minute. The concentration injected was 1.25 mg of polymer (0.25% solution for one minute). Calibration was achieved by determining peak counts of a series of narrow MWD polystyrenes supplied by Waters Associates. Peak molecular weights and values of $\bar{M}w$ and $\bar{M}n$ were supplied with the samples.

Such a curve plotted as log M versus elution volume is shown in Fig. 3.5 for the polystyrene standards.

Results and Discussion

Chromatograms of the copolymers and some polystyrene standards are shown in Fig. 3.4. Inspection and comparison of the chromatograms showed that all the copolymers may be considered to be of narrow MWD and free from extraneous homopolymers. To ascertain this from merely inspecting the GPC curves, the comparitive technique of MWD elucidation of an 'unknown' introduced by Bly[53,54] was found very useful. Provided efficient columns are used, the curve width features of a chromatogram are truly representative of the sample even though the true calibration remains unknown. Thus, comparison of a standard polymer curve to an unknown polymer curve can be made with the assurance that relative variations in curve features really represent the sample. The relative curve features and thus the relative size distributions can be obtained by this technique. If the polymer size distribution is the most probable or Gaussian-like, the relative polydispersity d can be calculated from

$$w_1/d_1 = w_2/d_2$$

Fig. 3.4. Gel Permeation Chromatograms of the copolymers and some polystyrene standards:

Solvent - THF

Temperature - 25°C

Columns - 10^6, 10^5, 10^4 Å

Concentration - 0.25% - 60 secs

Flow rate - 0.5 ml/min.

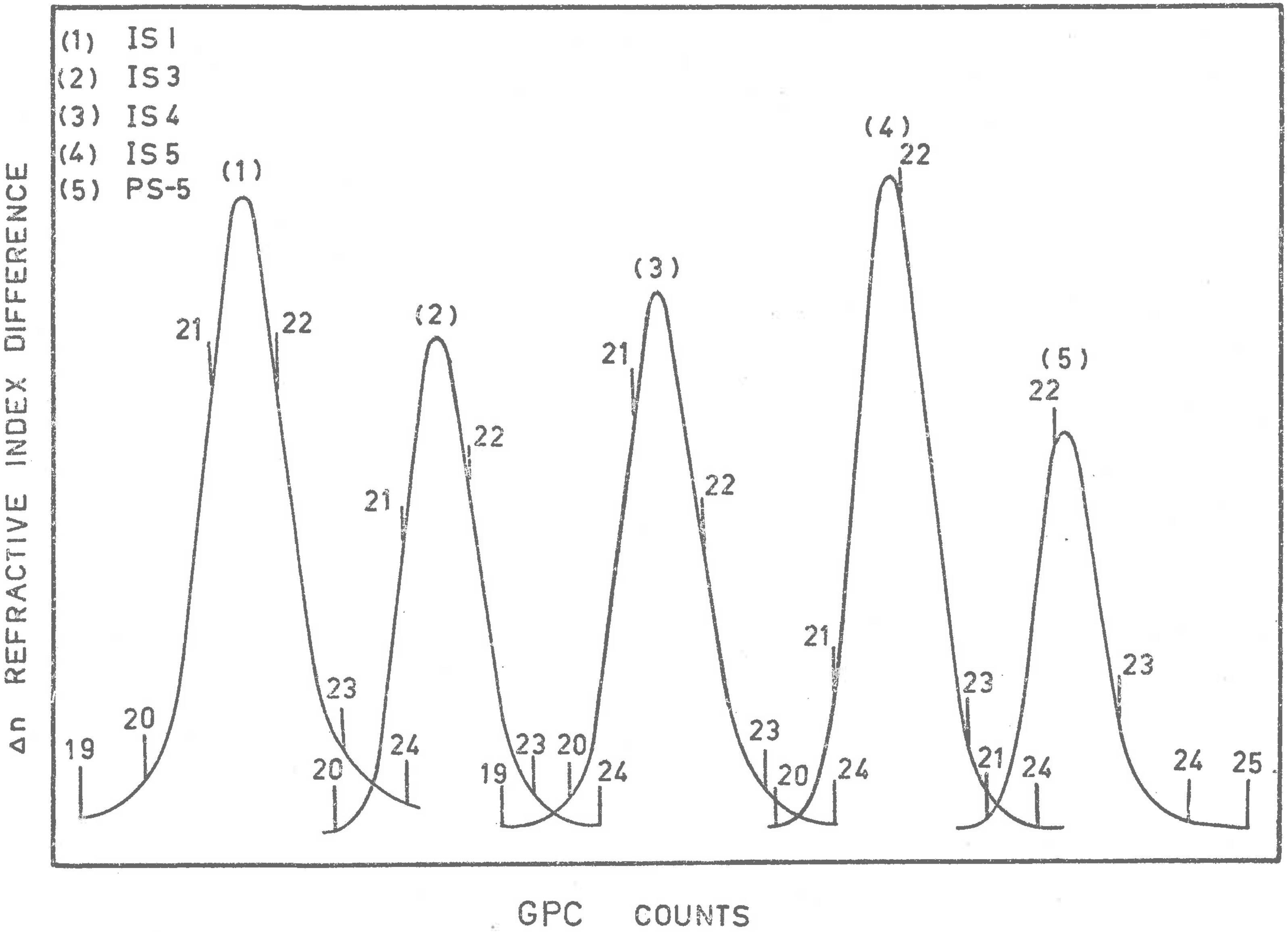
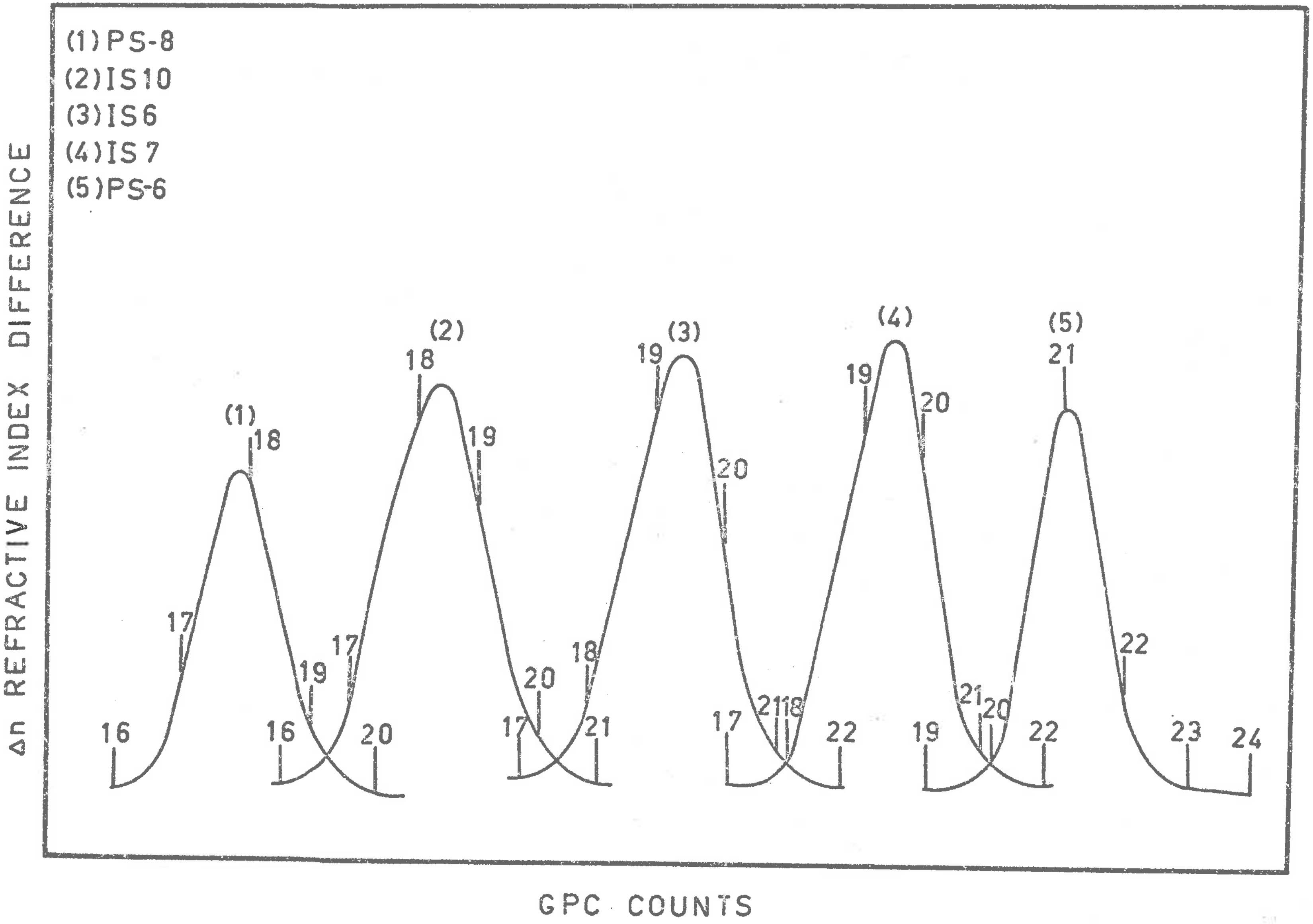

(1) IS 1
(2) IS 3
(3) IS 4
(4) IS 5
(5) PS-5
(1)
(2)
(3)
(4)
(5)
19
20
21
22
23
24
25
Δn REFRACTIVE INDEX DIFFERENCE
GPC COUNTS

Fig.3.4


(1) PS-8
(2) IS10
(3) IS6
(4) IS 7
(5) PS-6
Δn REFRACTIVE INDEX DIFFERENCE
GPC COUNTS
(1)
(2)
(3)
(4)
(5)
16
17
18
19
20
16
17
18
19
20
21
17
18
19
20
21
22
17
18
19
20
21
22
19
20
21
22
23
24

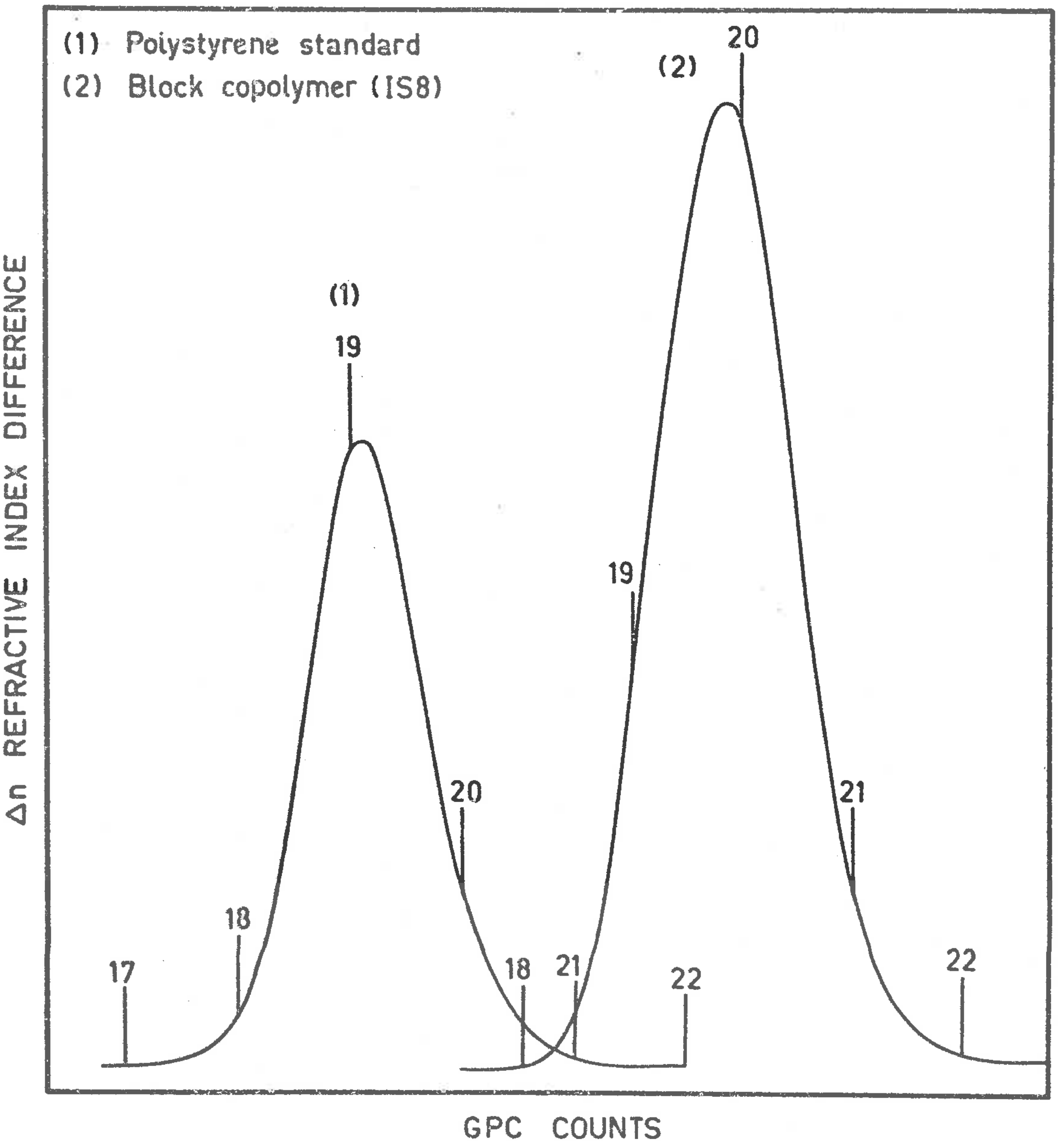

(1) Polystyrene standard
(2) Block copolymer (IS8)
(1)
(2)
17
18
19
20
18
21
22
19
20
21
22
Δn REFRACTIVE INDEX DIFFERENCE
GPC COUNTS

Fig. 3.5. Plot of log M against elution volume for the polystyrene standards.

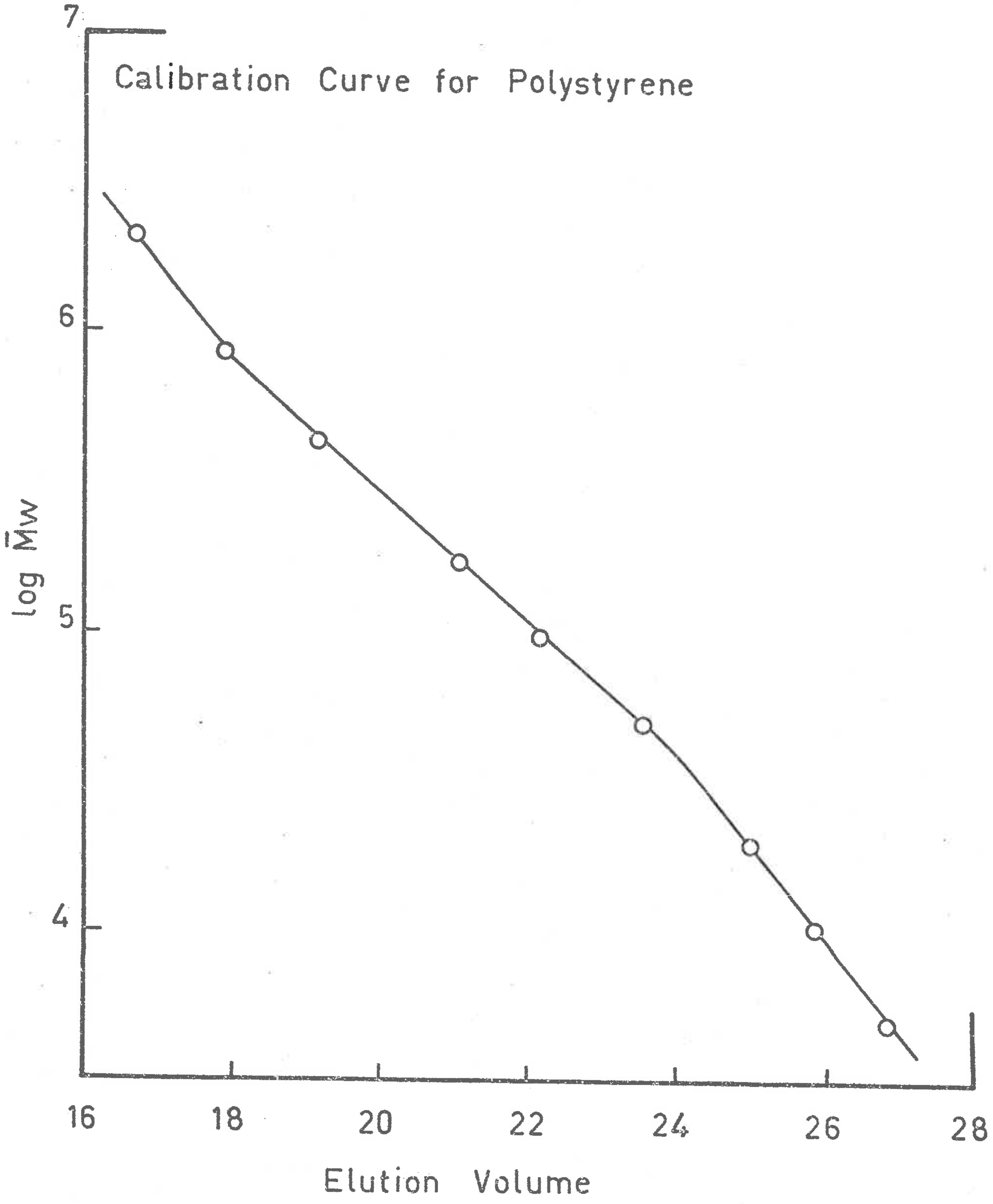

Calibration Curve for Polystyrene
log M̄w
7
6
5
4
16
18
20
22
24
26
28
Elution Volume

Fig.3.5

Here w is the width of the curve determined as the distance between the base line intercepts of lines drawn tangent to the points of inflection of the trace, d is $\bar{M}w/\bar{M}n$ and subscript 1 and 2 refer to different polymers, one of which is any standard. On this bases, comparison of the chromatograms of the block copolymers with those of the standard polystyrene samples showed them to have MWD's as narrow as the polystyrene standards. This is a rapid technique of obtaining comparative MWD's and is especially useful during the initial trial stages of the synthesis of novel copolymers.

The chromatograms were analysed quantitatively by integrating the curves at each half count and plotting the cumulative weight curve on normal-probability paper as the function of the number of counts. Such plots are shown in Fig. 3.6. These show that a linear plot is obtained over at least 95% of the chromatogram and Gaussian distribution over this range can be assumed. The standard deviation σ_c is determined from the difference in counts at 50% and 16% mark. To convert this to molecular weight σ_c must be divided by k, the slope of the calibration curve. The molecular weight at the 50% mark corresponds to the geometric mean $\bar{M}g$ and therefore the ratio $\bar{M}w/\bar{M}n$ may be computed from the relations:[55]

$$\sigma = \sigma_c/k \qquad 3.17$$

$$\bar{M}w = \bar{M}g \exp(\sigma^2/2) \qquad 3.18$$

$$\bar{M}w/\bar{M}n = \exp(\sigma^2) \qquad 3.19$$

The results of the standard deviation and the ratio $\bar{M}w/\bar{M}n$ calculated from the GPC curves are shown in Table 3.5. The values for the separate molecular weight averages $\bar{M}n$ (and $\bar{M}w$) included in this table have been computed with the aid of the calibration curve shown in Fig. 3.7.

Table 3.5: Molecular Weights and Standard Deviations (σ) Obtained from GPC Curves for the Copolymers

Polymer	Peak Count	σ	$\bar{M}n \times 10^{-5}$	$\bar{M}w/\bar{M}n$
IS1	21.23	0.287	0.94	1.08
IS2	21.38	0.312	1.02	1.10
IS3	21.56	0.230	0.96	1.05
IS4	21.36	0.277	1.07	1.08
IS5	21.84	0.285	0.96	1.08
IS6	19.40	0.317	2.41	1.10
IS7	19.53	0.287	2.42	1.08
IS8	19.85	0.272	2.25	1.07
IS9	18.10	0.327	4.90	1.11
IS10	18.35	0.352	4.68	1.13
PS-2	25.81	0.250		1.06

Fig. 3.6. Typical normal-probability plots of the cumulative weight data for the copolymers and a polystyrene sample.

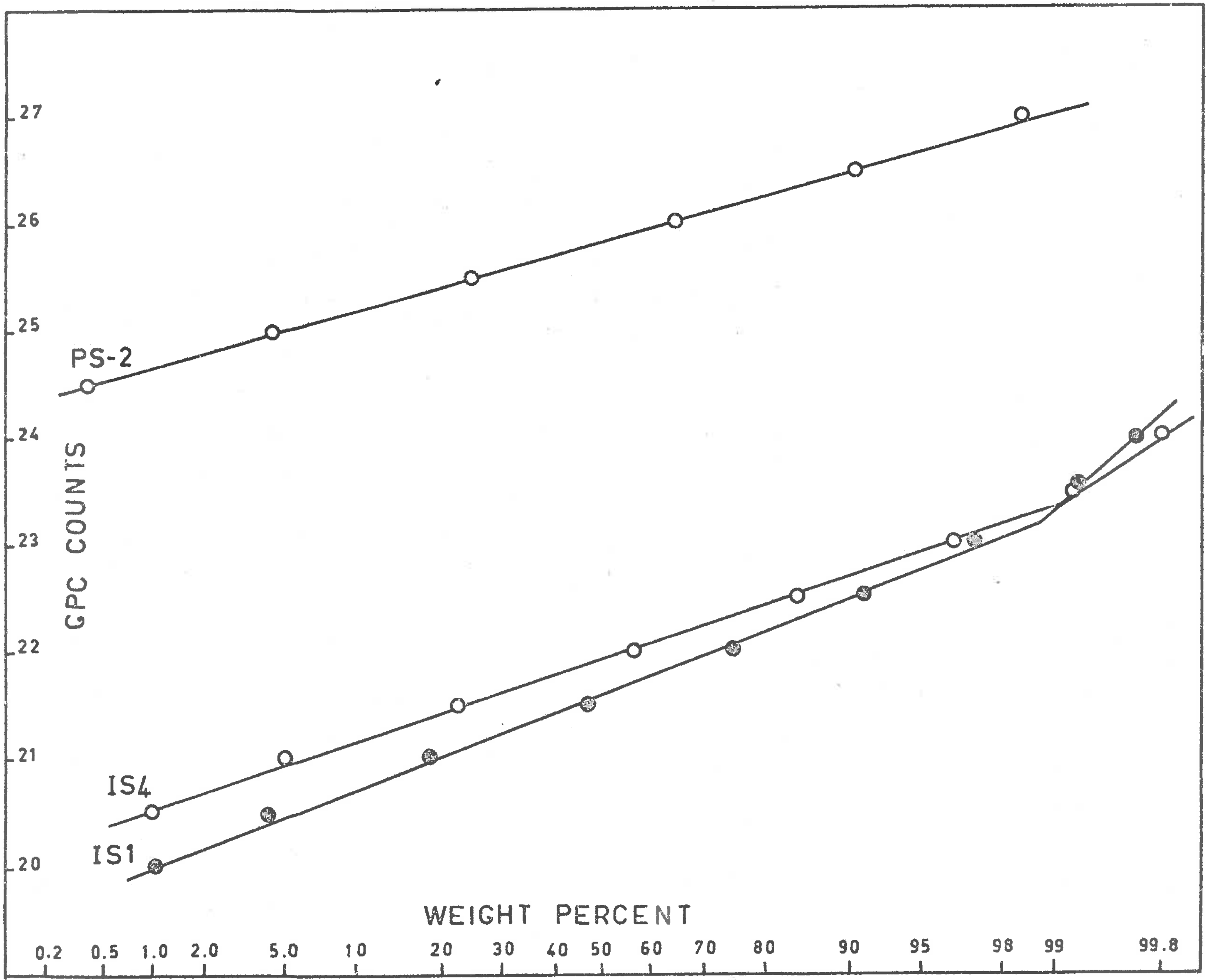

27
26
25
24
23
22
21
20
GPC COUNTS
PS-2
IS4
IS1
WEIGHT PERCENT
0.2
0.5
1.0
2.0
5.0
10
20
30
40
50
60
70
80
90
95
98
99
99.8

Fig.3.6

There are several ways of dealing with the experimental data of GPC. Many approaches to relate the GPC curve to the true MWD involve a computer to handle the calculations.[45-48] Recently a simpler graphical conversion procedure has also been reported.[56] As has been discussed before, the problems of obtaining absolute MWD's are complex. There is still no complete agreement as to a unique method which considers all factors involved.[50] The study of block copolymers presents a further problem: the extent to which any composition distribution may affect the chromatogram obtained. Any corrections attempted on GPC curves of copolymers should consider all these factors. The method of representing the cumulative curve of a GPC trace as a straight line on a normal-probability graph seems to have much to recommend it. One advantage 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 the more conventional methods of obtaining these parameters. 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 normal-probability curve may 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 of all the copolymers showed no evidence of a double inflection and it must be concluded that GPC cannot resolve narrow distributions of the type found in these copolymers. The distributions seem to follow a Gaussian law at least over the linear parts of the probability plots.

The normal calibration, using the polystyrene standards, of log M versus elution volume (Ve) for the column combination used, is shown in Fig. 3.5. The molecular weight data supplied by Waters Associates together with the determined peak counts are shown in Table 3.6. The values of the intrinsic viscosities $[\eta]$ determined in THF at 25°C are also shown. The viscosity determinations were carried out as detailed in Chapter 5.

Table 3.6: Molecular Weight, GPC, and Viscosity Data for the Polystyrene Standards

Polymer	$\bar{M}n \times 10^{-4}$	$\bar{M}w/\bar{M}n$	Peak Count	$[\eta]^{25°}_{THF}$, ml/g
PS-1	0.46	1.09	26.81	5.6
PS-2	0.97	1.06	25.81	9.5
PS-3	1.96	1.01	24.95	15.3
PS-4	4.90	1.04	23.53	30.3
PS-5	9.62	1.02	22.19	48.7
PS-6	16.40	1.05	21.07	73.4
PS-7	39.20	1.05	19.07	137.5
PS-8	77.30	1.12	17.86	236.2
PS-9	178.00	1.20	16.67	455.4

Figure 3.5 shows that the calibration curve is linear over the Ve interval 17.5-24 (counts). This covers a molecular weight range of 50,000-800,000. Over this interval the slope of the calibration is least, showing that it is the most sensitive range for the column combination used (since resolution is inversely proportional to the slope of the calibration). Since all the copolymers studied fall in this Ve range this column combination was used throughout the study.

The relevant data for the copolymers is shown in Table 3.7.

Table 3.7: Molecular Weight, GPC, and Viscosity Data for the Copolymers

Polymer	$\bar{M}n \times 10^{-5}$	Peak Count	$[\eta]^{25°}_{THF}$, ml/g
IS1	1.02	21.23	114.5
IS2	1.02	21.38	98.6
IS3	1.01	21.56	92.7
IS4	1.04	21.36	93.5
IS5	1.03	21.84	74.2
IS6	2.53	19.40	233.1
IS7	2.52	19.53	207.0
IS8	2.54	19.85	177.0
IS9	4.99	18.10	410.2
IS10	5.01	18.35	306.0

For the purpose of attempting a universal calibration, common for both the copolymers and homopolymer constituents, the product of the intrinsic viscosity and molecular weight was used as the universal parameter.[40] Such a universal curve is shown in Fig. 3.7 as a plot of $\log[\eta]M$ versus elution volume. The results of the copolymers can be well represented by the same curve which fits the points of the polystyrene standards. This shows that the hydrodynamic volume is a general size-parameter for GPC separation for both the copolymers and constituent homopolymers. Accepting this, the curve for the polystyrene standards can be used to give the molecular weight averages $\bar{M}n$ (and $\bar{M}w$) for the copolymers by making use of the measured $[\eta]$ for these systems. Results obtained in this way are shown in Table 3.5.

These results show that GPC for these block copolymers may be considered as a combination of molecular weight and viscosity. A similar conclusion was made by Crubisic, Rempp and Benoit[40] for the case of linear and branched homopolymers. Owing to the ease of both viscosity and GPC measurements, this method of calibration should prove very useful in obtaining quantitative results from GPC data of 'unknown' polymers. This would be especially useful in the field of copolymers where one deals with new materials for which calibration standards are not normally obtainable.

Fig. 3.7. Plot of log [η]M against elution volume for the copolymers and constituent homopolymers.

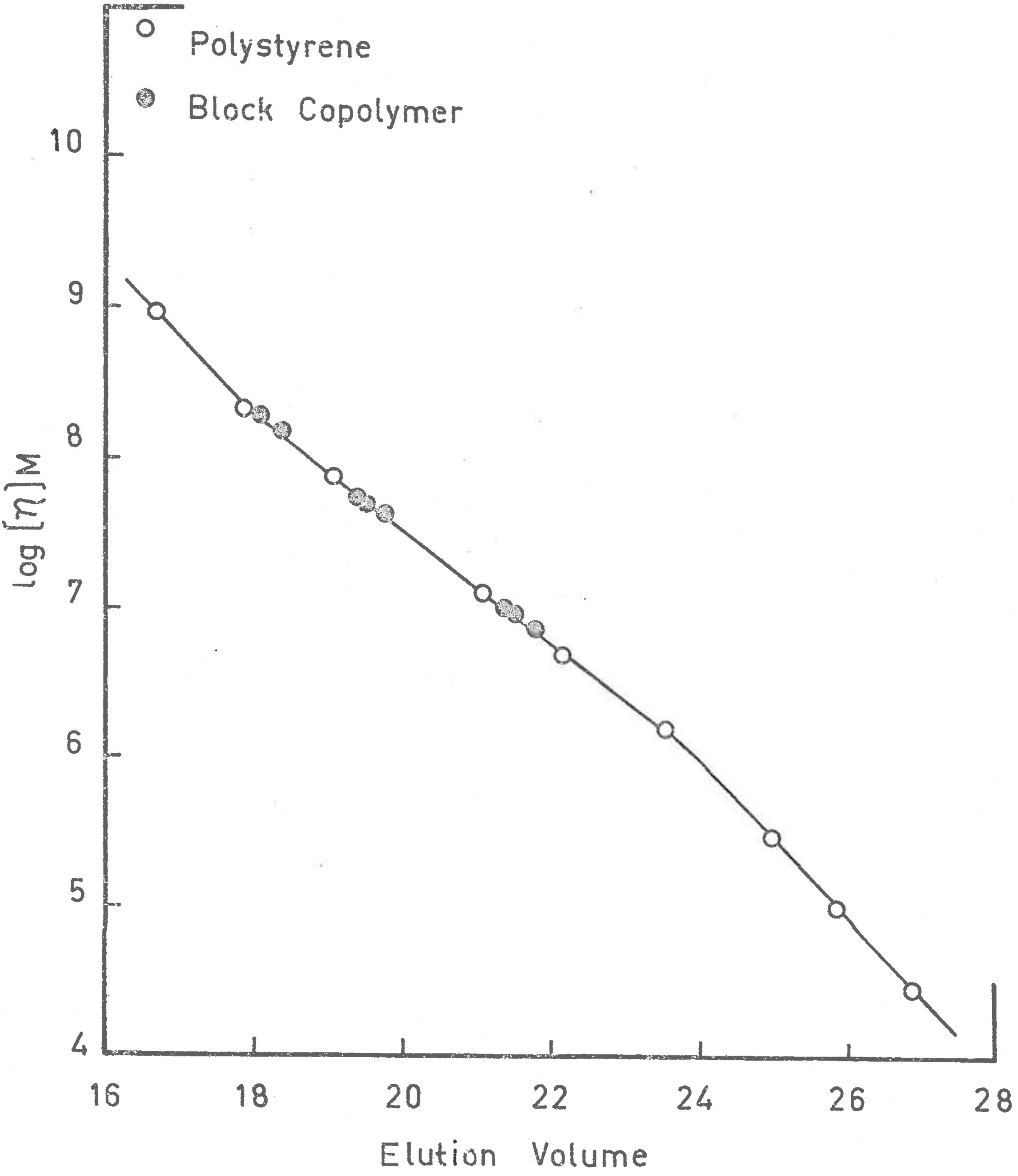

○ Polystyrene
● Block Copolymer
log [η] M
10
9
8
7
6
5
4
16
18
20
22
24
26
28
Elution Volume

Fig.3.7

DISCUSSION

For the purpose of comparison, the molecular weight averages $\bar{M}w$ and $\bar{M}n$ and the distributions obtained from them by the method of GPC, light scattering and osmometry are shown in Table 3.8.

Table 3.8: Molecular Weights and Distributions of the Copolymers as Determined by GPC, and Light Scattering (LS) and Osmometry (OP)

	GPC		LS and OP	
Polymer	$\bar{M}n \times 10^{-5}$	$\bar{M}w/\bar{M}n$	$\bar{M}n \times 10^{-5}$	$\bar{M}w/\bar{M}n$
IS1	0.94	1.08	1.02	1.04
IS2	1.02	1.10	1.02	1.05
IS3	0.96	1.05	1.01	1.07
IS4	1.07	1.08	1.04	1.03
IS5	0.96	1.08	1.03	1.05
IS6	2.41	1.10	2.53	1.06
IS7	2.42	1.08	2.52	1.04
IS8	2.25	1.07	2.54	1.03
IS9	4.90	1.11	4.99	1.07
IS10	4.68	1.13	5.01	1.08

Billmeyer[3] has discussed the accuracy involved in obtaining the ratio of $\bar{M}w/\bar{M}n$ from light scattering and osmometry. The error in $\bar{M}n$ is generally accepted to be of the order (± 4%). The determination of $\bar{M}w$ is subjected to a larger error, normally of the order (± 8%). Errors in determining $\bar{M}w$ for copolymers are even greater because a true $\bar{M}w$ can ohly be obtained by making measurements in at least three different solvents. Using a computer method to obtain $\bar{M}w$ should reduce the error in this parameter. $\bar{M}n$ can be obtained with equal accuracy for copolymers and homopolymers alike. According to Benoit[2] the number average molecular weight given by the usual expression:

$$\bar{M}n = \Sigma NiMi/\Sigma Ni$$

is unambiguous for homopolymers and copolymers alike. In view of this, comparision of the $\bar{M}n$ values obtained from GPC and those obtained from osmometry may be made as a test of the GPC method. As can be seen from Table 3.8 the comparison is good, showing the efficiency of the GPC method as well as the validity of the established universal calibration.

Comparative studies[52] have shown that GPC distributions are on the high side in contrast to fractional precipitation methods in which low molecular weight material may not precipitate.[57]

Values of $\bar{M}w/\bar{M}n$ from the classical light scattering and osmometry techniques are normally found between the values obtained by the above two methods.[52] The values from GPC shown in Table 3.8 may be somewhat smaller if suitable corrections for chromatogram broadening were applied. In view of this the molecular weight distributions obtained by the different techniques must be considered to be in good agreement.

Overall, it must be concluded that the block copolymers are of narrow distribution in both molecular weight and composition. Also they are completely free of extraneous homopolymer impurities. The values of $\bar{M}n$ (and $\bar{M}w$) obtained from GPC are in good agreement with those obtained by the classical methods. This shows the efficiency of the GPC method of separation of these block copolymers, as well as the validity of the universal calibration based on the hydrodynamic volume as the universal size-parameter.

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Chapter 4

THERMODYNAMIC PARAMETERS

INTRODUCTION

Development of Thermodynamic Theories of Homopolymer Solutions

To understand the meaning of the various thermodynamic parameters which may be obtained from osmotic pressure measurements on polymer solutions, it might prove helpful to go through the development of selected theories leading to these parameters.

The demand on any theory of solutions is that it be able to express, by appropriate mathematical relations, the properties of the solution with reference to those of the pure components. The ideal solution law, as described by Raoult's law, provides a sufficient basis for the treatment of simple molecule solutions. However, solutions for which the solute is a polymer of high molecular weight exhibit a very large deviation from ideality. Even at concentrations exceeding a few percent this deviation is so large that the ideal solution law is of little value as a basis for correlating the thermodynamic properties of polymer solutions. Previously the effect of the different molecular sizes of the components on the properties of their solutions had been taken into account through the energies of interaction, i.e., through the heat of mixing. It was first suggested in the mid-1930's that mixtures of molecules of different sizes would not have an ideal free energy of mixing, even if the heat of mixing is zero. It was later definitely established by Fowler and Rushbrooke[1] that such mixtures can deviate from the laws of ideal solutions even if mixing takes place without change of heat content and volume on mixing. The next major step was when Flory[2] and Huggins[3] succeeded independently in deriving an expression for the athermal entropy of mixing of two components, the molecules of which occupy one site and x sites each on the lattice model used.

In his original derivation for athermal polymer solutions, Flory[2] considered a polymer molecule as consisting of x chain segments, each equal in volume to a solvent molecule; x is, of course, the ratio of the molar volumes of the solute and solvent. Using a lattice containing $N_o = N_1 + xN_2$ sites and further letting z be the lattice coordination number or number of cells which are first neighbours to a given cell, he set out to calculate the number of ways (Ω) of arranging the N_1 solvent and N_2 polymer molecules on the lattice. Using Boltzmann relation $\Delta S = k \ln \Omega$, the athermal entropy of mixing becomes

$$\Delta S^*/R = -n_1 \ln \phi_1 - n_2 \ln \phi_2 \qquad 4.1$$

where n_1 and n_2 are the number of moles and ϕ_1 and ϕ_2 the volume fraction of solvent and solute respectively:

$$\phi_1 = N_1/(N_1 + xN_2)$$
$$\phi_2 = xN_2/(N_1 + xN_2) \qquad 4.2$$

We use a superscript asterisk* to denote a property of an athermal solution. Since the heat of mixing is zero we have for the free energy of mixing

$$\Delta G^*/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 \qquad 4.3$$

This is a very simple expression and replaces the expression for the ideal free energy of mixing for the case of polymer solutions. Of course equation 4.3 goes into the ideal free energy of mixing when x = 1, i.e., the solute and solvent molecular volumes are equal, in which case the volume fraction becomes the mole fraction. From equation 4.3 the change of the chemical potential on mixing can be obtained as

$$\Delta U_1^*/RT = \ln \phi_1 + (1 - 1/x)\phi_2$$
$$\Delta U_2^*/RT = \ln \phi_2 - (x - 1)\phi_1 \qquad 4.4$$

Equation 4.3 contains no lattice dependent parameters. This suggests that a similar expression might be derived without resorting to a lattice model. In fact Hildebrand[4] derived equation 4.3 by considering the free-volume theory, which assumes that the free volume is proportional to the molar volume. However, the model employed here, although useful, is no more realistic and offers no advantage over the lattice model.

In his original derivation Flory[2] neglected the effect of the finite coordination number of the lattice: he assumed that the probability of occupation of a site is independent of the knowledge of how a neighbouring site is occupied. Attempts to correct for this led to more complicated equations,[3,5,6]

To allow for the finite coordination number of the lattice we again consider N_1 solvent and N_2 polymer molecules distributed on the $N_o = N_1 + xN_2$ sites of a lattice. If the coordination number of the lattice is z then each solvent molecule has z nearest neighbours, but each polymer molecule has $qz = x(z-2)+2$ nearest neighbours and not xz as assumed by Flory. Now instead of considering site fractions we introduce nearest neighbour fractions defined by

$$\begin{aligned} \xi_1 &= N_1/(N_1 + qN_2) \\ \xi_2 &= qN_2/(N_1 + qN_2) \end{aligned} \qquad 4.5$$

Using these to calculate the probability that certain molecules will occupy certain series of sites, the chemical potential of mixing of polymer and solvent become

$$\begin{aligned} \Delta U_1^*/RT &= \ln \phi_1 + \ln(\xi_1/\phi_1)z/2 \\ \Delta U_2^*/RT &= \ln \phi_2 + \ln(\xi_2/\phi_2)zq/2 \end{aligned} \qquad 4.6$$

With these expressions the free energy of mixing can be calculated from

$$\Delta G^{*} = n_1\Delta U_1^{*} + n_2\Delta U_2^{*} \qquad 4.7$$

For a linear array of segments, $z=2$ and ΔG^{*} should have the ideal value. In fact the above equations do reduce to the ideal when $z=2$. From this it should not be surprising to find that deviations from the laws of ideal solutions increase with increasing z. Also if we let z go to infinity, Flory's original expression for ΔG^{*} (equation 4.3) can be obtained from equation 4.7.

However, it is found that for $z > 4$ the activity of the solvent in a polymer solution is very little different from when $z = \infty$, so that in general the use of equation 4.3, instead of the more complex equation 4.7, is quite justified.

We next consider the case of mixtures of molecules of different sizes in which the energies of interaction of the different types of nearest neighbour pairs are different. In this case there is a non-vanishing heat of mixing. In his original derivation Flory[2] assumed that the entropy of mixing in any solution can be put equal to the entropy of mixing of the corresponding athermal solution: he neglected any possible influence of the energies of interaction on the entropy of mixing.

Allowing for this, Flory-Huggins arrived at an expression for the general polymer solution for which the heat of mixing is given by

$$\Delta H/RT = \chi_1\phi_1\phi_2(n_1 + xn_2) \qquad 4.8$$

From this the changes of the partial molar heat contents on mixing are given by

$$\begin{aligned} \Delta H_1/RT &= \chi_1\phi_2^2 \\ \Delta H_2/RT &= x\chi_1\phi_1^2 \qquad 4.9 \end{aligned}$$

The changes in chemical potential on mixing for the two components are then

$$\begin{aligned} \Delta U_1/RT &= \ln\phi_1 + (1-1/x)\phi_2 + \chi_1\phi_2^2 \\ &= -\phi_2/x - ({}^1/_2 - \chi_1)\phi_2^2 \\ \Delta U_2/RT &= \ln\phi_2 - (x-1)\phi_1 + x\chi_1\phi_1^2 \qquad 4.10 \end{aligned}$$

and the free energy of mixing is

$$\Delta G/RT = n_1\ln\phi_1 + n_2\ln\phi_2 + \chi_1 n_1\phi_2 \qquad 4.11$$

This is normally known as the Flory-Huggins expression. The parameter χ_1 as defined by equation 4.8 is a dimensionless quantity and is known as the interaction parameter. It characterises the interaction energy per solvent molecule.

The quantity $kT\chi_1$ represents the difference in energy of a solvent molecule immersed in the pure polymer compared with one immersed in the pure solvent.

The parameter χ_1 consists of two terms, the first derived from the entropy of mixing and dependent on the coordination number z and the second derived from the heat of mixing. For practical purposes it is often convenient to write χ_1 as the sum of these two terms:

$$\chi_1 = \chi_S + \chi_H \qquad 4.12$$

This decomposition of χ_1 into two terms is particularly useful if it is independent of temperature; in this case χ_S and $T\chi_H$ are constants and χ_1 can be written as $\alpha + \beta/T$. This facilitates comparison of theory with experiment.

All of the thermodynamic relations derived thus far are appropriate, in general, only at concentrations which allow the randomly coiled molecules to overlap one another considerably. Under this condition the concentration of polymer segments can be considered to be uniform throughout the solution. At this stage the question arises as to what value of the concentration the deviation from the laws of dilute solutions becomes noticeable. For high polymers this is very small and explains why it is, in general, not possible to determine the molecular weight of polymers directly by the usual methods used for non-polymeric substances. Such methods as lowering of the freezing point, or elevation of the boiling point depend on the validity of the laws of ideal solutions. At the low concentrations for which ideal laws hold for polymer solutions, the changes in the property of the solvent are so small that they cannot be determined with any great accuracy. The only alternative is to measure these properties as a function of concentration and extrapolate to infinite dilution. This is what is normally done for the osmotic pressure.

It was first recognized by Flory[7] that the above theories, thus far developed, are not applicable to dilute solutions in which the polymer segments are not uniformly distributed throughout the solution. This problem was later taken up by Flory and Krigbaum[8,9] who attempted to derive an expression for the chemical potential of mixing of the solvent for this case. This theory has normally become known as the dilute-solution theory and includes some of the derivations and assumptions of the previous theories, with a further addition of the concept of an excluded volume.

A very dilute polymer solution can be considered as a dispersion of clouds of segments with a region of pure solvent separating each cloud. Flory and Krigbaum assumed these clouds as being approximately spherical and having a Gaussian distribution of segments about the centre. From a purely spatial consideration, in dilute solution, extensive overlap of these clouds is not favoured. But in this respect intermolecular interactions play an important role and must also be considered. In a poor solvent (χ_1 sufficiently positive) the preference for polymer - polymer contact will counteract repulsion between polymer molecules arising from their spatial requirements, to an extent depending on the magnitude of the interaction. In a good solvent (low χ_1) each molecule will tend to exclude all others from the volume it occupies. This leads to the concept of an excluded volume from which a polymer molecule effectively excludes all others.

Flory and Krigbaum approached the problem by considering small elements of volume dV in which uniformity of the segment distribution can be assumed, so that the Flory-Huggins expressions hold. One can then write expressions for the free energy of mixing of the solution in such elements of volume when the molecules are far apart and when their centres of mass are a distance a from each other. This process is accompanied by an increase in the free energy given by

$$\Delta G_{(a)} = kTX \exp[-3a^2/4<S^2>] \qquad 4.13$$

where $<S^2>$ is the mean-square radius of gyration. From this

Flory was able to calculate the chemical potential of the solvent on mixing. Considering two molecules, the probability that their centres of mass will be a distance a apart is given by a Boltzmann factor $\exp[-\Delta G_{(a)}/kT]4\Pi a^2 da$; so that the effect of $\Delta G_{(a)}$ when one molecule is at a fixed position is that the second molecule behaves as if the volume

$$U = \int_o^\infty [1-\exp(-\Delta G_{(a)}/kT)]4\Pi a^2 da \qquad 4.14$$

were excluded from it. This excluded volume can be calculated from equation 4.13 and 4.14 as

$$U = (1-2\chi)x\ v_2\ F(X) \qquad 4.15$$

where v_2 = volume of a polymer molecule. The function F(X) is given by

$$F(X) = 1 - X/2^{3/2}2! + X^2/3^{3/2}3! - \ldots \qquad 4.16$$

its value is unity when X = 0 and decreases monotonically with increasing X.

Equation 4.15 shows that U is a function of the interaction parameter χ and is zero when $\chi = 0.5$. The temperature at which this happens plays an important role in Flory's dilute-solution theory and is known as the theta (θ)- or Flory temperature. This temperature was defined by Flory as

$$\theta = \kappa_1/T\psi_1$$

where κ_1 and ψ_1 represent the enthalpy and entropy of dilution parameters respectively and are related to the enthalpy and entropy of dilution by

$$\Delta H_1 = RT\,\kappa_1\,\phi_2^2 \qquad 4.17$$

$$\Delta S_1 = R\,\psi_1\,\phi_2^2 \qquad 4.18$$

Of course all these related to the total interaction parameter χ by

$$\chi_1 = \kappa_1 + (1/2 - \psi_1) \qquad 4.19$$

If χ is split up into its enthalpy and entropy term, according to equation 4.12, then the terms χ_H and χ_S correspond to κ_1 and $1/2 - \psi_1$ respectively.[10-12] In his most recent paper, Flory[12] defines the term χ_H as the reduced enthalpy of dilution and χ_S as the reduced residual partial molar entropy.

The extension of the polymer molecule in space increases with U and Flory assumed that all linear dimensions of the polymer are increased by a constant factor α due to this excluded volume effect. Thus he obtained

$$X = 2C(1 - 2\chi)M^{1/2}/\alpha^3 \qquad 4.20$$

where C is essentially a constant and M is the molecular weight of polymer. Also

$$X = 2(\alpha^2 - 1) \qquad 4.21$$

so that

$$\alpha^5 - \alpha^3 = C(1 - 2\chi)M^{1/2} \qquad 4.22$$

This is an important relation which will be discussed further in Chapter 5.

From this, Flory was able to arrive at the chemical potential of mixing:

$$\Delta U_1/RT = -\phi_2/x - (^1/_2 - \chi)F(X)\phi_2^2 - \ldots. \qquad 4.23$$

Comparison of this with Flory-Huggins equation 4.10 shows that the effect of the dilute-solution is to decrease the coefficient of ϕ_2^2 (known as the second virial coefficient) by the factor F(X). At the Flory temperature, where $\alpha = 1$, $X = 0$ and $F(X) = 1$, so that the Flory-Huggins equation is recovered, i.e., under these conditions the excluded volume is zero so that there is no 'dilute-solution effect'.

Osmotic Pressure

Osmotic pressure measurements are widely used in polymer solution studies. The two major reasons for making such measurements are to obtain the number average molecular weight of the polymer and information on the thermodynamic properties of the solution.

The osmotic pressure is related to the chemical potential of mixing of the solvent by

$$\Pi = -(\mu_1 - \mu_1^o)/V_1 = \Delta\mu_1/V_1 \qquad 4.24$$

where V_1 is the molar volume of solvent. For ideal solutions Van't Hoff's law gives

$$\Pi/C_2 = RT/M_2 \qquad 4.25$$

where C_2 is the concentration of solute in g/cm^3 and M_2 is the molecular weight of solute. Any theory of polymer solution gives the osmotic pressure as a virial expansion in terms of concentration. Thus

$$\begin{aligned} \Pi/C_2 &= RT[1/M_2 + A_2C_2 + A_3C_2^2 + \ldots.] \\ &= (\Pi/C_2)_o[1 + \Gamma_2C_2 + \Gamma_3C_2^2 + \ldots.] \qquad 4.26 \end{aligned}$$

The coefficients of the expansion are known as virial coefficients, e.g., A_2 and A_3 are known as the second and third virial coefficients respectively. All theories must predict the ideal term of the expansion at infinite dilution, but can differ in their expression for the virial coefficients. In terms of the Flory-Krigbaum dilute-solution theory the second virial coefficient becomes

$$A_2 = \Gamma_2/M = (\bar{v}_2^2/V_1)(^1/_2 - \chi)F(X)$$
$$= (\bar{v}_2^2/V_1)\psi_1(1 - \theta/T)F(X) \qquad 4.27$$

where $\bar{v}_2$ is the specific volume of polymer and the other parameters have their usual meaning, as described in the dilute-solution theory.

The second and third virial coefficients are related by

$$\Gamma_3 = g\,\Gamma_2^2 \qquad 4.28$$

where g is a slowly increasing function of Γ_2 and has a theoretical value of 5/8, when considering solutions of hard spheres.[8] However, it has been shown[13] that this value is too high and that values near 0.25 are more nearly correct in good solvents. Using g = 0.25 reduces equation 4.26 to the convenient form

$$(\Pi/C_2)^{1/2} = (\Pi/C_2)_o^{1/2}[1 + \Gamma_2C_2/2] \qquad 4.29$$

The effect of the third virial coefficient is to produce curvature in plots of Π/C_2 versus C_2. Since Γ_3 should rapidly vanish as Γ_2 tends to zero, a decrease in the slope of the plot for poorer solvents should be paralleled by a more rapid disappearance of the curvature and at T = θ both become zero. Square root plots according to equation 4.29 usually show very little curvature for both good and poor solvents. Such plots are more convenient for extrapolation to obtain molecular weight and the second virial coefficient.

The thermodynamic behaviour of dilute polymer solutions depends on three factors: a) the molecular weight; b) the thermodynamic interaction parameters ψ_1 and κ_1, or ψ_1 and θ_1 which characterize the segment-solvent interaction; and c) configuration of the molecule in solution. Of course for block copolymers a fourth factor of composition might be expected to have an effect. The second virial coefficient is dependent on all three factors according to equation 4.27. The dilute-solution theory predicts that F(X) and therefore A_2 decreases with increasing M. Since F(X) approaches unity as T approaches θ, a plot of A_2 versus 1/T according to equation 4.27 gives the value of θ by extrapolating to $A_2 = 0$. The slope of the plot allows the calculation of ψ_1.

EXPERIMENTAL

Osmometry

The osmometer. Osmotic pressure measurements were made with a Hewlett-Packard/Mechrolab model 501 high speed membrane osmometer. This instrument provides a rapid means of measuring osmotic pressure by indicating hydrostatic head. This is accomplished automatically by using a photocell/electric-servo system. A schematic diagram of the instrument is shown in Fig. 4.1. Pressure is presented on a four digit odometer type readout (15) in centimetres of solvent. When solvent is contained on both sides of the membrane (13) the equilibrium odometer reading is taken as the solvent reference value (P_o). When polymer solution is contained in the sample stack an osmotic pressure between the two sides of the membrane is set up. This tends to make liquid flow through the membrane causing the bubble (5) in the capillary (8) to move. This movement is detected by the photocell (7) which activates the null-seeking electric-servo system. This adjusts the hydrostatic head to prevent this liquid flow and brings back the bubble to its equilibrium position. Because there is no net flow of solvent through the membrane the establishment of equilibrium is fast: from 5-15 minutes (depending on the solvent-polymer system). The new equilibrium position of the odometer is the solution reference value (P). The osmotic pressure Π for a particular concentration is expressed in centimetres of solvent and given by $\Pi = P-P_o$.

The osmometer was set up with a variable temperature probe giving an operating range, of the insulated sample chamber, from ambient to 65°C. The calibration chart of the temperature probe was checked by using an accurately calibrated thermistor probe. The sample-chamber temperature could be maintained to within ± 0.5°C. The instrument was also set up with a three

Fig. 4.1. Schematic diagram of the Hewlett-Packard membrane osmometer.

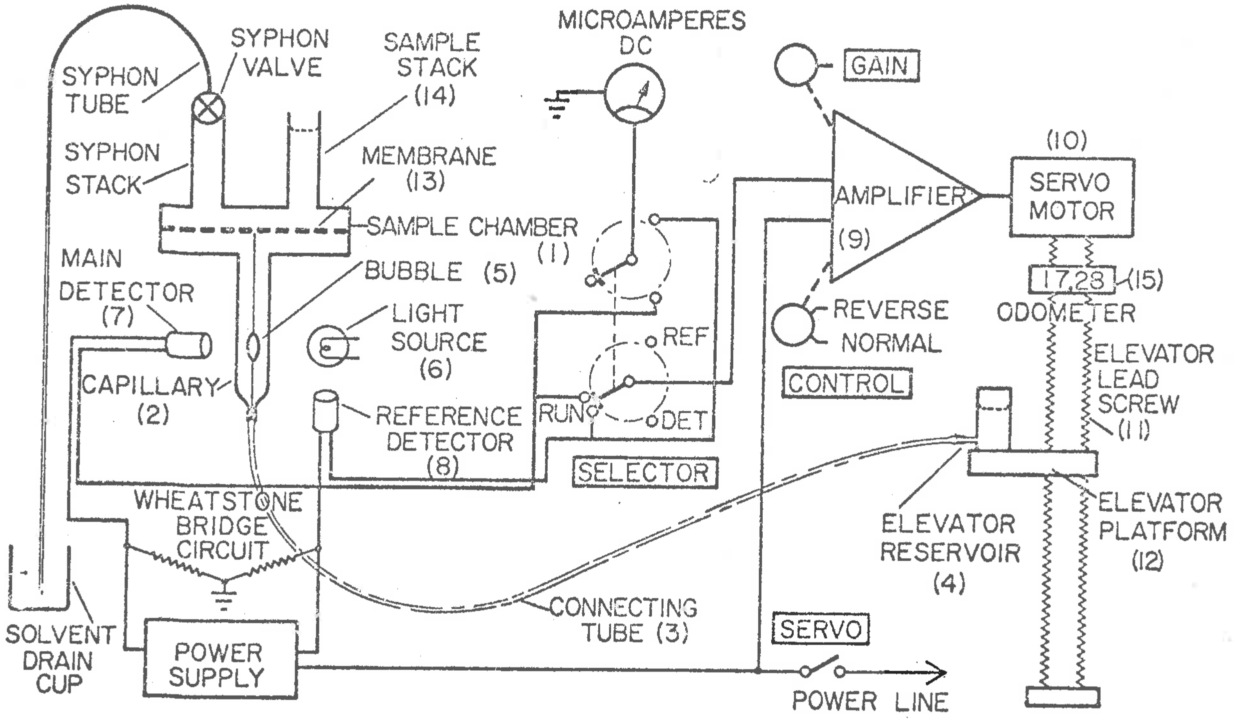

SYPHON TUBE
SYPHON VALVE
SAMPLE STACK (14)
MICROAMPERES DC
GAIN
SYPHON STACK
MEMBRANE (13)
SAMPLE CHAMBER (1)
AMPLIFIER (9)
(10) SERVO MOTOR
MAIN DETECTOR (7)
BUBBLE (5)
LIGHT SOURCE (6)
17,28 (15)
ODOMETER
REVERSE
NORMAL
CONTROL
REF
RUN
DET
SELECTOR
CAPILLARY (2)
REFERENCE DETECTOR (8)
ELEVATOR LEAD SCREW (11)
WHEATSTONE BRIDGE CIRCUIT
ELEVATOR PLATFORM (12)
ELEVATOR RESERVOIR (4)
CONNECTING TUBE (3)
SOLVENT DRAIN CUP
POWER SUPPLY
SERVO
POWER LINE

Fig.4.1

speed chart recorder which gave a recorded trace of establishment of equilibrium. This proved very useful in following the stability of the instrument over a period of time, especially after the initial setting up of a new membrane.

Membrane conditioning. Non-aqueous type (0-8) membrane filters (from Schleicher and Schuell) were used. These were supplied in a 25% isopropanol/water solution. Conditioning for use with a particular solvent consisted of successively soaking them for eight hours in each of the following liquids:

1) water/isopropanol, 50%/50% by volume
2) isopropanol, 100%
3) isopropanol/toluene, 50%/50%
4) toluene, 100%.

If the solvent to be used was other than toluene, they were soaked for another eight hours in each of:

1) toluene/solvent, 50%/50%
2) final solvent, 100%.

Just before a new membrane was installed it was heated in the particular solvent to 60°C for about 30 minutes, with gentle agitation to completely degass it.

Handling of solutions. For each polymer-solvent system the osmotic pressure was measured for at least four different concentrations. These were obtained by sequential dilution of the most concentrated solution. Both solvents and solutions were filtered through a G4 filter by means of dry nitrogen pressure prior to use. All solvents used were treated as described previously (Chapter 3). For the higher temperature range, 0.02% of antioxidant (N-phenyl-beta-naphthylamine) was added to the solvent. All solvents and solutions were degassed before introducing them into the osmometer by heating just above the operating temperature. This prevented any bubbles forming in the osmometer assembly and allowed thermal equilibrium to be attained rapidly. The operation of the osmometer was periodically checked by measuring a standard solution of polystyrene of known $\bar{M}n$. In any case, this was routinely done after the instillation of every new membrane.

Treatment of data. The difference between odometer readings of the solvent (P_o) and the solution (P) gives directly the osmotic pressure of the solution in centimetres of solvent: $\Pi = P-P_o$. The reduced osmotic pressure is

$$\Pi/C = (P - P_o)/C$$

where C is the concentration in gm/cm^3.

According to equation 4.26

$$\Pi/C = RT[1/M + A_2C + ...]$$

Here T is the temperature of the solvent in contact with the membrane, i.e., the sample chamber temperature in °K. R is the gas constant having the value 0.08208 litre-atmosphere/degree mole. The value of R, in the appropriate units to be used in the above calculation, is given by

$$R = 0.08208 \times 1033.3/d$$

where d = density of solvent in the elevator reservoir in gm/cm^3 and 1 atmosphere = 1033.3 gm/cm^3. The osmotic pressure measurements were treated according to both equation 4.26 and 4.29, as will be discussed later.

Cloud-point Titration

Introduction. The theta temperature (or Flory temperature) is a very important parameter in both thermodynamic and hydrodynamic studies of polymer solutions. For this reason it is very important to be able to determine this parameter experimentally. Also this theta temperature must fall within a workable temperature range if it is to be of practical use. Use of solvent mixtures to achieve this theta condition is undesirable because of the complications which arise in the analysis of osmotic pressure and light scattering data made in mixed solvents. Fortunately, the interpretation of viscosity measurements are not complicated by using solvent mixtures.

The problem can also be removed from the analysis of light scattering data by using solvent-nonsolvent which are isorefractive. This eliminates the problem of preferential absorption. As a priori, it is impossible to predict the theta behaviour of block copolymers (or copolymers in general) in a given solvent system. Some indication may be obtained from the cohesive energy densities of the respective homopolymers in the particular solvent, but this is far from satisfactory. For these reasons finding a useful theta condition of a copolymer of given composition is a process of trial and error. Because of this it is desirable to find a rapid method of obtaining knowledge of this theta condition. The cloud-point titration (or turbidimetric titration) should offer such a method. This technique was first developed by Elias[14-17] for determination of theta compositions of homopolymers. This was later modified and extended by Cornet and coworkers[18] to the determination of theta temperature as well as theta composition. Recently Napper[19] attempted to give some form of theoretical explanation to the method.

Apparatus

The solution under study was contained in a 100 ml cylindrical glass cuvette having a domed ground-glass lid.

This fitted into a thermostatically controlled vat. A constant voltage mercury lamp was focused on the entrance window of the vat and used to illuminate the solution. A photomultiplier was focused on the exit window of the vat directly opposite the entrance window. This photomultiplier was used to detect the light transmitted through the solution by feeding its output directly into the input of a galvanometer. The intensity could be read directly on the linear scale of the galvanometer. The solution in the cuvette was electrically stirred at a constant slow rate. The rate was adjusted by a voltage regulator so as to be effective without causing floculation of the polymer precipitate (about 200 revolutions per minute). The titrating non-solvent was added by means of an accurately graduated micro-burette, at an adjusted rate of about 0.5 ml per minute. The delivery was through a stainless steel capillary tubing sealed onto the end of the burette and immersed into the solution through a hole in the lid of the cuvette. The temperature of the solution was monitored by means of a graduated thermistor probe immersed in the solution. With this set up, the appearance of any turbidity in the solution caused a change in the light transmission which was detected by the photomultiplier. The change could be read on the galvanometer. This apparatus allowed the 'first cloud-point' of polymer-solvent system, with concentration as low as 0.001% by weight of polymer, to be detected. The SOFICA light scattering apparatus (Chapter 3) was found to have the main requirements for this experimental set up. With the minimum of changes this instrument could easily be made to perform such a task.

Treatment of data. Solutions of concentration strength between 1 and 0.001% by weight of polymer in the solvent system were titrated with non-solvent until the first appearance of turbidity. At least ten points were obtained for a range of concentrations at each fixed temperature. The results were treated according to the method of Corret and coworkers.[18] Plots of volume fraction of non-solvent ($\phi_{n.s.}$) versus log of volume fraction of polymer (ϕ_p) gave straight lines, which when extrapolated to pure polymer ($\phi_p = 1$) gave the theta mixture at that particular temperature. When the values of $\phi_{n.s.}$ at $\phi_p = 1$, for at least three different temperatures, were plotted against the titration temperature it gave a straight line from which the theta mixture could be read off at any desired temperature. If this line was further extrapolated to $\phi_{n.s.} = 0$, an estimate of the theta temperature for the pure solvent could be obtained. This approach has the advantage of providing a complete curve from which the desired working temperature under theta conditions can be easily read off. This is very useful when the theta behaviour of a system is not know a priori, as is usually the case for copolymers.

RESULTS

Theta Conditions Having Practical Applications

After having carried out preliminary tests on several prospective solvent systems, the solvent methyl ethyl ketone (MEK) was found to be the most useful. This solvent gave a practically useful theta temperature for the block copolymers in the composition range 25-50% by weight of polystyrene. For compositions on either side of this resort to theta mixtures was necessary. Copolymer IS5 had a practically inaccessible theta temperature in MEK (-10°C) and for this the isorefractive pair[20] MEK/isopropanol (IPA) was used. Copolymer IS1 would not dissolve in MEK and for this the solvent mixture methyl isobutyl ketone (MIBK)/IPA was found most useful.

The determined theta conditions for the whole composition range of block copolymers studied are shown in Table 4.1.

Table 4.1. Practically Useful Theta Conditions from Cloud-Point Titration Data in Methyl Ethyl Ketone, or Mixed Solvents, for the Block Copolymers: Values in Brackets from Osmotic Pressure Data.

Polymer	θ°C (MEK)	Theta Composition at 30°C Volume % IPA
IS1	insoluble	5.6 (in MIBK)
IS2	- (49)	
IS3	46 (48)	
IS4	45 (44)	
IS5	-10 (-10)	7.2 (in MEK)

Second Virial Coefficients

The second virial coefficients obtained at various temperatures in toluene, cyclohexane and MIBK are tabulated in Table 4.2. For consistency these values were all obtained from $(\Pi/c)^{1/2}$ versus c plots according to equation 4.29 (some representative curves have been shown in Fig. 3.1).

Table 4.2. Second Virial Coefficients A_2($cm^3gm^{-2}mole \times 10^4$) for the Copolymers at Various Temperatures (°C) in the Solvents Toluene, Cyclohexane and MIBK.

Polymer	Toluene				Cyclohexane				Methyl Isobutyl Ketone			
	20°	30°	45°	60°	20°	30°	45°	60°	20°	30°	45°	60°
IS1	9.48	9.73	10.08	9.94	8.28	8.65	9.10	9.51	1.10	1.20	1.31	1.39
IS2	9.13	9.45	9.82	9.95	7.61	7.74	9.04	8.69	1.45	1.67	1.70	1.77
IS3	9.03	9.24	9.39	9.05	7.26	7.55	8.01	8.60	1.42	1.58	1.80	1.91
IS4	7.24	7.69	8.00	7.89	4.65	4.88	5.44	6.09	1.38	1.56	1.87	2.07
IS5	6.40	6.59	6.68	6.04	2.30	2.97	4.15	5.50	1.83	1.93	2.04	2.21
	22°	30°	40°	50°	22°	30°	40°	50°	22°	30°	40°	50°
IS6	7.24	7.57	7.67	7.72	6.34	6.68	6.84	7.25	1.05	1.13	1.21	1.31
IS7	6.46	6.68	6.82	-	5.30	5.63	5.71	6.02	1.18	1.21	1.30	1.37
IS8	5.78	6.10	6.29	6.43	3.66	4.29	4.55	4.90	1.30	1.48	1.68	1.86
IS9	5.03	5.24	5.37	-	4.39	4.40	4.52	4.84	1.13	1.18	1.25	-
IS10	4.71	4.86	5.08	5.24	3.13	3.52	3.50	3.98	1.42	1.60	1.84	-

As can be seen from the results, the A_2 values depend markedly on composition, especially for the more selective solvent cyclohexane. For this reason attempts to correlate the dependence of the second virial coefficient on molecular weight must be done on a series of block copolymers having the same composition. The systems studied offered two such series; these will be identified by the code 25/75 (representing a composition of 25% polystyrene by weight) and 50/50 (containing equal weight percentage of each polymer). Such correlations on these two series were carried out on the basis of the empirical log A_2/log M relationship. Results in the solvents, toluene, cyclohexane and MIBK are shown graphically in Fig. 4.3. This shows that the observed decrease in A_2 with increasing molecular weight can be conveniently expressed as a linear relationship between log A_2 and log M, in the limited range of M studied. The slope of the plots gave the exponent of M in the empirical relation, $A_2 = kM^{-y}$. Values of the exponent y are listed in Table 4.3.

Table 4.3. The Molecular Weight Dependence of the Second Virial Coefficient (A_2) for two Composition of the Copolymers in Three Solvents at 30°C: Expressed as the Exponent y in the Equation $A_2 = kM^{-y}$

Polymer Code	Solvent	y
25/75	TOL	0.33
	C-HEX	0.33
	MIBK	0.01
50/50	TOL	0.30
	C-HEX	0.20
	MIBK	0.18

Derived Parameters from A_2/T Data

Some plots of A_2 versus $^1/T$ are shown in Fig. 4.2. Extrapolation of these plots to $A_2 = 0$ yields θ according to equation 4.27. Values of the θ temperature thus obtained are shown in Table 4.4. Fig. 4.4 presents the data in graphical form as a plot of θ against the composition of the copolymer in mole percent polystyrene in the solvents, toluene, cyclohexane, MIBK and MEK. Table 4.5 lists the thermodynamic

Fig. 4.2. Plots of the osmotic second virial coefficient A_2 against $^1/T$ for the copolymers in various solvents.

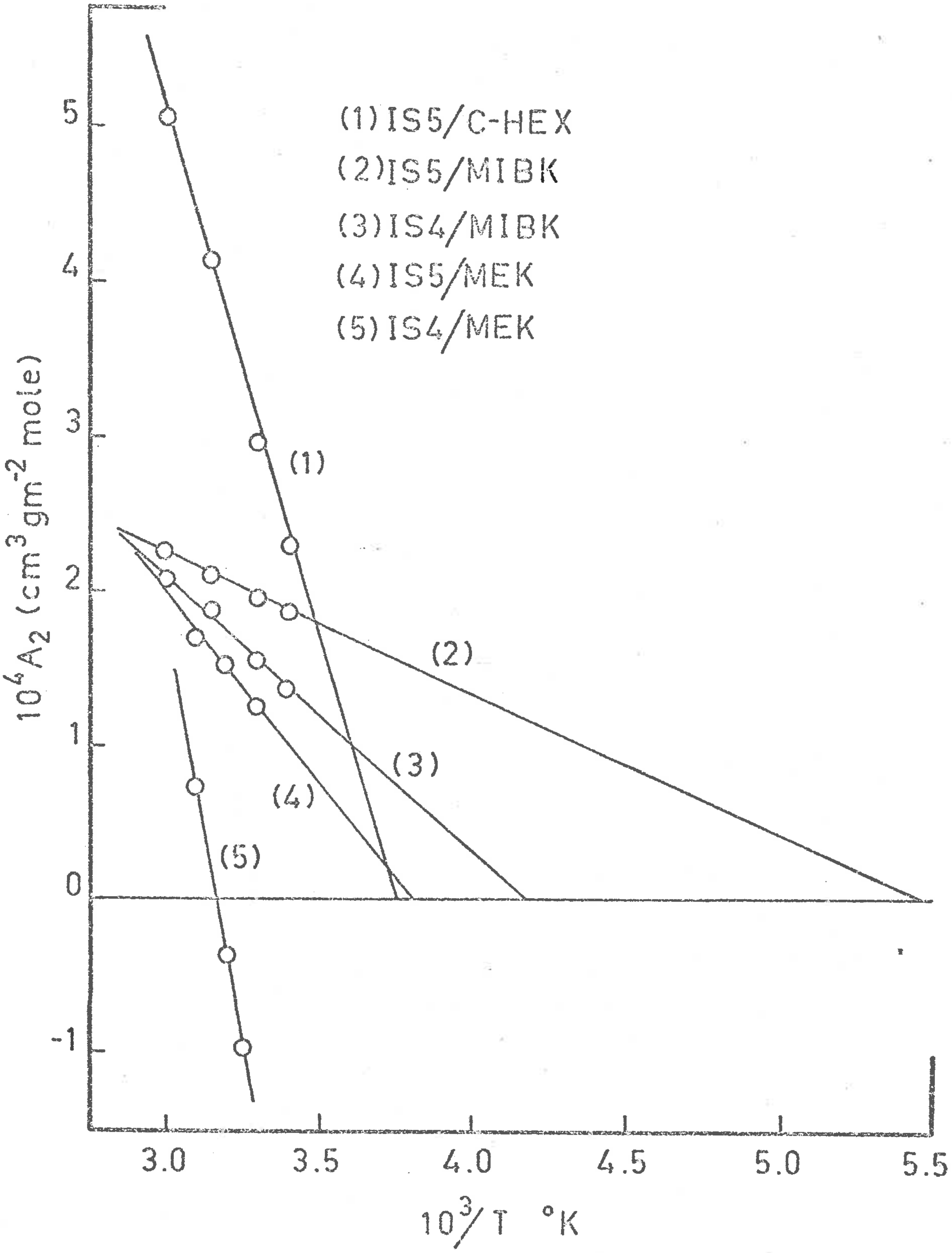

(1) IS5/C-HEX
(2) IS5/MIBK
(3) IS4/MIBK
(4) IS5/MEK
(5) IS4/MEK
(1)
(2)
(3)
(4)
(5)
5
4
3
2
1
0
-1
$10^4 A_2$ (cm^3 gm^{-2} mole)
3.0
3.5
4.0
4.5
5.0
5.5
$10^3/T$ °K

Fig.4.2

parameters, ψ_1, κ_1 and χ_1 of the copolymers in toluene, cyclohexane and MIBK. Figs. 4.5 and 4.6 represent the same results graphically in terms of composition in mole percent of polystyrene in the copolymer.

Table 4.4. Theta Temperatures (θ) for the Copolymers Derived from Osmotic Data in Three Different Solvents

	θ(°K)		
Polymer	TOL	C-HEX	MIBK
IS1	133	159	201
IS2	148	177	190
IS3	146	182	215
IS4	185	221	240
IS5	175	267	183
IS6	134	165	214
IS7	158	172	190
IS8	181	224	244
IS9	153	174	188
IS10	179	221	243
PS[+]	160	307	-

[+] from reference 34.

Table 4.5. The Thermodynamic parameters ψ_1, κ_1 (30°C) and the Interaction Parameter χ_1 for the Copolymers Derived from Osmotic Data in Three Solvents

	Toluene			Cyclohexane			Methyl Isobutyl Ketone		
Polymer	ψ_1	κ_1	χ_1	ψ_1	κ_1	χ_1	ψ_1	κ_1	χ_1
IS1	0.161	0.071	0.409	0.171	0.090	0.419	0.038	0.025	0.487
IS2	0.179	0.087	0.407	0.182	0.106	0.424	0.046	0.029	0.483
IS3	0.176	0.085	0.409	0.188	0.113	0.425	0.063	0.045	0.482
IS4	0.209	0.127	0.419	0.196	0.143	0.447	0.095	0.075	0.480
IS5	0.189	0.110	0.420	0.312	0.275	0.463	0.069	0.041	0.473
IS6	0.122	0.054	0.432	0.139	0.076	0.437	0.042	0.030	0.488
IS7	0.135	0.071	0.435	0.216	0.072	0.445	0.038	0.024	0.486
IS8	0.159	0.095	0.436	0.173	0.128	0.455	0.095	0.076	0.481
IS9	0.102	0.051	0.450	0.102	0.059	0.456	0.035	0.022	0.486
IS10	0.127	0.075	0.448	0.136	0.099	0.463	0.102	0.082	0.480
PS$^+$	0.111	0.058	0.448	0.381	0.384	0.504			

$^+$ from reference 34.

DISCUSSION

The second virial coefficient can be obtained from osmotic pressure data by plotting the reduced osmotic pressure as a function of concentration; extrapolation to zero concentration yields the number average molecular weight ($\bar{M}n$) and the slope gives the second virial coefficient (A_2). The data for the copolymers was treated in two ways: a) by plotting (Π/c) versus c and b) by plotting $(\Pi/c)^{1/2}$ versus c. The former assumes an insignificant contribution from the third virial coefficient and the latter assumes a value of $g = 0.25$ in equation 4.28. As is well known, the value of A_2 obtained from a set of osmotic pressure measurements is influenced by the treatment of the third virial coefficient A_3 in the series expansion for the osmotic pressure. Various methods have been proposed for treating the data.[21-23] According to Stockmayer[13,24] the g-factor is strictly dependent on the nature of the solvent and also on the molecular weight; of course for copolymers an extra parameter in the form of the composition should be included. From practical considerations $g = 0.25$ is a reasonable choice and has been found to be a good approximation for both good and poor solvents.[21]

All the data on the block copolymers was treated according to this assumption. The plots in all solvents were found to be good straight lines (exhibiting no curvature) as shown in

Fig. 3.1. By contrast the (Π/c) versus c plots did show some curvature at the higher concentrations. For this reason such plots were harder to extrapolate and the values of A_2 (and $\bar{M}n$) obtained were generally higher. This effect was most pronounced for toluene which is a good solvent for both sequences of the copolymer. In such cases a significant contribution from the third virial coefficient must be expected. On the other hand in MIBK which is a poor solvent for both sequences of the copolymer no curvature was observed. Plots from both methods were parallel and gave the same A_2 (and $\bar{M}n$) values. In a poor solvent A_3 is negligible so that the method of plotting the data should be insensitive to the g-value. This is in accordance with experience on homopolymers. Data in cyclohexane showed the effect of composition on A_2 to the best advantage. This solvent is selective (or preferential): it is a good solvent for the polyisoprene sequence of the block but a theta solvent for the polystyrene sequence at 34°C. Curvature of the (Π/c) versus c plots was found to decrease with increasing polystyrene content. In fact for IS5 (containing 78% polystyrene) the linear plot gave the same value for A_2 as the square-root plot and exhibited no curvature.

The problem of the second virial coefficient of flexible chain polymers is complex and in the case of block copolymers can be assumed to have three types of interactions. In the first place, there is the problem of interchain interactions; in the second, the problem of intrachain interactions; and finally, the problem of the coupling of the inter- and intrachain interactions. According to the dilute solution theory of Flory, A_2 was expressed as a function of these interactions by equation 4.27:

$$A_2 = \bar{v}_2^2/\bar{V}_1(1/2 - \chi)F(X)$$

Orofino and Flory[25] expanded this approach by deriving a relationship between the intrinsic viscosity [η] and the expansion factor (α), arriving at the expression

$$A_2 = (2^{5/2}\pi N_A/3^3\Phi)([\eta]/M)\ln[1+(\pi^{1/2}/2)(\alpha^2-1)] \qquad 4.30$$

where N_A is Avogadros number, Φ is a constant and M the molecular weight of polymer. Thus, when examining the values of A_2 for the copolymers in the various solvents, three factors must be considered:

1) the effect of the solvent on the intrinsic viscosity and hence on the expansion factor,

2) the effect of the molecular weight, and

3) the effect of the extra interactions arising from the chemically different segments comprising the chain.

All these three effects will be discussed in turn.

The first of these effects, i.e., the nature of the solvent will be considered in a more quantitative fashion in Chapter 5 when dealing with configurational parameters. Here it will suffice to discuss the observations in qualitative terms. Toluene is a good solvent for both polystyrene and polyisoprene so that A_2 would be expected to be large for the copolymers in this solvent because of the larger polymer-solvent interaction. Next would be cyclohexane, which is a good solvent for polyisoprene but a theta solvent for polystyrene. We will refer to this as a selective or preferential solvent. MIBK is at the other extreme, being a poor solvent for both polystyrene and polyisoprene. This is well examplified by the A_2 values obtained (Table 4.2), where in all cases the largest value of A_2 was in toluene, next was cyclohexane and the smallest value in MIBK. When considering the effect of composition on A_2 the values in toluene and cyclohexane can be seen to decrease monotonically with increasing polystyrene content - the largest decrease being observed in cyclohexane. In MIBK the A_2 values showed an increase with increasing polystyrene content. These observations can be explained by noting that cyclohexane is the most selective solvent and increasing the polystyrene content of the copolymer effectively causes the solvent to become poorer. Also, toluene, although a good solvent for both sequences of the chain is slightly better for polyisoprene. Also, MIBK, although a poor solvent for both polystyrene and polyisoprene, is a slightly better solvent for the former. Previous attempts to make such correlations of the effect of solvent on A_2, in terms of the effect on the constituent homopolymers, were not successful because of the limited range of composition studied and the non allowance of the molecular weight effect.[26]

The second effect, i.e., that of the molecular weight has been summarized in Table 4.3. In all solvents A_2 was found to decrease with increasing molecular weight. All the data was well represented by linear relations on the basis of the empirical equation, $A_2 = kM^{-y}$. This is in accordance with observations made on homopolymers[27,28] and as predicted by theory. The values of y ranged from about 0.3 in toluene to 0.01 in the poor solvent MIBK. The dilute solution theoty predicts a smaller decrease in A_2 with increasing M than is generally observed experimentally. More recent two-parameter theories (which will be discussed further in Chapter 5) predict an upper limit for y of 0.15 over a restricted range of molecular weights.[29] Contrary to this, many values as high as 0.3 have been reported in the literature[29,30] for a variety of homopolymers in different solvents. Because of this the seemingly high values of y obtained for the block copolymers in toluene and cyclohexane, in comparison to theoretical

Fig. 4.3. Plots of log A_2 against log $\bar{M}n$, $A_2 = KM^{-y}$, for two composition of the copolymers in toluene, cyclohexane and MIBK.

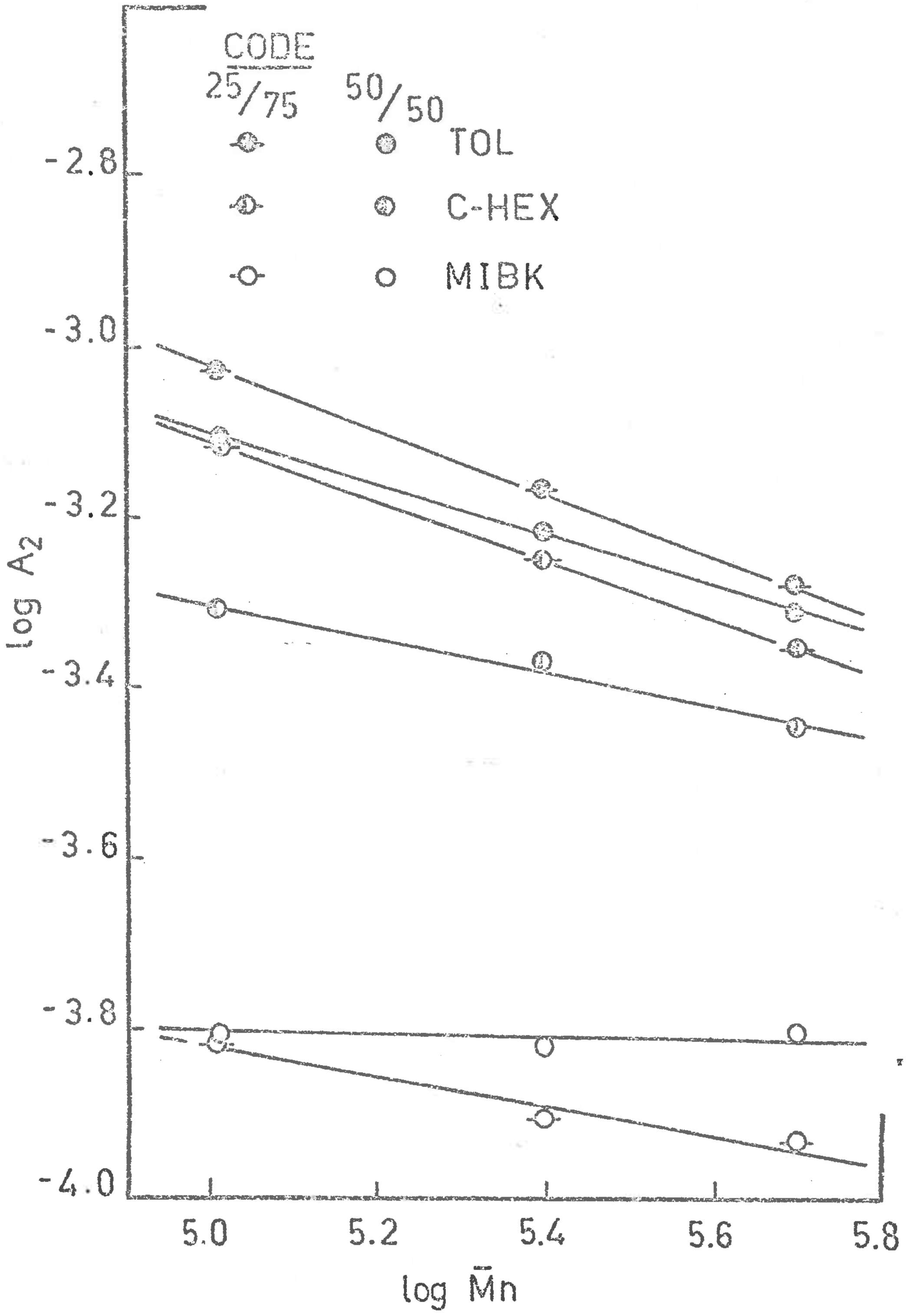

CODE
25/75
50/50
TOL
C-HEX
MIBK
-2.8
-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
log A_2
5.0
5.2
5.4
5.6
5.8
log $\bar{M}n$

Fig.4.3

predictions, are not characteristic of the copolymer system studied. They are in accordance with similar observations on homopolymers. Also Kotaka and coworkers[31] obtained a y value of 0.31 for a series of statistical copolymers of (styrene-MMA). In this respect it seems that the copolymers studied cannot be differentiated from their homopolymer counterparts.

The third factor affecting A_2 in copolymers is that due to the extra interactions arising from heterocontacts. Because of the incompatibility of the two homopolymers constituting the chain, such interactions would be expected to be repulsive in nature. These extra repulsions should cause an expansion of the chain and hence an increase in viscosity. This should have the effect of increasing A_2. The consequences of these heterocontact interactions can be best studied by considering their effects on the thermodynamic parameters. These will be discussed later in this chapter.

The theta conditions using MEK as solvent are summarized in Table 4.1. The importance and practical application of these will be dealt with in Chapter 5. As can be seen the agreement between the two methods employed (osmometry and cloud-point titration) is very satisfactory. This is gratifying, both from the point of view of justifying the experimental set up of the cloud-point titration technique and establishing its applicability to block copolymer systems (in the same manner as has been applied to homopolymers.[14-19]) The agreement between this method and the osmometric method is encouraging and to some extent indicative that under these conditions a true theta state for the copolymers might be realized.

Theta temperatures in toluene, cyclohexane and MIBK are listed in Table 4.4. These were obtained from plots of A_2 versus $^1/_T$. These plots were linear as shown in Fig. 4.2. In toluene, points at the highest temperature (i.e. 60°C) showed a slight downward curvature (as can be seen from the A_2 values listed in Table 4.2.) This probably shows the significant contribution of the A_3 factor in this particular solvent, as previously noted. No such effect was exhibited for cyclohexane and MIBK solutions. Unfortunately, the osmometer could not be operated below ambient temperature, so that in good solvents such as toluene extrapolation to zero A_2 could produce an error of up to ± 10°C in the determination of the θ temperature. In reasonably poor solvents, such as cyclohexane and MIBK only a short extrapolation to zero A_2 is necessary and the θ temperature could be obtained with a higher accuracy.

When dealing with copolymers one is justified to question the validity of the theta condition concept. The concept of the theta condition for solutions of flexible chain homopolymers has been fully established by Flory.[18,33] As discussed previously the theta condition is achieved when the osmotic second virial coefficient A_2 is zero. At this point the average dimensions of the polymer are determined solely by short-range interactions, which in a homopolymer defines the unperturbed configuration. The definition of the theta condition as being that at which $A_2 = 0$ is a practically convenient approach and is unambiguous. In block copolymers the theta condition is also realized when $A_2 = 0$; but here it can be achieved in two ways: either A_2 of the individual homopolymers comprising the chain simultaneously go to zero, or the sum of the A_2's is zero. In the latter case an 'average' theta condition for the whole copolymer is obtained which defines an 'average' unperturbed configuration. It can be appreciated that these two approaches will possibly lead to different, but nevertheless well defined, configurations of the copolymer molecule. One might expect that the theta temperature and the configuration associated with it may depend intimately on the composition of the block copolymer and on the nature of the solvent.

Thermodynamic theories of polymer solutions are based on the interactions between solvent molecules and segments comprising the chain. For this reason it was considered that comparison of the copolymer thermodynamic parameters with those of the parent homopolymers should be made in terms of the mole fraction. Fig. 4.4. displays graphically the θ temperature as a function of composition in four solvents, toluene, cyclohexane, MIBK and MEK. These plots show that in toluene the θ temperature for the copolymers exhibit a maximum at about the middle of the composition scale. This must be indicative of extra repulsive interactions between the different homopolymer segments in the copolymer chain. This is in accordance with similar observations made on block copolymers in thermodynamically good solvents.[26,28,32] In MIBK and MEK, which are poor solvents for both sequences of the copolymer chain, similar maxima in the plots of θ versus composition are observed. In these solvents the position of the maximum appears to be shifted to a lower mole fraction of polystyrene; this shift being greatest in the poorer of the two solvents (MEK). These observations lead us to the conclusion that the theta temperature of these copolymers exhibits the same trend with composition in both good and poor solvents. However, in cyclohexane, a preferential solvent for polyisoprene, the behaviour is markedly different. The plot of θ versus composition displays an almost linear relationship between the value for polystyrene (θ = 307°K) and that for polyisoprene (θ = 100°K). In the context of the above explanation, the absence of a maximum in the θ versus

Fig. 4.4. Theta temperature plotted against composition of the copolymers, in mole % polystyrene, in the solvents toluene, cyclohexane, MIBK and MEK.

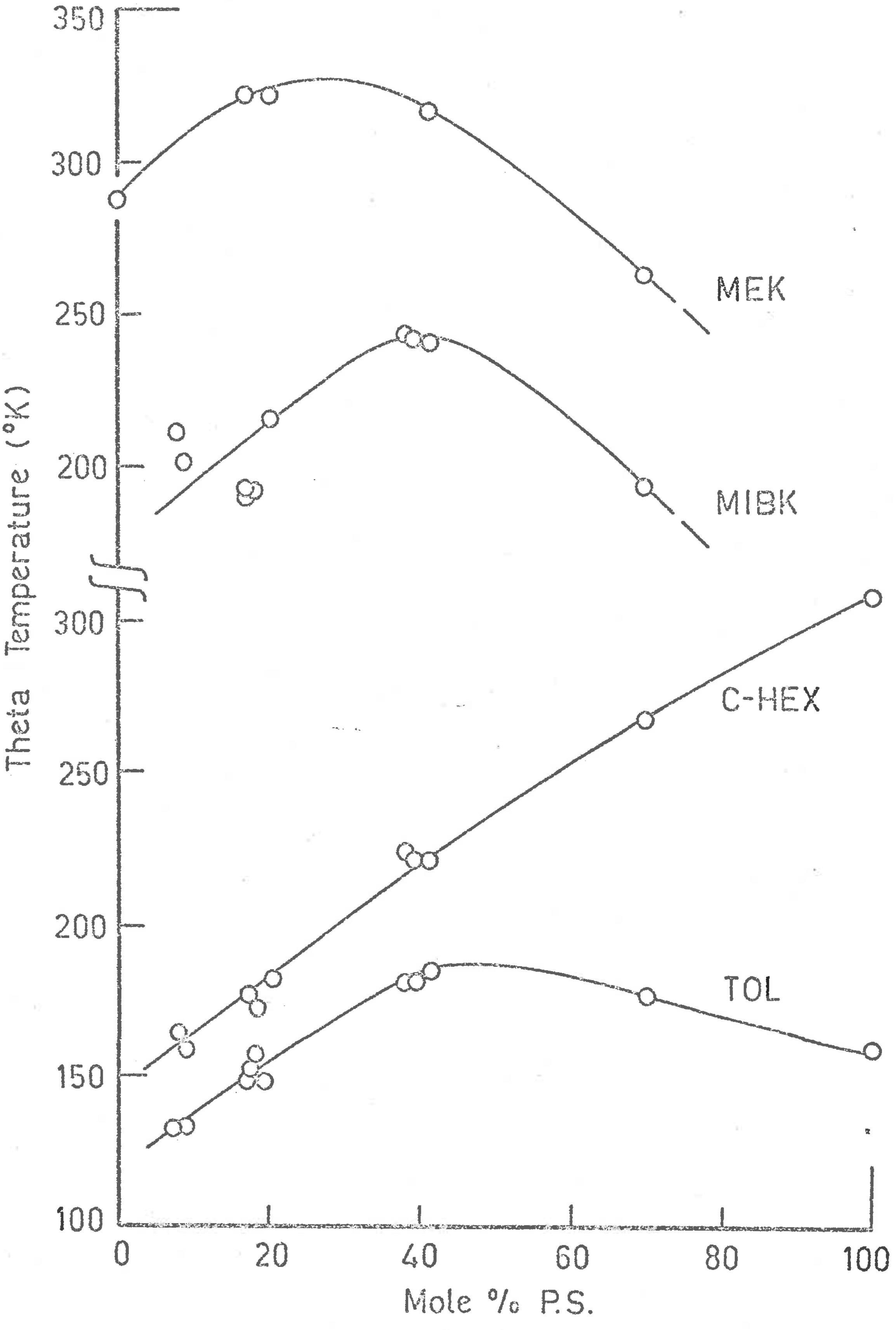

350
300
250
200
300
250
200
150
100
Theta Temperature (°K)
MEK
MIBK
C-HEX
TOL
0
20
40
60
80
100
Mole % P.S.

Fig. 4.4

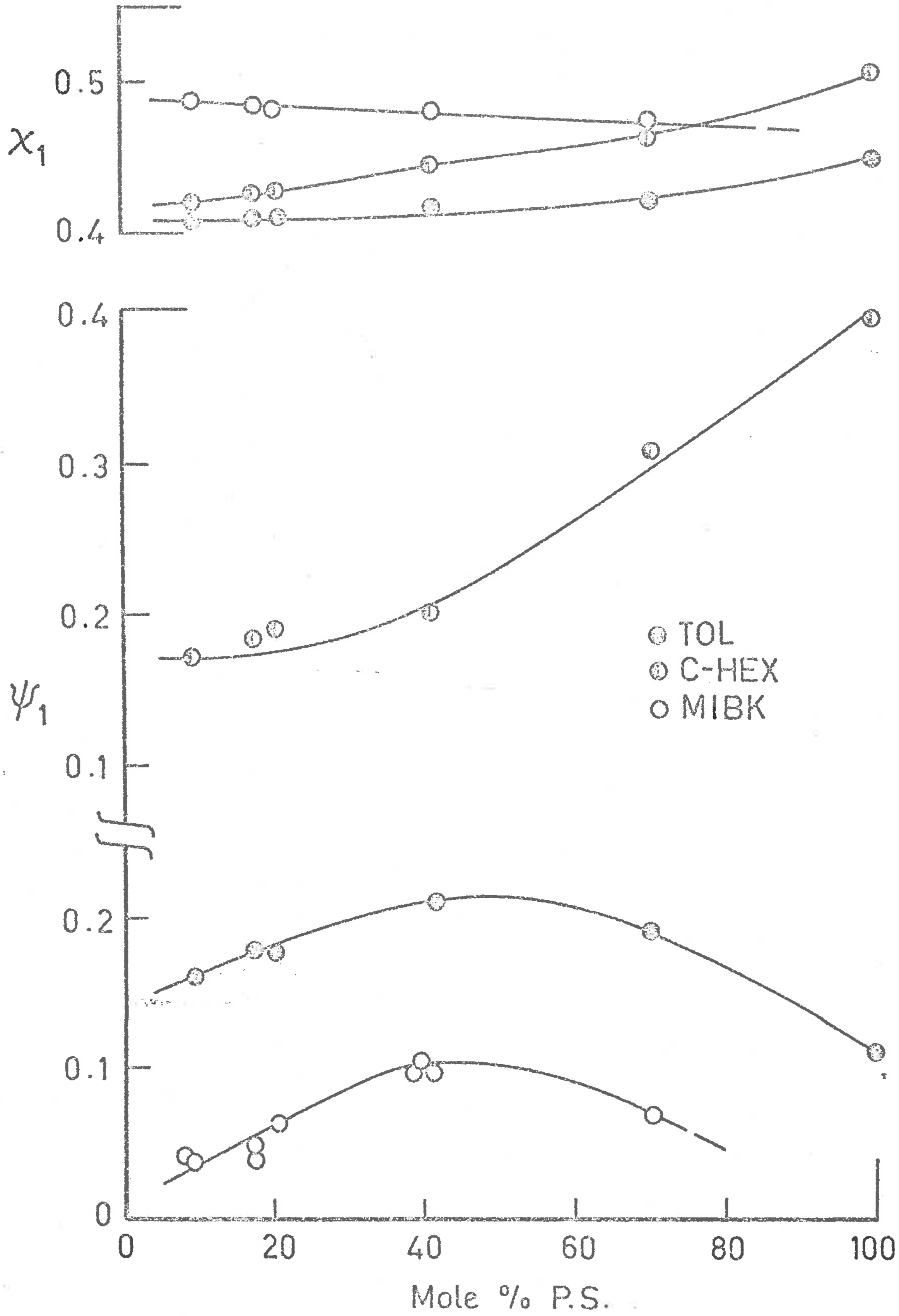
composition plot in cyclohexane would indicate the absence of repulsive forces due to heterocontacts. The only way such interactions could be absent is for the polystyrene and polyisoprene sequences of the chain to be non interacting; that is for interpenetration of the two sequences to be a minimum in this solvent. This would lead to at least partial intramolecular phase separation.

In summary the results suggest a basic difference in configuration of the block copolymers depending upon the specific solvent. The preferential solvent displays a linear change of θ with composition. This suggests that the contribution to A_2 from each kind of segments are simply additive with respect to the total. The maxima appearing in θ versus composition plots for non-preferential solvents suggest a random structure in which heterocontacts play an important role. In the very good solvent (toluene), the maximum is at the point at which the greatest number of heterocontacts would be expected: in the middle of the composition scale.

Figures 4.5 and 4.6 show the thermodynamic parameters, χ_1, ψ_1 and κ_1 as a function of composition in the solvents toluene, cyclohexane and MIBK. In both toluene and MIBK the plots of ψ_1 and κ_1 pass through a maximum at the middle of the composition scale. Again this can be explained as

Fig. 4.5. Interaction parameter χ_1 and the entropy of dilution parameter ψ_1 plotted as a function of composition of the copolymers.

Fig. 4.6. Enthalpy of dilution parameter κ_1 plotted as a function of composition.



0.5
X_1
0.4
0.4
0.3
0.2
ψ_1
0.1
0.2
0.1
0
● TOL
◉ C-HEX
○ MIBK
0
20
40
60
80
100
Mole % P.S.

Fig. 4.5

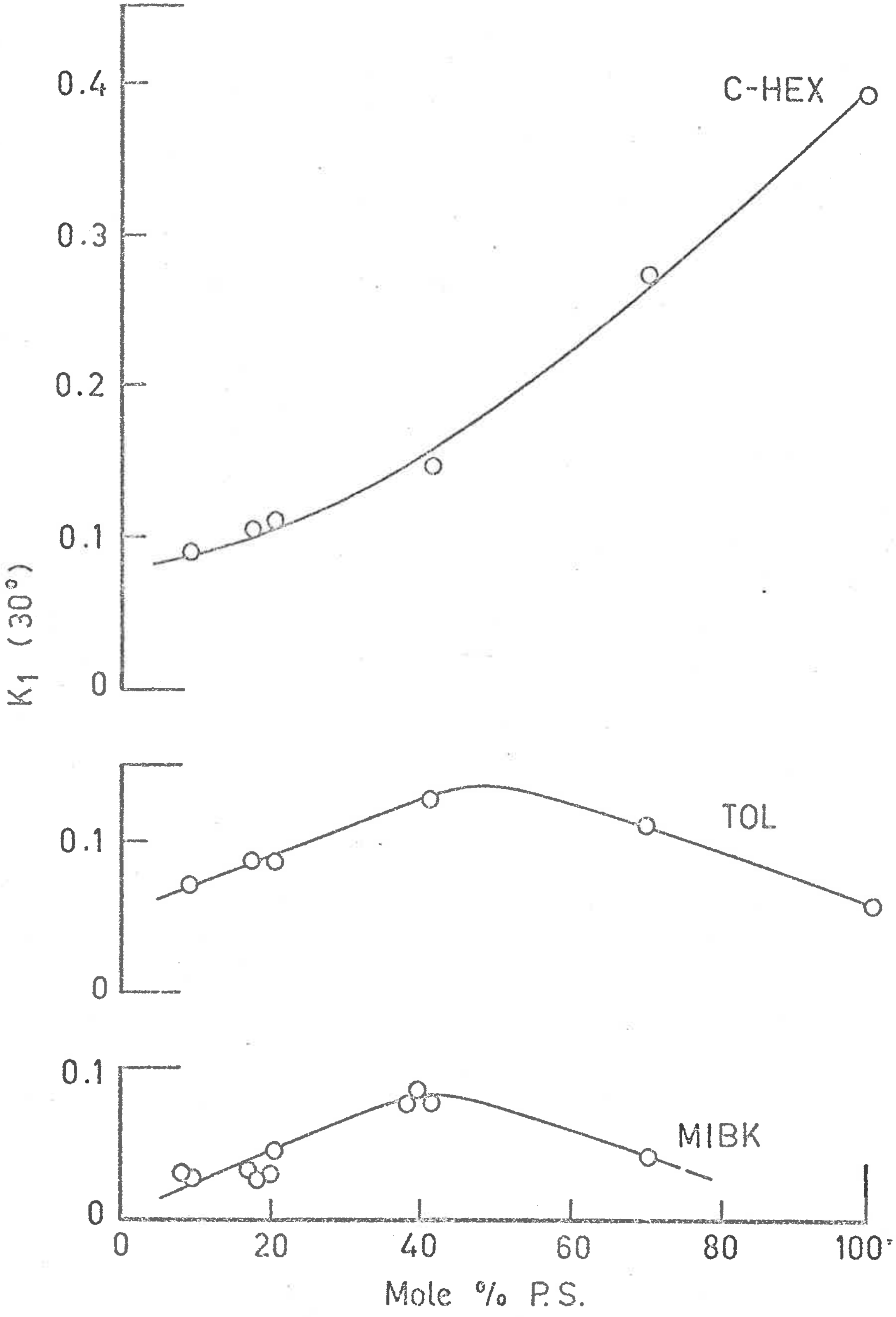


Fig.4.6

presumably due to the extra repulsive interactions present in the copolymer which causes it to become more expanded than it would be otherwise. This increased expansion permits more degrees of freedom of a solvent molecule in relation to its segmental environment. This would give rise to a large entropy of dilution parameter in comparison to the pure homopolymers. The expansion of the copolymer is indicated as being greatest in the middle of the composition scale for here the greatest number of heterocontacts are possible. Another way of looking at this large ψ_1 value, in relation to the homopolymers, is to consider that the 'unsolvated' block copolymer has more restricted configurational freedom than an equivalent homopolymer of the same molecular weight. As solvent is taken up this configurational restriction is removed.

In contrast to the results in toluene and MIBK, the thermodynamic parameters of the copolymers in cyclohexane again behave differently. In this solvent the values of ψ_1 (and κ_1) actually exhibit a slight negative deviation when plotted as a function of composition. This deviation is in the opposite direction to that observed in toluene and MIBK. A feasable explanation for this, which is in agreement with the context of the present argument, is similar to that given for the behaviour of the θ temperature in this solvent. In a highly preferential solvent, such as cyclohexane, the two homopolymer sequences of the copolymer chain have the minimum interpenetration. In this solvent the polystyrene domain would be collapsed while the polyisoprene would be expanded. In actual fact the polystyrene domain would be collapsed to a greater extent than it would otherwise be in this solvent because of the inevitable close proximity of the polyisoprene segments. For this reason the entropy of dilution parameter ψ_1 (and κ_1) exhibit a negative deviation from the linearity between the two homopolymer values. This evidence again suggests at least partial intramolecular phase separation in this selective solvent.

The total interaction parameter χ_1 shows an almost linear relationship when plotted as a function of composition in all solvents (Fig. 4.5). This parameter is given by equation 4.31, i.e.,

$$\chi_1 = (\kappa_1 - \psi_1 + {}^1/_2)$$

This linear behaviour with composition shows the self compensating effect of κ_1 and ψ_1 in determining χ_1 and also shows the extra thermodynamic information which may be obtained on these copolymer systems by splitting χ_1 into its components. As discussed in the polymer solution theories, the magnitude of χ_1 parameter can be taken as a measure of the solubility of a polymer in the particular solvent. At $T = \theta$, $\chi_1 = 0.5$; as the solvent power increases χ_1 decreases. The same trend is shown for the block copolymers: the value of χ_1 decreases in going from MEK-MIBK-cyclohexane-toluene, showing that the solvent power increases in this direction. This trend is as expected from the known solubility behaviour of the constituent homopolymers in these solvents. Also the slope of the χ_1 versus composition plots is in the direction predicted from knowledge of the solubility of the homopolymers. In MEK and MIBK the χ_1 values decrease as the polystyrene content of the copolymer increases, i.e., as the solvent becomes better. In toluene and cyclohexane χ_1 values decrease as the polystyrene content decreases - the decrease being greatest in cylcohexane as would be anticipated. In this respect the χ_1 parameter appears to play a similar role in describing the thermodynamic behaviour of both homopolymer and copolymer solutions.

The molecular weight dependence of the thermodynamic parameters is worth noting. Within the proposed accuracy of its measurements, the θ temperature appears to be independent of molecular weight in all solvents; behaving similar to homopolymers in this respect. The parameters ψ_1 and κ_1 show a definite decrease with increasing molecular weight in both toluene and cyclohexane (but the general shape of the curve when the parameters are plotted as a function of composition is the same independent of molecular weight). In the poor solvent (MIBK) both ψ_1 and κ_1 are virtually independent of molecular weight and the values for all the copolymers follow one curve when plotted as a function of composition (Figs. 4.5 and 4.6). This molecular weight dependence can be seen by comparing values of copolymers having the same composition but different molecular weights. Such a comparision is offered by the two series previously coded 25/75 and 50/50. The interaction parameter χ_1, shows negligible dependence on molecular weight. Although, the values in toluene and cyclohexane seem to indicate a slight increase of χ_1 with increasing molecular weight, this increase is small and could be absorbed by the experimental error involved. However, an increase, if authentic, is in the right direction with what would be expected from experience with homopolymers Although, from theory it is hard to conceive the dependence of the parameters ψ_1 and κ_1 on chain length, it is a fact observed experimentally for homopolymers and it merely reflects some deficiency in the polymer solution theory. However, it must not be overlooked that this molecular weight dependence for the block copolymers might be more conceivable for such systems because of their more complex nature.

If we assume the theta condition concept and the thermodynamic equations derived from the dilute solution theory, originally for flexible homopolymers, to be applicable to block copolymers, or at least as a reasonable working assumption, then we have derived similar thermodynamic parameters as can be derived for homopolymers. Any deviations from the ideal behaviour expected have been explained in terms of the extra repulsive interactions present due to heterocontacts. The results obtained have been explained with these limitations in mind. They are very useful as a comparative study of a series of such copolymers in determining the various effects of solvent, composition and molecular weight on the parameters measured. From the results it seems that a proper theory which would account for the solution behaviour of block copolymers must take account of the composition of the polymer but must also include the contribution to the entropy and enthalpy of dilution from the heterocontacts. In preferential solvents the indication is that such heterocontact interactions may give rise to intramolecular phase separation and therefore a change in the configuration of the copolymer molecule. This point will be taken up throughout the following chapters.

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Chapter 5

CONFIGURATIONAL PARAMETERS

INTRODUCTION

In this chapter the configurational properties of the block copolymers in various solvents will be discussed. The initial and basic information needed is the intrinsic viscosity in the particular solvent, The combination of this with appropriate theories gives a method of obtaining information about these configurational parameters. The theories used are those initially derived for flexible homopolymers, so that extension to copolymers is always questionable and must be carried out with some reservations. Some of the various mathematical models and theories put forward in an attempt to explain the configurational solution behaviour of flexible homopolymer chains will be first discussed.

In Chapter 4 thermodynamic theories of polymer solutions were discussed and it was shown how these are determined by the interaction between the solvent molecule and the polymer segments. Such theories do not consider how the segments are distributed in space. This consideration gives rise to the problem of configurations, which arise because a certain flexibility of the polymer molecules is assumed. If a molecule was completely rigid it could take up different positions in space only as a whole and the question of chain configurations does not arise. In chains built up from single-bonded carbon atoms, intramolecular rotation around the carbon-carbon bonds is possible. This will obviously alter the relative position of the atoms considerably. Due to Brownian motion the configuration will be constantly changing. As a consequence the number of configurations which a long chain molecule may assume is very large. This necessitates adopting a statistical approach. The dimension of a polymer most widely used to characterize its spatial or configurational character is the distance r from one end group to the other of the chain molecule. An average value of this quantity is required and is usually expressed as the root-mean-square (rms) distance between its ends, $(\bar{r}^2)^{1/2}$. Another important measure of the effective size of a polymer is the rms distance of the elements of the chain from its centre of gravity. This quantity is designated $(\bar{S}^2)^{1/2}$ and often referred to as the radius of gyration of the molecule. For linear polymers both these quantities are simply related by

$$(\bar{r}^2)^{1/2} = 6^{1/2}(\bar{S}^2)^{1/2} \qquad 5.1$$

To deduce appropriate averages over the total population of configurations, for an ensemble of chain molecules, various models of the polymer chain have been used. The simplest model is the hypothetical random flight or freely jointed chain, consisting of Z links, each of fixed length b, joined in linear succession. This assumes that the direction of a link is not influenced in any way by the direction of any other link. The probability that such an array has a given end-to-end distance r can be calculated by the classical random flight method. [1,2] The most important result of the calculation is that the end-to-end distance is proportional to the square root of the number of links:

$$(\bar{r}_o^2)^{1/2} = Z^{1/2}b \qquad 5.2$$

(The subscript zero indicates the unperturbed or random flight end-to-end distance). The behaviour of many more complicated models can be explained in terms of that of the random chain. Because of this the concept has proved very useful. One of the most unrealistic properties of the random chain, when compared to an actual polymer molecule, is that it neglects any correlation between the direction of successive links. If the angle between neighbouring links is fixed and equal to ϕ, then the mean square end-to-end distance is calculated to be

$$\bar{r}^2 = Zb^2(1 + \cos\phi)/(1 - \cos\phi) \qquad 5.3$$

(for large Z and ϕ not too close to zero). This shows that the chain with fixed bond angles resembles the random chain in that the rms end-to-end distance is still proportional to the number of links.

Another very useful concept, due to Kuhn,[3] is that of the equivalent chain. The equivalent chain is regarded as consisting of the same number of links as the actual chain and of a bond length a of such magnitude that the rms end-to-end distance is the same, so that $r^2 = Za^2$. This length a is termed the statistical chain element or effective bond length; for the chain with fixed bond angles

$$a^2 = b^2(1 + \cos\emptyset)/(1 - \cos\emptyset) \qquad 5.4$$

There are many instances of chains which do not satisfy the condition of random chains; but in the absence of long-range interactions an equivalent random chain can always be found, the links of which equal the statistical chain element. If the equivalent chain and the actual chain have the same rms end-to-end distance and the same contour length, then it is assumed that all the statistical properties of the two chains also agree. The statistical behaviour of the chain can then be studied from the behaviour of the equivalent chain. The usefulness of this concept is easily realised.

All the models so far considered are unrealistic in the sense that they make no allowance for the finite volumes of the atoms constituting the chain. Consideration of this effect raises the question of the excluded volume (as discussed in

Chapter 4). Many authors have approached this problem along different lines. Some have attempted a purely mathematical treatment. However, by far the most fruitful approach has been Flory's[4] treatment along lines resembling the dilute solution theory of polymers (discussed in Chapter 4). This treatment assumes that the distribution of the polymer segments, when the excluded volume effect is taken into account, is similar to that without it, so that all linear dimensions are increased by a factor α, known as the expansion factor. This leads to an expression for α in terms of the lattice parameters (of Chapter 4) as

$$\alpha^5 - \alpha^3 = C(1 - 2\chi)M^{1/2} \qquad 5.5$$

This equation directs attention to a number of important characteristics of the expansion factor α. It predicts that α should increase slowly with molecular weight. It also predicts that the rms end-to-end distance of the molecule $(\bar{r^2})^{1/2}$ should increase more rapidly than in proportion to $M^{1/2}$. This comes from the theory of random chain configuration according to which the unperturbed rms end-to-end distance $(\bar{r}_o^2)^{1/2}$ is proportional to $M^{1/2}$, whereas $(\bar{r^2})^{1/2} = \alpha(\bar{r}_o^2)^{1/2}$. Also, if χ can be regarded as a measure of the 'goodness' of a solvent, such that it is smaller in a good solvent, then according to equation 5.5 the molecule is more extended in a better solvent.

These conclusions have practical applicability. They show that the perturbation effect of the excluded volume can be removed by making measurements under theta conditions (when $T = \theta$, $\chi = {}^1/_2$ and $\alpha = 1$). Dimensions obtained under these conditions are termed unperturbed dimensions and are determined solely by short-range interactions. Such interactions operate between atoms or groups separated by only a small number of valence bonds. In the presence of the excluded volume effect, long-range interactions are also present. These operate between non -bonded groups which are separated in the basic chain structure by many valence bonds.

Since the first formulation of Flory's excluded volume theory (equation 5.5) great efforts have been devoted to test this theory both theoretically and experimentally.[5,6] In his original derivation Flory assumed a spherical distribution of segments about the centre of molecular mass. After a number of attempts to refine the defects in the Flory theory, by using slightly different models (an ellipsoid model), very similar equations for α have been proposed by Kurata, Stockmayer and Roig;[7] Fixman;[8] and Ptitsyn.[9] All these equations express α as a function of a single parameter z, given by

$$z = (3/2\pi)^{3/2} \beta a^{-3} Z^{1/2} \qquad 5.6$$

for a chain of Z links of the effective length a. Here β

is the binary cluster integral and defined as

$$\beta = \int_0^\infty [1 - \exp(-w(r)/kT)] 4\Pi r^2 dr \qquad 5.7$$

where w(r) is the pair potential, which represents the potential energy for solute-solute interactions. Obviously the variable z involves two independent parameters: a representing the short-range interactions and β representing the long-range interactions. Thus the theories available to date are generally called two-parameter theories.

In terms of z the Kurata-Stockmayer-Roig (KSR) equation[7] and the Fixman[8] equation are respectively formulated as

$$\alpha^3 - \alpha = {}^4/_3[4\alpha^2/(1 + 3\alpha^3]^{3/2} z \qquad 5.8$$

$$\text{and} \quad \alpha^3 - 1 = 2z \qquad 5.9$$

These two equations are in good quantitative agreement[6] for the whole range of z, despite their totally different methods of derivation. In contrast, Flory's equation (5.5) when expressed in terms of z gives a coefficient for z which is twice as large as that needed to secure agreement with the exact expression for the expansion factor, in the region of small z.[8,10,11] The KSR type equation is also in good agreement with computational results of mean-square end-to-end displacements for a diamond lattice chain obtained by Wall and Erpenbeck.[12] These factors, in conjunction with other experimental observations,[13,14] have led to the conclusion that α^3-type equations better describe the behaviour of a single polymer coil in solution than Flory's α^5-type equation. References to these equations when used for the study of the block copolymers will be made throughout this chapter.

VISCOMETRY

Introduction

Viscosity is probably the most widely measured property of polymer solutions. The ease of obtaining measurements and the information which can be deduced from them, makes viscometry a very useful and widely used technique in polymer solution studies. Viscometry is used principally to obtain information on the molecular weight and on the dimensions of macromolecules. If the measurements are carried out at the theta point, or if they are corrected thereto by suitable extrapolation procedures, information on the unperturbed dimensions (short-range interactions) can be obtained directly. Measurements under set conditions of molecular weight, solvent system and temperature can give information on the dimensions (long-range interactions) under these conditions. Extension of this technique and ideas to the study of block copolymers (and copolymers in general) must always be treated with certain reservations. Of course justification for such extensions must eventually come from the experimental results and the way they can be explained in the context of available theory.

Ever since the formulation of the Flory-Fox[15-17] dilute solution theory of viscosity, the technique of viscometry has become a well accepted and widely used method of obtaining information on the configurational parameters of linear polymers. In this work the Flory-Fox treatment has been extended to the study of copolymers. Of course it must be realized that the acceptance of the viscosity treatment for homopolymer solutions does not automatically make the same treatment valid for copolymer solutions. There is evidence to suggest[18-21] that viscosity relations similar to those for homopolymers may also hold for copolymers. However, the results are often contradictory in their conclusions. While some authors[20-22] found that the intrinsic viscosities $[\eta]$ and chain dimensions of block copolymers are larger than those of either homopolymer of equal degree of polymerization, others[23-25] made the opposite observations. Inagaki[26] tried to explain this apparent contradiction as being due to a composition effect. However, his observations were made on the polystyrene-poly(methylmethacrylate) block system in one solvent and of course cannot be generally valid. One might anticipate that the results obtained from viscosity measurements will depend on the nature of the solvent, the composition and the compatability of the polymeric species constituting the copolymer. From this it is evident that the viscosity behaviour of block copolymers cannot be quantitatively predicted from a knowledge of the constituent homopolymers. Earlier attempts to relate the viscosity behaviour of a copolymer to that of a mixed polymer system have failed because of this.

Theory

The most general expression relating the viscosity of a polymer solution η, the viscosity of the solvent η_o and the concentration of the solution c, is given by a series expansion:

$$\eta_{SP}/c = (\eta - \eta_o)/\eta_o c = A + Bc + Cc^2 + \ldots \quad 5.10$$

where η_{SP}/c is the viscosity number. This equation has been found to fit the experimental data of a large number of polymer-solvent systems. In dilute solution, terms in c^2 and higher powers of c can be neglected. Equation 5.10 now becomes

$$\eta_{SP}/c = A + Bc = [\eta] + Bc \quad 5.11$$

where $[\eta] = \lim_{c=o} (\eta_{SP}/c) = A$
and is known as the intrinsic viscosity or limiting viscosity number. When $B = k_H[\eta]^2$, equation 5.11 reduces to the familiar Huggins[27] equation:

$$\eta_{SP}/c = [\eta] + k_H[\eta]^2 c \quad 5.12$$

The Huggins viscosity slope constant k_H is a dimensionless parameter which should be independent of the molecular weight of the polymer and should give a measure of the intermolecular interactions. A variation of the Huggins equation is that due to Kraemer and is expressed in the form

$$\ln(\eta_{rel})/c = [\eta] - k^{1}[\eta]^{2}c \qquad 5.13$$

where $\eta_{rel} = \eta/\eta_o$ and is known as the relative viscosity. The viscosity slope constant k^1 is similar to k_H and is known as the Kraemer parameter. Expansion of the logarithm into powers of c in equation 5.13 and comparison with equation 5.12 shows that $k_H + K^1 = 0.5$. Plotting both η_{SP}/c and $\ln(\eta_{rel})/c$ against c on the same graph provides a certain check on the extrapolation. Both curves must give the same limiting value at zero concentration and the sum of their slopes must equal 0.5.

The intrinsic viscosity [η] of homopolymers has been the subject of many investigations. Its value as a measure of molecular weight, of solvent power and of shape and structure of polymers has been well established.[5,28-30] This information is afforded by the Flory-Fox treatment of viscosity, suggested a number of years ago.[5,15-17] In this treatment the polymer molecules are represented as random coil structures with a Gaussian distribution of chain segmants about their molecular centre of gravity. The polymer molecules are also considered to be extended to different degrees in different solvents and at different temperatures, due to their interactions with the solvent molecules. The degree of extension is defined by the expansion factor α, where α is related to the polymer dimensions by the equation

$$\alpha^2 = \bar{r}^2/\bar{r}_o^2 \qquad 5.14$$

where $\bar{r}^2$ is the mean square end-to-end distance for the polymer under set conditions of solvent and temperature and $\bar{r}_o^2$ is the unperturbed mean square end-to-end distance under theta conditions.

According to the Flory-Fox treatment of viscosity, the relation between intrinsic viscosity $[\eta]$ and molecular weight M is given by

$$[\eta] = \Phi(\bar{r}^2)^{3/2}/M \qquad 5.15$$

where Φ is a viscosity constant originally assumed to be the same for all systems. Using equation 5.14 the above equation can be rearranged in the form

$$[\eta] = \Phi(\bar{r}_o^2/M)^{3/2}M^{1/2}\alpha^3 \qquad 5.16$$

$$= K\,M^{1/2}\alpha^3 \qquad 5.17$$

$$\text{where} \quad K = \Phi(\bar{r}_o^2/M)^{3/2} \qquad 5.18$$

and is a constant characteristic of the polymer. Under theta conditions $\alpha = 1$, so that equation 5.18 reduces to

$$[\eta]_\theta = K M^{1/2} \qquad 5.19$$

The proportionality of $[\eta]_\theta$ to $M^{1/2}$ at the θ point, over several decades of M, has been confirmed by numerous investigations[31,32] for anumber of polymer-solvent systems and is perhaps the most convincing test of the Flory-Fox treatment of viscosity. Comparison of equations 5.19 and 5.17 gives an alternative expression for the expansion factor:

$$\alpha^3 = [\eta]/[\eta]_\theta \qquad 5.20$$

These equations give a method of experimentally finding the expansion factor of a polymer-solvent system at any desired temperature from measurements of intrinsic viscosities. It also allows the determination of the dimensions of a polymer molecule under set conditions. The only assumption to be made is a value for the viscosity constant Φ. Experimental evidence has shown this constant to have values from 1.9×10^{23} to 2.6×10^{23} (cgs units), with a weighted mean of 2.2×10^{23}. According to some recent light scattering experiments,[33,34] critically interpreted, the value of Φ applicable at the theta point is about 2.5×10^{23}. More recent theoretical calculations[35] have shown Φ to have a value of 2.68×10^{23} at the theta point. Theoretical considerations[6,36] have also shown that Φ must depend on the form of the spatial distribution of the units of the chain molecule . For this reason systems removed from the theta point appear to require a small downward adjustment of Φ owing to perturbation of the form of the spatial distribution, due to the excluded volume effect. This means that the value of Φ will to some extent depend on the solvent power. Such dependence has been found experimentally.[6,37,38]

The application of the Flory-Fox theory to homopolymers is well established. However, extension to solutions of block copolymers must be carried out with some reservations. A Gaussian distribution of chain segments about the molecular centre of gravity may not be strictly applicable to block copolymers. These limitations must be considered when interpreting the data for block copolymers using theories developed originally for homopolymers.

Experimental

All the copolymers were examined viscometrically in three different solvents; toluene, cyclohexane and methyl isobutyl ketone (MIBK). These solvents were chosen because of their differing behaviour towards the parent homopolymers of the blocks. Toluene is a good solvent for both polystyrene and polyisoprene; cyclohexane is a good solvent for polyisoprene but poor for polystyrene; and MIBK is a poor solvent for both parent homopolymers. Measurements were also carried out in theta solvents. All the solvents were treated as discussed in Chapter 3. Both polymer solutions and solvents were filtered through a sintered glass G4 filter by means of dry nitrogen pressure before use. The viscometer used was the suspended level or Ubbelohde type, designed to allow dilutions to be made in situ. This featured a capillary having a slow, monotonic increase in diameter and longitudinal curvature of the wall from the centre of the capillary to the extremity. This feature has been shown[39] to reduce the kinetic energy correction to a negligible factor. The viscometer was incorporated in an apparatus similar to that previously described by Steel.[40] This apparatus makes use of a photo-electric timing device which automatically operates an electric timer. A narrow beam of light is focussed on the capillary tubing of the viscometer above the measuring bulb. As the liquid meniscus passes through the beam of light, some of the beam is deflected to the side due to reflection at the interface between the inner wall of the tube and the air which then occupies the outside of the tube. The deflected beam illuminates a light dependent resistor which markedly lowers its electrical resistance. This resistance change activates a trigger circuit causing a crystal timer to start. A similar beam of light focussed below the measuring bulb is also deflected, as the meniscus passes, onto a second light dependent resistor which causes the timer to stop. The viscometer mounted on a frame was contained in a water bath. The temperature of the bath could be kept constant to within ±0.01°C by means of a thermistor controlled heater unit. Using this set up flow times could be determined with an accuracy of ±0.005 seconds. Flow times of solvent used were all in excess of 200 seconds, as shown in Table 5.1.

Table 5.1. Solvent Flow Times in the Viscometer at 30°C

Solvent	Flow Times (secs)
Toluene	215.728
Cyclohexane	407.858
MIBK	229.871

The solutions of the copolymers were tested for non-Newtonian behaviour over a four-fold increase in flow times, compared to the flow times normally used. Over the concentration range used no non-Newtonian behaviour was observed so that no correction was necessary.

BASIC ANALYSES OF THE DATA

Intrinsic Viscosity

All the viscosity data was treated according to both equation 5.12 and 5.13. The results of the copolymers in all solvents were well represented by these two equations. The plots were linear over the concentration range studied. Plots from both equations extrapolated to the same point at infinite dilution. From the definition it follows that the sum of the two slope constants, k_H and $k^1 = 0.5$. The observed values for the copolymers were 0.5 ± 0.02. Some representative plots are shown in Fig. 5.1. Intrinsic viscosities in toluene, cyclohexane, MIBK and in a theta solvent are shown in Table 5.2.

Table 5.2. Intrinsic Viscosities $[\eta]$ of the Copolymers in Toluene, Cyclohexane, MIBK at 30°C and in a Theta Solvent

Polymer	$[\eta]$, ml/g			
	TOL	C-HEX	MIBK	$[\eta]_\theta$
IS1	88.0	92.1	43.2	41.3
IS2	80.1	89.8	42.9	40.3
IS3	75.7	79.0	40.2	39.1
IS4	75.5	63.7	42.8	37.5
IS5	59.2	41.6	34.6	33.5
IS6	201.0	237.0	78.7	65.0
IS7	172.5	178.5	74.1	63.3
IS8	139.1	144.2	65.3	58.6
IS9	345.5	426.7	94.5	89.1
IS10	263.5	272.0	84.8	82.3

Fig. 5.1. Viscosity plots according to both the Huggins (——) and Kraemer (----) equations for the copolymers in three solvents.

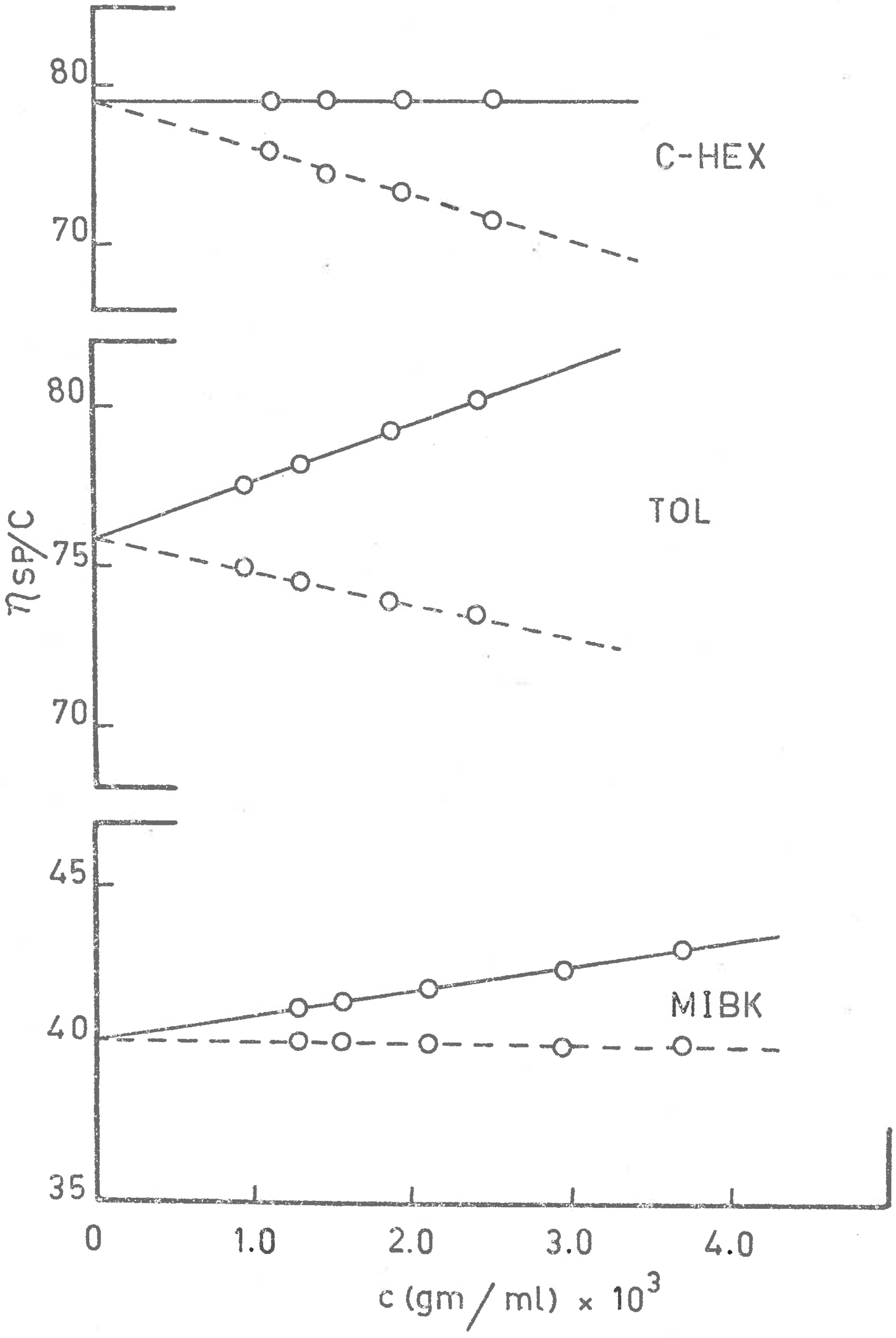


Fig. 5.1

The Huggins and Kraemer Viscosity slope constants for the whole composition range of the copolymers are listed in Table 5.3.

Table 5.3. The Huggins (k_H) and Kraemer (k^1) Viscosity Slope Constants in Toluene, Cyclohexane and MIBK at 30°C.

	TOL		C-HEX		MIBK	
Polymer	k_H	k^1	k_H	k^1	k_H	k^1
IS1	0.30	0.20	0.27	0.21	0.44	0.06
IS2	0.29	0.20	0.02	0.50	0.41	0.10
IS3	0.33	0.16	0.06	0.43	0.46	0.04
IS4	0.46	0.06	0.57	-0.06	0.30	0.20
IS5	0.39	0.14	0.52	-0.02	0.56	-0.06

Mark-Houwink-Sakurada Equation

The dependence of the intrinsic viscosity on molecular weight can be conveniently expressed by the empirical Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K\,M^a \qquad 5.21$$

Double logarithmic plots of log $[\eta]$ versus log $\bar{M}n$ for the copolymers of constant composition were found to be linear.

Such plots were performed on the two series of copolymers coded 25/75 and 50/50. Within each of these series the composition is constant at 25 and 50 weight percent of polystyrene and the molecular weight changes from 10^5 to 5×10^5. The constants of the MHS equation determined for these two series of copolymers in toluene, cyclohexane and MIBK are shown in Table 5.4. The relevant values for polystyrene and polyisoprene are also given.

Table 5.4. Mark-Houwink-Sakurada Constants, $[\eta] = K \bar{M}n^{a}$, of the Copolymers in Three Solvents at 30°C

Code	Solvent	10^2K	a
25/75	TOL	1.0	0.79
	C-HEX	1.9	0.74
	MIBK	9.4	0.53
50/50	TOL	1.8	0.72
	C-HEX	0.4	0.85
	MIBK	9.4	0.53
PS+	TOL	1.1	0.72
	C-HEX	8.0	0.50
PI+	TOL	2.0	0.73
	C-HEX	2.0	0.70

+ from reference 66.

The accuracy in obtaining these MHS constants is low with only three points, nevertheless, they should give a reasonable representation of the behaviour over the limited molecular weight range studied (10^5 - 5 x 10^5). For the 50/50 series in toluene the MHS constants are very close to those of the component homopolymers in this solvent. The 25/75 series show a slightly larger a exponent and smaller K parameter. In MIBK, because of the low composition gradient of [η], all the points could be approximated by one straight line (irrespective of composition) in the log [η] versus log M plot. The experimental points could be best represented by the equation, $[\eta] = 9.36 \times 10^{-2} \bar{M}n^{0.53}$. The MHS constants obtained show that MIBK is close to a theta solvent. Both the K and a parameters are of the right order of magnitude for such a theta condition in comparison to homopolymers. In cyclohexane, for both the 25/75 and 50/50 series, the a exponent is above and the K parameter is below either of the parent homopolymers.

According to the Flory-Fox[17] theory the exponent a in the Mark-Houwink-Sakurada equation must lie between the limits 0.5 to 0.8, for linear flexible chains without drainage effects. The lower limit is for rather tightly coiled chains in theta solvents and the upper limit for highly swollen polymers in very good solvents. In fact, most synthetic linear polymers are found to have a values somewhere between these limits.[6,41] The results on the copolymers also show that they have a values between this range (except 50/50 in cyclhexane for which a = 0.85 - this case will be further dealt with in Chapter 6). These results suggest that the block copolymers have a normal viscosity behaviour similar to homopolymers: they can be considered as semi-permeable coils exhibiting no drainage effects.

Expansion Factor

The expansion factor as defined by equation 5.14:

$$\alpha^2 = \bar{r}^2/\bar{r}_o^2$$

is normally referred to as the linear expansion factor. From the original Flory-Fox[17] viscosity theory the expansion factor can also be defined according to equation 5.20, i.e.

$$\alpha^3 = [\eta]/[\eta]_\theta$$

However, this assumes that Φ is a constant independent of the solvent. As already pointed out recent evidence suggests that this is not strictly correct, so that equation 5.20 should be redefined as

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \qquad 5.22$$

where α_η is the hydrodynamic expansion factor ($\alpha_\eta < \alpha$) and is defined by the equation[6]

$$\Phi = \Phi_o(\alpha_\eta/\alpha)^3 \qquad 5.23$$

This equation indicates that Φ is not strictly a constant but decreases with increasing molecular weight and solvent power. This is now a generally accepted view and similar conclusions have also been advanced by Ptitsyn and Eisner[42,43] and Yamakawa and Kurata.[44,45] The exact form of the expression between α and α_η is not known over a large range of α values and for this reason some authors often neglect to differentiate between these two expansion factors. In this study on the copolymers we have used equation 5.22 to calculate α_η and relation 5.23 to convert α_η to α, assuming that $\Phi_o = 2.68 \times 10^{23}$ and for all conditions other than theta, $\Phi = 2.2 \times 10^{23}$.

Measured values of α_η for the copolymers and constituent homopolymers are shown in Table 5.5. The values of $[\eta]_\theta$ used were those measured directly under theta conditions and listed in Table 5.2. The linear expansion factors α calculated according to equation 5.23 are shown in Table 5.6.

Table 5.5. Hydrodynamic Expansion Factor (α_η) of the Copolymers and Constituent Homopolymers in Three Solvents at 30°C

	α_η		
Polymer	TOL	C-HEX	MIBK
IS1	1.287	1.306	1.015
IS2	1.257	1.306	1.021
IS3	1.246	1.264	1.009
IS4	1.262	1.193	1.045
IS5	1.208	1.074	1.010
IS6	1.457	1.539	1.066
IS7	1.397	1.413	1.054
IS8	1.334	1.350	1.037
IS9	1.571	1.686	1.020
IS10	1.474	1.489	1.010
PS10[+✚]	1.224	1.000	1.068
PS25	1.311	1.000	1.068
PS50	1.381	1.000	1.068
PI10[+]	1.324	1.361	1.036
PI50	1.496	1.515	1.036

[+] calculated from data in references 66, 67, 68

[✚] code of the homopolymers, 10, 25, 50, refers to a molecular weight of 10^5, $2.5\text{x}10^5$ and $5\text{x}10^5$ respectively.

Table 5.6. Linear Expansion Factor (α) of the Copolymers and Constituent Homopolymers in Three Solvents at 30°C

Polymer	α		
	TOL	C-HEX	MIBK
IS1	1.390	1.410	1.096
IS2	1.358	1.411	1.103
IS3	1.346	1.365	1.090
IS4	1.364	1.288	1.129
IS5	1.305	1.161	1.091
IS6	1.573	1.662	1.151
IS7	1.508	1.526	1.138
IS8	1.441	1.458	1.120
IS9	1.697	1.820	1.101
IS10	1.592	1.609	1.091
PS10	1.322	1.000	1.153
PS25	1.416	1.000	1.153
PS50	1.491	1.000	1.153
PI10	1.430	1.470	1.119
PI25	1.533	1.562	1.119
PI50	1.616	1.636	1.119

Some observations on the tabulated values of the expansion factor are worth noting. The values are similar in toluene and cyclohexane but are very much smaller in MIBK, showing that this is a poor solvent for both the copolymers and constituent homopolymers. Also the α values lie between the homopolymer values in the respective solvents. In toluene and cyclohexane α increases with molecular weight (as can be seen by comparing series 25/75 and 50/50) in accordance with behaviour of homopolymers and as predicted by theory.[5] In MIBK there is no definite trend with molecular weight. In this solvent α is not very sensitive to molecular weight, a behaviour which might be expected in a sufficiently poor solvent.

Perturbed Dimensions

Under conditions where α is not equal to unity, i.e., under conditions perturbed by the volume effect, the dimensions assumed by a macromolecule in solution are known as perturbed dimensions. The quantity normally used is the rms end-to-end distance $(\bar{r}^2)^{1/2}$, or the rms radius of gyration $(\bar{S}^2)^{1/2}$, the two of course being related for a Gaussian chain by equation 5.1. For the purpose of comparisons of chains of differing molecular weight the normalized form

$(\bar{r}^2)^{1/2}/M^{1/2}$, known as the root mean square displacement length, is used. Since the theory of chain configurations is based upon the random coil governed by Gaussian statistics, the normalizing factor applied to the end-to-end distance should strictly be the root of the number of links (Z) in the polymer chain. In the case of homopolymers, however, comparison between polymers of different chain lengths may be made on the basis of either the number of segments (N) in the chain or the molecular weight (M) of the chain, since both are directly proportional to the number of links. When considering block copolymers this proportionality does not apply due to the different molecular weights of the segments and in some cases the different number of links in the segments. For the case of poly(isoprene:styrene) blocks: polystyrene has a segmental molecular weight $M_o = 104$ and for polyisoprene $M_o = 68$. Also polystyrene contains two carbon-carbon links in the backbone while polyisoprene contains four such links in the backbone (one of which is a double bond) for the cis- and trans-1,4 isomer. The 3,4 addition isomer contains only two links in the backbone. This shows that for this system use of $M^{1/2}$ as the normalizing factor would cause weighting in favour of polystyrene in terms of both molecular weight and the number of links in the respective monomeric segments. Use of $N^{1/2}$ would still cause weighting in favour of polystyrene in terms of the number of links in the respective monomeric segments. For this reason it seems that the correct normalizing factor to use is $Z^{1/2}$. After allowing for the double bond in the backbone and the isomeric composition (5% 3,4 structure) of the polyisoprene, the appropriate Z for the block copolymers was calculated by the equation

$$Z = \bar{M}n[w2/104 + (1-w)3.8/68] \qquad 5.24$$

where w is the weight fraction of polystyrene in the block. When comparing the variation of copolymer dimensions with composition the correct procedure was considered to be a comparison in terms of link percent (or link fraction) polystyrene. This consideration of the correct composition variable to use when studying changes of copolymer dimensions as a function of composition is an important one. Using plots of $(\bar{r}^2)^{1/2}M^{1/2}$ as a function of weight percent for such a study, as some authors[20,22,46] have done, can lead to a distortion of the true picture.

The end-to-end distance $(\bar{r}^2)^{1/2}$ in toluene, cyclohexane and MIBK, calculated using equation 5.15 (and a value of $\Phi = 2.2 \times 10^{23}$) are listed in table 5.7.

Table 5.7. Root-Mean-Square End-To-End Distance of the Copolymers in Toluene, Cyclohexane and MIBK

	$(\bar{r}^2)^{1/2} \times 10^8$ cm		
Polymer	TOL	C-HEX	MIBK
IS1	350	355	276
IS2	339	352	275
IS3	331	336	268
IS4	334	316	277
IS5	307	273	257
IS6	623	658	456
IS7	592	598	446
IS8	552	559	429
IS9	936	1005	608
IS10	857	866	587

Using a value of Φ equal to 2.2×10^{23} for the copolymers is justified by other experimental evidence on copolymers.[20,21,47,48] Further justification may be obtained from the directly measured values of $(\bar{S}^2)^{1/2}$ in MIBK by light scattering. As discussed earlier this value is only an apparent value but in MIBK, which has a high refractive index, it should be close to the true value (Chapter 3). For this reason the value of Φ calculated should also be close to the true value. An absolute value of $(\bar{S}^2)^{1/2}$ is difficult, if not impossible, to obtain for block copolymers.[49] Obtaining such a value requires measurements in at least three solvents having different refractive indicies. In each of these solvents the copolymer should be extended by the same amount. This is difficult to achieve, practically, due to the limitation on the volume effect in each solvent. For this reason the method of light scattering has no advantage over the viscosity method for determining dimensions of block copolymers. On the contrary viscometry has the advantage of giving a true dimension and possessing a higher order of accuracy than light scattering measurements.

Table 5.8 shows the values of the root-mean-square displacement length in two different normalized forms, together with the values for the parent homopolymers in toluene, cyclohexane and MIBK.

Table 5.8. Root-Mean-Square Displacement Length, $(\bar{r}^2)^{1/2}/M^{1/2}$ and $(\bar{r}^2)^{1/2}/Z^{1/2}$, of the Copolymers in Three Solvents

Polymer	Wt.% PS	$(\bar{r}^2)^{1/2}/M^{1/2}\times10^8$ cm			Link% PS	$(\bar{r}^2)^{1/2}/Z^{1/2}\times10^8$ cm		
		TOL	C-HEX	MIBK		TOL	C-HEX	MIBK
IS1	13.5	1.09	1.11	0.86	5.1	4.85	4.92	3.83
IS2	24.7	1.06	1.10	0.86	10.1	4.90	5.09	3.98
IS3	28.2	1.04	1.06	0.84	11.9	4.89	4.96	3.96
IS4	52.2	1.04	0.98	0.86	27.3	5.41	5.11	4.48
IS5	78.2	0.96	0.85	0.80	55.2	5.80	5.16	4.85
IS6	11.8	1.24	1.31	0.91	4.4	5.45	5.76	3.99
IS7	25.5	1.18	1.19	0.89	10.5	5.47	5.52	4.12
IS8	48.5	1.09	1.11	0.85	24.5	5.61	5.67	4.36
IS9	25.1	1.32	1.42	0.86	10.3	6.13	6.58	3.98
IS10	49.7	1.21	1.22	0.83	25.4	6.23	6.30	4.27
PS	100	0.89	0.67	0.71	100	5.91	4.83	5.16
PI	0	1.17	1.19	0.86	0	4.54	4.66	3.55

The values in Table 5.8 show that the root-mean-square displacement length of the copolymers, for constant composition, increases with increasing molecular weight, in the same manner as do the homopolymers. This effect shows up in toluene and cyclohexane, but in MIBK the parameter is virtually insensitive to changes in molecular weight. This is in accordance with the theory of random chain configuration which predicts that $(\bar{r}^2)^{1/2}$ should increase more rapidly than in proportion to the square root of the molecular weight (or number of links). The results also indicate that in toluene and cyclohexane the copolymer molecules are extended by about the same amount for compositions containing 30 or less weight percent polystyrene. Above this composition the dimensions of the copolymer in toluene increase while those in cyclohexane remain almost constant. The dimensions in MIBK are below those in these two solvents.

Figure 5.2 shows the results of $(\bar{r}^2)^{1/2}Z^{1/2}$ plotted graphically in terms of link percent polystyrene. These plots show that positive deviations from linearity between the parent homopolymer values occur in all three solvents. In toluene and MIBK the deviation appears to be a maximum at about the middle of the composition scale. This may be interpreted in terms of extra repulsive interactions, between the chemically different segments, causing expansion of the copolymer molecule. The implication is that maximum expansion occurs when the chain consists of equal number of unlike links; there is then the possibility of maximum number of heterocontacts. This also implies that there

Fig. 5.2. Plots of $(\bar{r}^2/Z)^{1/2}$ against composition of the copolymers, link % polystyrene, in toluene, cyclohexane and MIBK.

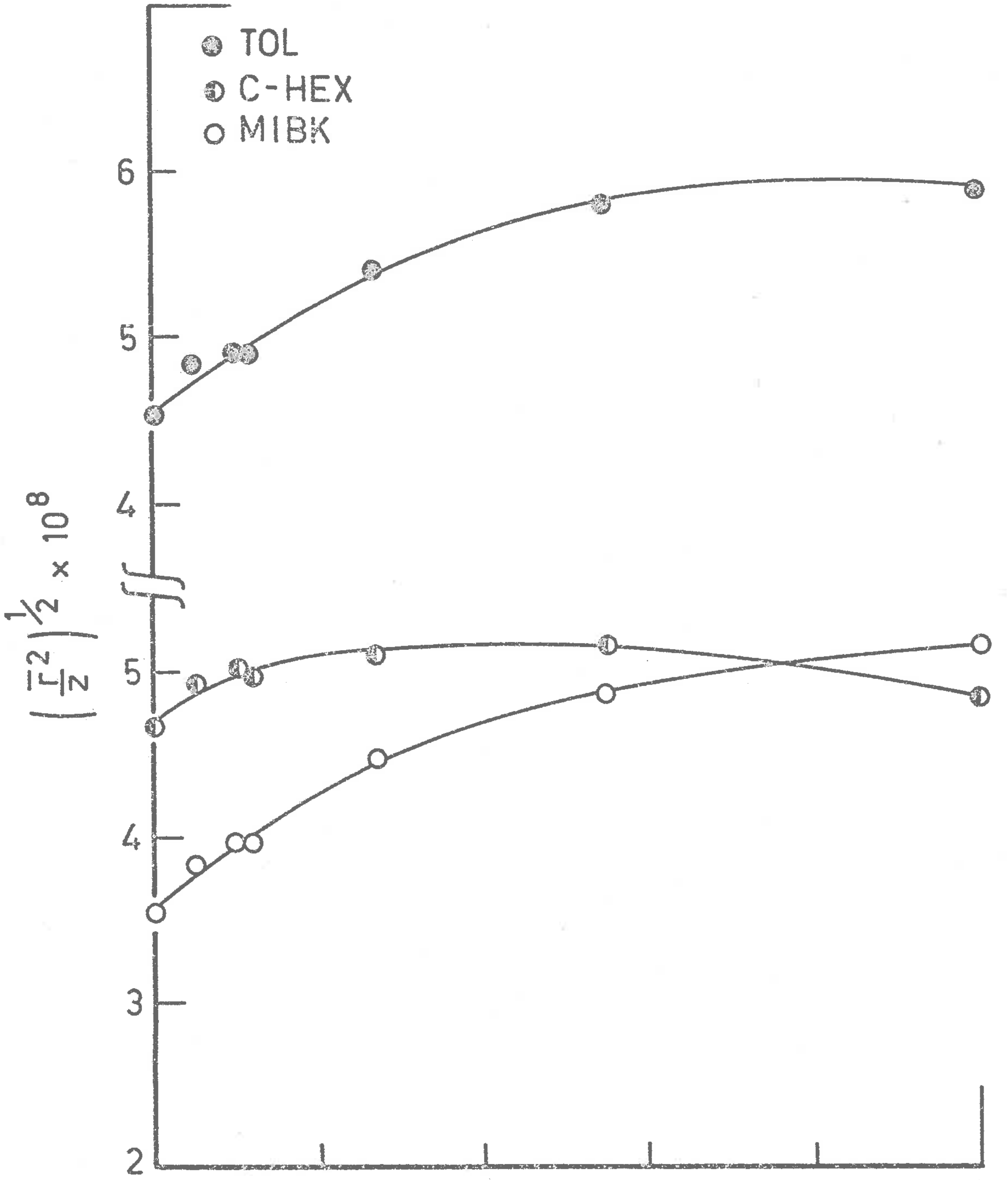

● TOL
◑ C-HEX
○ MIBK
6
5
4
5
4
3
2
$\left(\overline{r}^2_z\right)^{\frac{1}{2}} \times 10^8$
0
20
40
60
80
100
Link % P.S.

Fig. 5.2

must be sufficient mixing of the segments to give rise to these extra repulsions. This conclusion is consistent with the one arrived at by considering the behaviour of the thermodynamic parameters of these systems (Chapter 4). The results in cyclohexane show that the dimensions of the copolymer molecule are larger than those of both homopolymer constituents. Also the dimensions in this solvent show very little composition dependence. The conclusion from these results is that the perturbed dimensions of the copolymer molecule is always greater than the composition average dimension calculated from the constituent homopolymers. This conclusion comes from considering results in three solvents which have intrinsically different behaviour towards the constituent homopolymers of the block.

Unperturbed Dimensions

Under theta conditions the dimensions assumed by a macromolecule are known as unperturbed dimensions. Under such conditions the intrinsic viscosity is given by equation 5.19, i.e.

$$[\eta]_\theta = K_\theta M^{1/2}$$

where $$K_\theta = \Phi_o(\bar{r}_o^2)^{3/2}/M^{3/2}$$

Having measured $[\eta]_\theta$ for all the copolymers the values of K_θ were calculated directly using the above equation. This allows the calculation of the parameter $(\bar{r}_o^2)/M$, which is normally used as a measure of the unperturbed dimensions of a polymer molecule. This parameter is independent of molecular weight and is regarded as a constant for a particular polymer system. In some cases this parameter has been shown to have a small dependence on the solvent. However, such solvent effects are small and only of secondary importance at the most. This parameter may also exhibit a temperature coefficient usually expressed as $d \ln (\bar{r}_o^2)/dT$. However, this is normally small and seldomly exceeds about 1×10^{-3} degree^{-1} in magnitude.[36] The unperturbed dimension data for the copolymers is tabulated in Table 5.9.

Table 5.9. Unperturbed Parameters of the Copolymers in Various Forms

Polymer	$10^2 K_\theta$	$10^8 (\bar{r}_o^2)^{1/2}$	$10^{17} (\bar{r}_o^2)/M$	σ	C_∞	C_∞^*
IS1	12.9	250	6.15	1.70	5.20	5.18
IS2	12.6	248	6.05	1.77	5.56	5.61
IS3	12.3	245	5.95	1.78	5.62	5.76
IS4	11.6	244	5.73	1.79	6.70	6.86
IS5	10.4	234	5.33	2.13	8.40	8.35
IS6	12.9	394	5.16	1.69	5.14	5.12
IS7	12.6	390	6.05	1.77	5.59	5.65
IS8	11.6	381	5.73	1.91	6.47	6.68
IS9	12.6	549	6.05	1.77	5.58	5.63
IS10	11.6	5.37	5.75	1.92	6.57	6.74
PS	8.2	-	4.49	2.44	9.90+	-
PI	11.9	-	6.89	1.71	4.70+	-

* calculated value from equation 5.28

\+ from references 36, 69.

The parameter $(\bar{r}_o^2/M)$ is a measure of the polymer chain dimensions under those circumstances in which the polymer chain has no net interaction with its environment. Under these conditions the chain dimensions are only influenced by the configuration entropy, that is, the polymer chain will have that particular end-to-end distance which allows the rest of the chain to exist in the largest possible number of configurations. Under these conditions the chain dimensions are influenced by: a) length of the chain, b) bond angles along polymer backbone and c) steric interactions between different portions of the chain. In the case of the copolymers the first two factors can be taken into account by dividing ($\bar{r}_o^2$) by Z (as described in the previous section). Any difference in ($\bar{r}_o^2$/Z) is now dependent only on the steric character of the chain. If block copolymers exist in the same configuration as the homopolymers (i.e. random coil) then they should have a steric character intermediate between those of the homopolymers. The fact that this is true for these copolymers can be seen from the results in Table 5.9.

The steric factor (or stiffness parameter) σ, is defined as

$$\sigma = (\bar{r}_o^2/r_{of}^2)^{1/2}$$

This simply expresses the ratio of the unperturbed rms end-to-end distance measured under theta conditions to that calculated assuming free rotation about each single bond of the chain. Of course this ratio is always greater than one and can be used as a measure of the hindrance to free rotation about

about the carbon-carbon bond. In effect σ is a measure of the steric effects operating. The σ values calculated for the block copolymers and constituent homopolymers are shown in Table 5.9. As can be seen the values of the blocks lie intermediate between those of the homopolymers. In fact if σ is plotted as in Fig. 5.3 in terms of the composition the values are well approximated by a straight line joining the values for the homopolymers. This means that the σ values for the copolymers, over the entire composition range studied, can be approximated by the simple additivity relation

$$\sigma_{AB} = Z_A\sigma_A + Z_B\sigma_B$$

where Zi is the link fraction of species i.

Recently Flory[36] has pointed out that the characteristic ratio:

$$C_\infty = (\bar{r}_o^2/nb^2)_\infty \qquad 5.25$$

is to be preferred over $(\bar{r}_o^2/M)$ as a basis for comparing the average dimensions of various random coil chains. Of course the former ratio is calculated from the latter by the relationship

$$C_\infty = (\bar{r}_o^2/M)_\infty(Mb/b^2) \qquad 5.26$$

where Mb is the mean molecular weight per skeletal bond and

Fig. 5.3. Plot of the steric factor, $\sigma = (\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$, as a function of the copolymer composition.

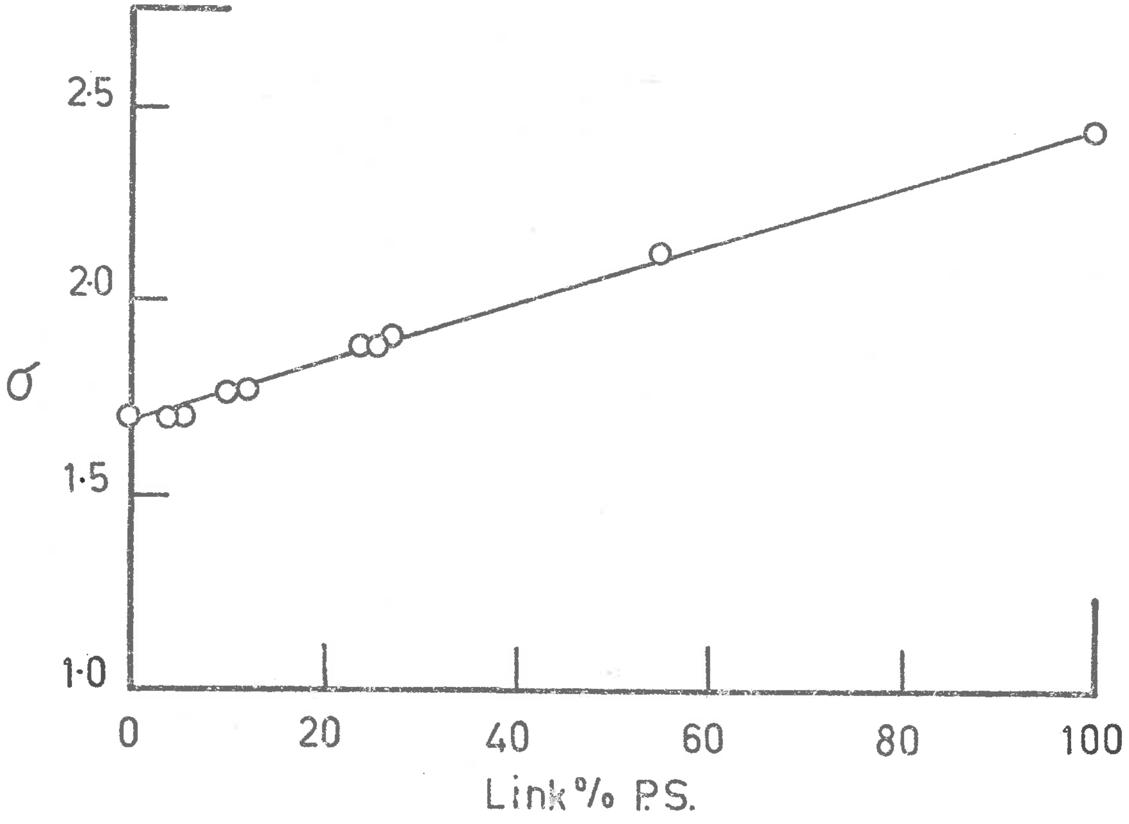


Fig. 5.3

(nb^2) represents the value which ($\bar{r}_o^2$) would assume if correlation between bond directions did not exist. This meas that (nb^2) is the mean-square end-to-end length for a random flight chain of n bonds each being of length b. The characteristic ratios of the block copolymers were calculated from equation 5.26. In the case of the copolymers the values of Mb/b^2 can be calculated from the relation

$$b^2/Mb = \sum_i w_i (nb^2)_i / M_i$$

where M_i is the molecular weight of individual segments and w_i is the weight fraction. The value of $(nb^2)_i$ for the polystyrene and polyisoprene segments was calculated by considering the length of the carbon-carbon bond (1.53Å), the double bond (1.34Å) and allowing for the appropriate isomeric composition of polyisoprene in the copolymer (Chapter 2). The values of $(nb^2)_i$ for polystyrene and polyisoprene were calculated as 4.68Å and 8.61Å respectively.

Stockmayer and coworkers[18] have suggested that the unperturbed mean-square end-to-end distance of an A-B binary copolymer may be given by the simple relation:

$$\bar{r}_o^2/M = w_A(\bar{r}_o^2/M)_A + w_B(\bar{r}_o^2/M)_B \qquad 5.27$$

where w is the weight fraction and the values in parentheses represent those of the homopolymers. They further pointed out that the values of $(\bar{r}_o^2/M)$ for polymer chains may be influenced by interactions extending over a few skeletal chain atoms, so that the above equation might be inadequate for random copolymers, in which the average sequence length is short, but it should suffice for block copolymers. An equivalent relation to 5.27 may be written in terms of the characteristic ratios:

$$C_\infty = xC_\infty^A + (1-x)C_\infty^B \qquad 5.28$$

where x is the mole fraction and the super script denotes quantities characteristic of the parent homopolymers. Calculated values of C_∞ by the above equation are shown in the last column in Table 5.9. As can be readily seen the agreement between calculated and experimental values of C_∞ is good. This shows that the unperturbed dimensions of the block copolymers are a linear function of the dimensions of the constituent homopolymers over the whole composition range. This suggests that the effect of long-range interactions must be zero under these conditions. This situation is similar to homopolymers under theta conditions. Very recently[47,48] measurements on polystyrene-poly(methyl-methacrylate) block copolymers in theta solvents have also revealed that the unperturbed dimensions of this system can be well approximated by a simple additivity relationship between the homopolymers.

This is in contrast to earlier results obtained by Burnett and coworkers[22] and Krause[23] also working with the polystyrene-poly(methyl-methacrylate) system. The former authors obtained unperturbed dimensions which passed through a maximum when plotted as a function of composition, while the values obtained by Krause were actually lower than the values for the constituent homopolymers. It must be recognized however, that both these authors did not measure the unperturbed dimensions directly but obtained them by extrapolating data in good solvents. Such extrapolations must be treated with caution - as will be shown later in this chapter.

FURTHER ANALYSES OF THE DATA

Short-Range Interactions

In view of the current status of two-parameter theories (discussed in the introduction to this chapter) it was thought of interest to extend the theories to examine the dilute solution properties of the block copolymers. In cases where theta solvent data is available the unperturbed dimensions or short-range interactions can be computed directly as outlined in the previous section. Under circumstances where such data is not available it has been often argued, from considerations of two-parameter theories, that the short-range interactions may be estimated from good solvent data.

This requires employing an appropriate extrapolation procedure that separates the effects of the short-range and long-range interactions.[6,34,51-53] However, the conditions of applicability of such extrapolations must be fully realized in order to obtain correct estimates. It is especially fruitful to find a suitable extrapolation procedure for copolymers for which data in theta solvents is often non-existing or hard to obtain. In this study an attempt was made to determine the short-range interactions for the block copolymers from viscosity-molecular weight and second virial coefficient-molecular weight data. The solvents used were a good solvent (toluene), a preferential solvent (cyclohexane) and a poor solvent (MEK). The results thus obtained were compared with the directly measured ones. This allowed the relative merit of the extrapolations employed to be assessed as well as testing the applicability of two-parameter theories to solutions of block copolymers.

<u>$[\eta]$-M relations</u>. If the $[\eta]$-M method is to be used an effective relation describing the dependence of $[\eta]$ on M must be employed. The basic equation always used is the Fox-Flory viscosity equation - equation 5.17:

$$[\eta] = K M^{1/2} \alpha^3$$

The dependence of the expansion factor α on M also needs to be known. Due to minor variations employed in this dependence a number of theories have developed. Three different equations suggested for obtaining K_θ from $[\eta]$-M data will be considered below.

1. Fox-Flory-Schaefgen (FFS) method:

The early theoretical treatment of Flory[5] led to the formulation of the well known excluded volume equation (equation 5.5). Combining this with equation 5.17 gives

$$[\eta]^{2/3}/M^{1/2} = K^{2/3} + C(1-2\chi)K^{5/3}\ (M/[\eta]) \qquad 5.29$$

so that K can be obtained from the intercept of a plot of $[\eta]^{2/3}/M^{1/3}$ against $M/[\eta]$. The method is ingenious but its application, however, often leads to underestimation of K and it cannot be recommended for general use in good solvent systems.[54]

2. Kurata-Stockmayer (KS) method:

In an extensive publication,[6] Kurata and Stockmayer proposed a new method for obtaining the unperturbed dimensions from $[\eta]$-M data. This approach utilized a slight modification of an equation due to Kurata Stockmayer and Roig[7] (equation 5.8) who assumed an ellipsoid model for the polymer molecule. The basic equations in terms of the viscosity expansion factor become:

$$\begin{aligned} \alpha_\eta^3 - \alpha_\eta &= 1.10\, g(\alpha_\eta) z \\ g(\alpha_\eta) &= 8\, \alpha_\eta^3/(3\, \alpha_\eta^2 + 1)^{3/2} \\ z &= (3/2\pi)^{3/2}\, B\, A^{-3}\, M^{1/2} \\ A^2 &= \bar{r}_o^2/M \end{aligned} \qquad 5.30$$

Where B is related to the solute-solvent interaction parameter χ and defines the long-range interactions. The parameter A of course defines the short-range interactions. In addition one now defines α_η, the viscosity expansion factor, as

$$[\eta] = K_\theta M^{1/2} \alpha_\eta^3 \qquad 5.31$$

Combination of equations 5.30 and 5.31 gives

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363\Phi_o B[g(\alpha_\eta) M^{2/3}/[\eta]^{1/3}] \qquad 5.32$$

Extrapolatins according to this equation have been shown to result in a common intercept for good and poor solvent data for many systems.[6] Despite this the method lacks attraction because of the cumbersome form of equation 5.32 and the lengthy procedure of the extrapolation.

3. Stockmayer-Fixman (SF) method:

More recently, Stockmayer and Fixman[55] have proposed another equation for estimating the parameter K_θ from viscosity-molecular weight data. In this approach earlier equatins developed by Fixamn[8] led to a very simple closed form expression for the linear expansion factor (equation 5.9):

$$\alpha^3 = 1 + 2z$$

In comparing this with an earlier expression of the viscosity expansion factor obtained from perturbation calculations:[44]

$$\alpha_\eta^3 = 1 + 1.55z + O(z)^2 \qquad 5.33$$

they concluded that the viscosity expansion factor could be approximated by the relation

$$\alpha_\eta^3 = 1 + 1.55z \qquad 5.34$$

without higher terms. A combination of equation 5.34 with equation 5.31 leads to the formulation of the simple equation:

$$[\eta] = K_\theta M^{1/2} + 0.51\Phi_o BM \qquad 5.35$$

$$\text{or} \quad [\eta] = \Phi_o A^3 M^{1/2} + 0.51\Phi_o BM$$

This equation clearly separates the effects of short- and long-range interactions into two separate terms. The data is presented as plots of $[\eta]M^{-1/2}$ versus $M^{1/2}$; the intercept gives the short-range interaction parameter (K_θ or A) and the slope gives the long-range interaction parameter B. This method has been shown[55] to yield the correct value for K_θ in both good and bad solvents. Equation 5.35 can be said to describe the dilute solution properties or intrinsic viscosities of flexible chain polymers in all solvents, provided drainage effects are negligible.

In estimating the short-range interactions for the block copolymers from $[\eta]$-M data, equation 5.35 was used. The results are summarized in Table 5.10. The values in cyclohexane are those at 46°C (the reason for this will become evident in Chapter 6).

Table 5.10. Short-Range Interaction Parameter for the Copolymers, Calculated from $[\eta]$-M Relation

Code	Solvent (°C)	$10^2 K_\theta$	$10^{11} A$	$10^{11} A^*$
25/75	TOL (30°)	12.8	782	778
	MIBK (30°)	12.8	782	
50/50	TOL (30°)	11.5	754	
	MIBK (30°)	12.4	773	757
	C-HEX (46°)	11.6	756	

* measured directly in theta solvent.

The plots of $[\eta]\bar{M}n^{-1/2}$ versus $\bar{M}n^{1/2}$ were straight lines, except series 25/75 in toluene which showed a slight curvature at the highest molecular weight. The plots are shown in Fig. 5.4. Values for 25/75 in cyclohexane could not be extrapolated with any great accuracy because of the high curvature of the plot.

Equation 5.35 should hold for both good and poor solvents. However, it has been found from studies on homopolymers[56] that the equation has an upper limit of applicability; the range of linearity expressed as $\alpha_\eta < 1.4$. The same limit was found to hold for the block copolymers (actually $\alpha_\eta < 1.5$). This explains why the 25/75 series in cyclohexane showed curvature at the highest molecular weight (IS9 in this solvent has a value of $\alpha_\eta = 1.68$).

Table 5.10 shows the values of K_θ and $(\bar{r}_o^2)^{1/2}/M^{1/2}(\equiv A)$ obtained from equation 5.35. For comparison the values of A obtained from direct measurement in theta solvents are included for the relevant copolymers. As can be seen the two methods are in excellent agreement in predicting the short-range interactions of the copolymers. This means that the same extrapolation procedure as used for homopolymers can also be used for the copolymers to obtain a measure of the short-range interactions. The results suggest that the intrinsic viscosity of the copolymers can be described by equation 5.35 in both good and poor solvents. In preferential solvents the applicability of this equation depends on the temperature (see Chapter 6).

From the results in Table 5.10 it can be seen that the values of K_θ show no specific solvent effect. This conclusion is arrived at by considering K_θ values in four intrinsically different solvents: both a good and poor solvent, a preferential solvent and a theta solvent. K_θ can therefore be regarded as characteristic of the polymer series and independent of the solvent - in the same manner as it is for homopolymers.[36] The results also show that there is no measurable difference in the value of K_θ obtained at 30°C to that obtained at 46°C. This negligible temperature coefficient might be expected from a consideration of the values for the constituent homopolymers.[36]

A_2-M relations. The use of different methods, to measure the short-and long-range interactions in solution, which complement each other is desirable both to minimize the uncertainties in estimating the interaction parameters and to confirm certain theories. Such an approach is especially valuable when trying to assess the validity of certain theories derived for homopolymers and extended to copolymers. Two such methods are the $[\eta]$-M and A_2-M approaches in estimating the unperturbed dimensions and the long-range interactions of macromolecules. Unfortunately the latter method has not enjoyed the same success as the former. The reasons being partly theoretical and partly due to the low sensitivity of the second virial coefficient towards variation in M.

The first problem in using the A_2-M method is to establish an appropriate closed expression for A_2 in terms of the parameters A and B. Kurata and coworkers[14] have suggested a closed expression for A_2 corresponding to the third power law equations of the excluded volume effect. The above authors used the same ellipsoid method which was used to obtain expressions (5.8 and 5.9) for the excluded volume. By using the Fixman equation for the expansion factor (equation 5.9) they arrived at the expression

$$A_2\bar{M}n^{1/2} = 1.65 \times 10^{23}A_{\pi}^3 + 0.968 \times 10^{23}B_{\pi}\bar{M}n^{1/2} \qquad 5.36$$

(the subscript π is used to differentiate the parameters from the ones derived using the viscosity method). This expression should only be used in the range $\alpha_\eta > 1.2$: for data in relatively good solvents. The equation predicts that a plot of $A_2M_n^{1/2}$ versus $M_n^{1/2}$ should give a straight line from which the two parameters A and B can be determined from the intercept and the slope. If instead of using the Fixman equation for the excluded volume, an equation due to Ptitsyn:[9]

$$\alpha^2 = [3.68 + (1 + 9.36z)^{2/3}]/4.68 \qquad 5.37$$

is used, then the expression obtained is the same in form to equation 5.36 but with different coefficients:

$$A_2\bar{M}n^{1/2} = 2.83 \times 10^{23}A_{\pi}^3 + 1.67 \times 10^{23}B_{\pi}\bar{M}n^{1/2} \qquad 5.38$$

The results of the copolymers were treated by the above method using the second virial coefficient obtained from the osmotic work (Chapter 4). All plots of $A_2Mn^{1/2}$ versus $Mn^{1/2}$ were linear and are shown in Fig. 5.5. The values of the A parameter are tabulated in Table 5.11. The subscripts Π_1 and Π_2 refer to values obtained by equations 5.36 and 5.38, which for the purpose of the discussion will be referred to as equations I and II respectively. For comparison the values obtained by the viscosity method are also included and distinguished by the subscript η. The ratio of the values of A obtained by the two methods is also included in Table 5.11.

Table 5.11. Comparisons of the Short-Range Interaction Parameter (A) Obtained by $[\eta]$-M and A_2-M Methods

Code	Solvent	$A \times 10^{11}$				
		A_η	A_{Π_1}	A_{Π_2}	A_{Π_1}/A_η	A_{Π_2}/A_η
25/75	TOL	782	1059	885	1.35	1.13
	C-HEX	778	1018	850	1.31	1.09
50/50	TOL	754	981	820	1.30	1.80
	C-HEX	756	823	687	1.09	0.91

The discrepancies between A_η and A_Π is as expected from experience with homopolymers.[57-59] Since the agreement between A_η and A, obtained from the viscosity method and from direct

Fig. 5.4. Plots of $[\eta]M^{-1/2}$ against $M^{1/2}$, Stockmayer-Fixman extrapolation, for the copolymers in three solvents.

Fig. 5.5. Plots of $A_2M^{1/2}$ against $M^{1/2}$ for the copolymers in three solvents.

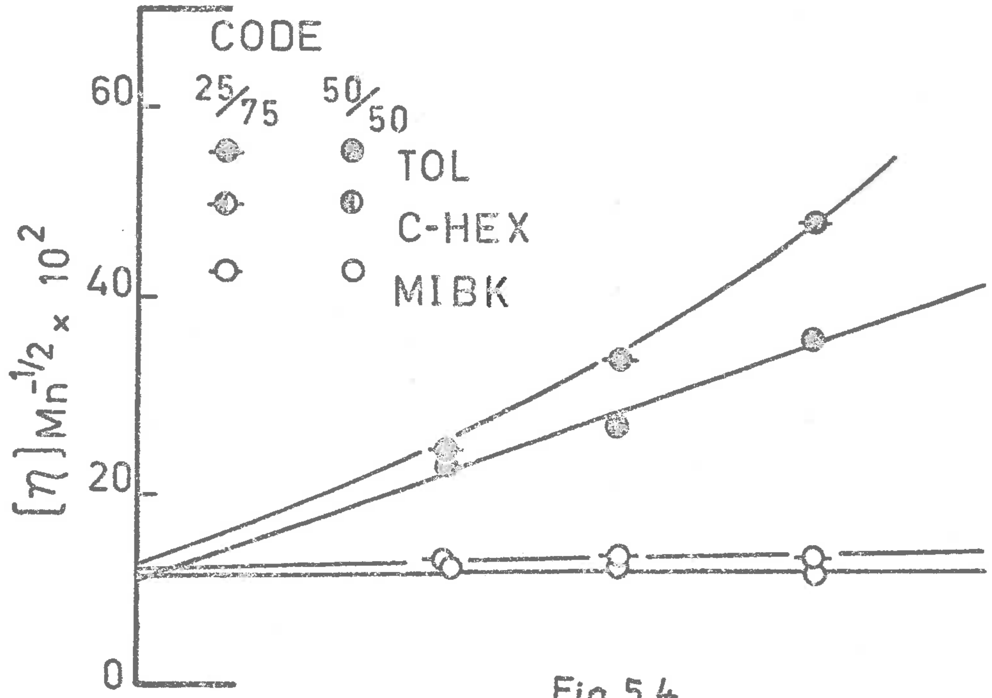

CODE
25/75
50/50
TOL
C-HEX
MIBK
60
40
20
0
$[\eta]\,Mn^{-1/2}\times 10^2$

Fig.5.4

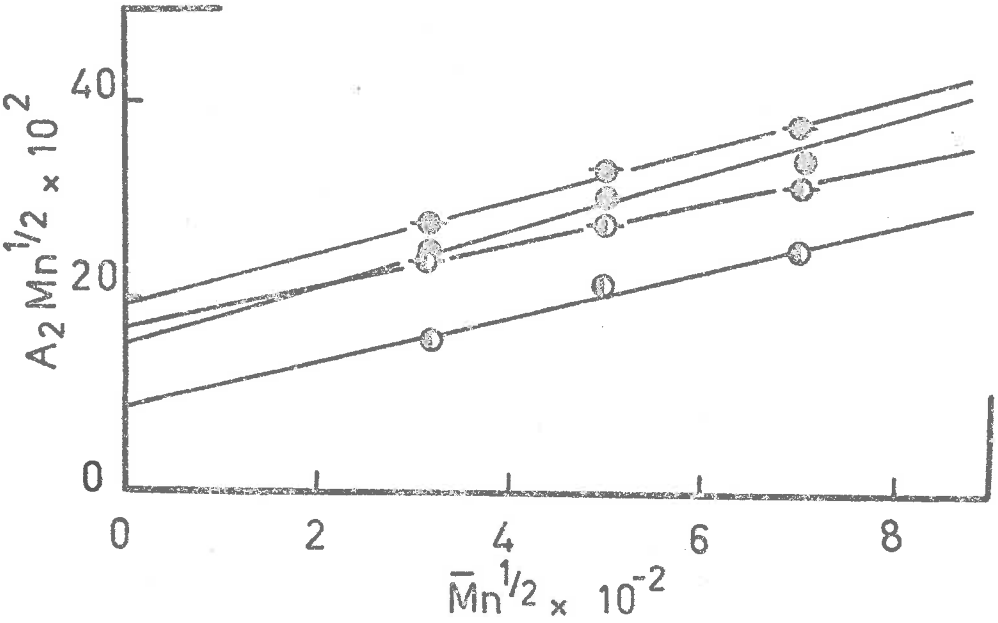

40
20
0
$A_2\,Mn^{1/2}\times 10^2$
0
2
4
6
8
$\bar{M}n^{1/2}\times 10^{-2}$

Fig.5.5

measurements in theta solvents is good, the conclusion must be that it is the A_2-M method which gives rise to the discrepancy in the A parameter. This is in agreement with the experimental observation[14] that the viscosity-method is superior for determining unperturbed dimensions to the A_2-method. To understand this difference between A_η and A_Π, from a theoretical point, it is desirable to establish a correlation between $[\eta]$ and A_2 in terms of M. This is most conveniently expressed by the osmometric dimensionless ratio, defined as $A_2\bar{M}n/[\eta]$. The coefficients of equations I and II are based on a treatment which makes use of the limiting value of a 'penetrating' function[14] equal to 0.180 (when $\alpha > 1.35$). This determines the range of applicability of equation I. This numerical value of 0.180 yields a value for the dimensionless ratio of about 60. An alternative expression[9] for the 'penetrating' function produces a limit of 0.311 and gives rise to equation II. Here $A_2\bar{M}n/[\eta]$ is about 110, which is in closer agreement with the experimentally observed 100-140 obtained for ordinary synthetic polymers.[6,60] This suggests a better correlation between $[\eta]$ and A_2.

The results of the copolymers listed in Table 5.11 show that the use of equation II gives better agreement between A_η and A_Π (about 10%) than the use of equation I. The reason for this can be appreciated by considering the dimensionless ratio of the copolymers, shown in Table 5.12.

Table 5.12. Osmometric Dimensionless Ratio of the Copolymers in Three Solvents at 30°C

Polymer	$A_2\bar{M}n/[\eta]$ TOL	$A_2\bar{M}n/[\eta]$ C-HEX	$A_2\bar{M}n/[\eta]$ MIBK
IS1	118	96	28
IS2	112	93	40
IS3	119	97	40
IS4	106	80	38
IS5	115	70	57
IS6	59	71	36
IS7	98	79	41
IS8	111	76	58
IS9	76	54	62
IS10	92	65	94

As can be seen the values in toluene are very close to the limit predicted by equation II, while those in cyclohexane are generally lower but lie between the two limits predicted by equation I (60) and equation II (110). This possibly shows why equation II gives values of A_{Π} closer to A_{η} than does equation I. It also shows why the values obtained for the

50/50 series in cyclohexane lie above A_{II} if equation I is used and below A_η if equation II is used. The above procedure could not be used for data in MIBK because this is a poor solvent and is outside the range of applicability of equations I and II (as indicated by the small $A_2\bar{M}n/[\eta]$ values).

The failure of the A_2-method in obtaining the correct A parameter is partly due to the low sensitivity of A_2 on M and partly due to the inadequacies underlying the theory. To this end a refinement of the theories of the excluded volume effect and its relation to A_2 appears to be necessary. Recent theoretical[61,62] work is continuing along these lines. However, from the results it can be concluded that the second virial coefficients of these block copolymers can be approximated by equations of the form I and II, with the same accuracy and limitations as found for homopolymers and also some random copolymers.[63]

Long-Range Interactions

Interaction parameter B. The long-range interaction parameter B can be estimated from equation 5.35 and equation 5.36 in the same manner as can the parameter A. The values of B obtained by both the $[\eta]$-M and A_2-M methods are shown in Table 5.13.

Table 5.13. Long-Range Interaction Parameter for the Copolymers Obtained by [η]-M and A_2-M Methods

		$B \times 10^{28}$		
Code	Solvent	B_η	B_{Π_1}	B_{Π_1}/B_η
25/75	TOL	26.3	27.2	1.03
	C-HEX	-	22.5	-
50/50	TOL	25.6	28.7	1.12
	C-HEX	24.8	23.3	0.94

As can be seen the agreement between B_η and B_Π is reasonable (about 10%) and is at least as good as that obtained for homopolymers.[13] From this it can be concluded that the long-range interaction parameter for the copolymers can be estimated in different solvents by using the appropriate extrapolation procedures. The accuracy and limitations of these extrapolations are the same as experienced with homopolymers. This again shows the applicability of two-parameter theories to these block systems.

Binary cluster integral β. Another approach to the problem of long-range interactions of macromolecules is to measure the binary cluster integral β. This may be taken to represent the excluded volume of a pair of segments; assuming that the ternary and higher order clusters may safely be disregarded in dilute solutions. In most polymer solutions β will be positive, since for appreciably negative values the polymer becomes insoluble. Under theta conditions $\beta = 0$. Mathematically β is defined as in equation 5.7 in terms of the pair potential of average force, which represents the potential energy for solute-solute interactions. However, as has been pointed out[64] this pair potential also depends on the solvent-solute and solvent-solvent interactions. For this reason β should be recognized as playing the role of a parameter and one should not take its physical interpretation, as an excluded volume, too literally. Despite this its usefulness in current two-parameter theories has been widely proved.

The equation derived by Kurata, Stockmayer and Roig[7] (equation 5.8) was used to calculate β for the block copolymers. The values of α used were those shown in Table 5.6. For the calculation the effective segment length was defined as $a^2 = \bar{r}_o^2/Z$, where Z represents the number of links (as previously defined). Using this notation the KSR equation becomes:

$$(\alpha^3 - \alpha)(1 + {}^1/_3\alpha^2)^{3/2} Z^{-1/2} = ({}^4/_3)^{5/2}({}^3/_{2\pi a^2})^{3/2}\beta$$

With this definition β becomes the excluded volume for a pair of links. The β values calculated for the copolymers, together with those of the constituent homopolymers are shown in Table 5.14.

Table 5.14. Binary Cluster Integral for the Copolymers in Three Solvents at 30°C

	$\beta \times 10^{24}$ (cm^3)		
Polymer	TOL	C-HEX	MIBK
IS1	1.44	1.54	0.29
IS2	1.49	1.78	0.35
IS3	1.47	1.58	0.32
IS4	2.25	1.68	0.67
IS5	2.97	1.40	0.77
PS	4.96	0	1.66
PI	1.40	1.58	0.31
IS6	1.67	1.88	0.29
IS7	1.68	1.61	0.31
IS8	1.72	1.82	0.37
IS9	1.72	2.22	0.16
IS10	1.91	1.99	0.13

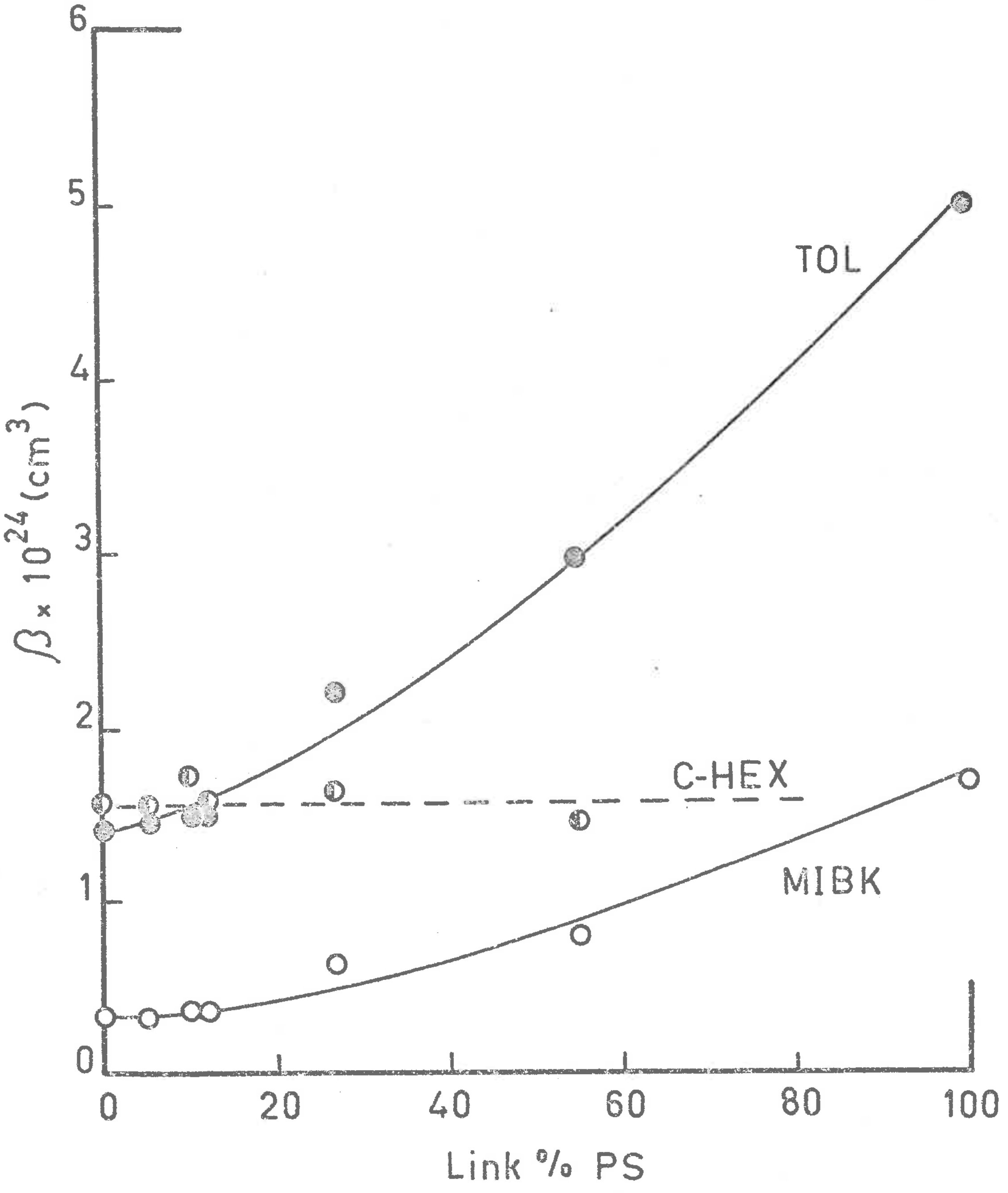
To fully describe the repulsive long-range interactions in a binary copolymer, three types of binary cluster integrals must be defined: β_{11}, β_{22} describing the interactions between like segments and β_{12} describing the interactions between unlike segments. By making use of the Zeroth approximation[65] the average binary cluster integral for the copolymer can be written in the form:

$$\begin{aligned}\bar{\beta} &= \beta_{11}x^2 + \beta_{22}(1-x)^2 + 2x(1-x)\beta_{12} \qquad 5.39\\ &= \sum_i \beta_{ii}x_i^2 + 2\sum_{i<j}\beta_{ij}x_i x_j\end{aligned}$$

where x_i is the mole fraction of species i. This equation is strictly applicable only to a random distribution of disconnected segments, where the probability of contacts can be taken to be directly proportional to the number of such segments.

The calculated values of β listed in Table 5.14 are shown plotted as a function of copolymer composition in Fig. 5.6. These plots show that in toluene and MIBK, β increases from the value of pure polyisoprene to that of polystyrene: the values fall on a smooth curve intermediate between the homopolymer values. This behaviour is as expected if the composition dependence of β is similar in form to that described in equation 5.39. This must suggest that in these two solvents the different segments of the copolymer are

Fig. 5.6. Plots of the binary cluster integral β against composition of the copolymers, in three solvents.



$\beta \times 10^{24}\,(cm^3)$
0
1
2
3
4
5
6
0
20
40
60
80
100
Link % PS
TOL
C-HEX
MIBK

Fig.5.6

sufficiently mixed to give this type of behaviour. This is consistent with conclusions made from the thermodynamic results (Chapter 4). In cyclohexane the behaviour is different. The values of β over the composition range studied (12-78 weight percent polystyrene) are virtually independent of composition. Considering the error involved, a horizontal straight line passing through the value for pure polyisoprene could well represent these points. This would imply that in this solvent we are primarily looking at the polyisoprene sequence of the copolymer chain - the polystyrene sequence contributing little to the β value. Since β for polystyrene in cyclohexane is zero, this must imply that no heterocontacts are present. The suggestion is that in this solvent there is minimum interpenetration of the polystyrene and polyisoprene domains, i.e., partial intramolecular phase separation must exist. This is consistent with the conclusion arrived at by a consideration of the thermodynamic results in this solvent (Chapter 4).

The excluded volume integral can be related to the long-range interaction parameter B, by the relationship

$$B = \beta/M_o^2 \qquad 5.40$$

for homopolymers. For a copolymer the relation becomes

$$B = \beta/M_{oc}^2 \qquad 5.41$$

where $M_{oc} = \sum_i M_{oi} x_i$ and x_i is the mole fraction. When using link fractions the relation becomes

$$B = \beta/Z_{oi} \qquad 5.42$$

where $Z_{oi} = \Sigma M_{oi} x_i / Z_{oi}$ and Z_{oi} is the number of links in species i.

The values of B obtained from the [η]-M plots (for the 25/75 and 50/50 series in toluene) were converted to values of β using the above relationships. The calculated values of β were 1.51×10^{-24} and 2.44×10^{-24} respectively. These compare very favourably with the directly measured values of 1.49×10^{-24} and 2.25×10^{-24} shown in Table 5.14. Considering the two entirely different approaches of obtaining this parameter the correlation must be considered to be good.

In order to split up β into its components and thus obtain an estimate of the value of β_{12}, the excluded volume integral for heterocontacts, we have firstly explored the validity of using equation 5.39. In arriving at this equation the assumption made is that a random distribution of segments exists in the copolymer. This may not be strictly correct. However, for block copolymers this should be semi-quantitatively a good approximation. If the above assumption is valid then β_{12} should be independent of copolymer composition, but may still vary with the solvent. The calculated values of β_{12} are shown in Table 5.15.

Table 5.15. Values of the Binary Cluster Integral for Heterocontacts (β_{12}) for the Copolymers Calculated by Equation 5.39, in Three Solvents

	$\beta_{12} \times 10^{24}$ (cm^3)		
Polymer	TOL	C-HEX	MIBK
IS1	1.46	1.41	0.12
IS2	1.31	2.43	0.66
IS3	1.17	1.78	0.18
IS4	1.88	2.35	0.57
IS5	0.97	3.01	-0.17

The values of β_{12} are shown plotted as a function of composition in Fig. 5.7. Considering the accuracy and the assumptions made in arriving at this parameter, the values in toluene and MIBK are reasonably approximated by two horizontal straight lines. These give an average value of β_{12} of 1.36 in toluene and 0.30 in MIBK. However, the values in cyclohexane show a definite composition dependence. These results suggest that at least in toluene and MIBK the segments of the copolymer chain are sufficiently mixed to make equation 5.39 a reasonable approximation. If the contention that in

Fig. 5.7. Plots of the binary cluster integral for heterocontacts β_{12} against composition of the copolymers.

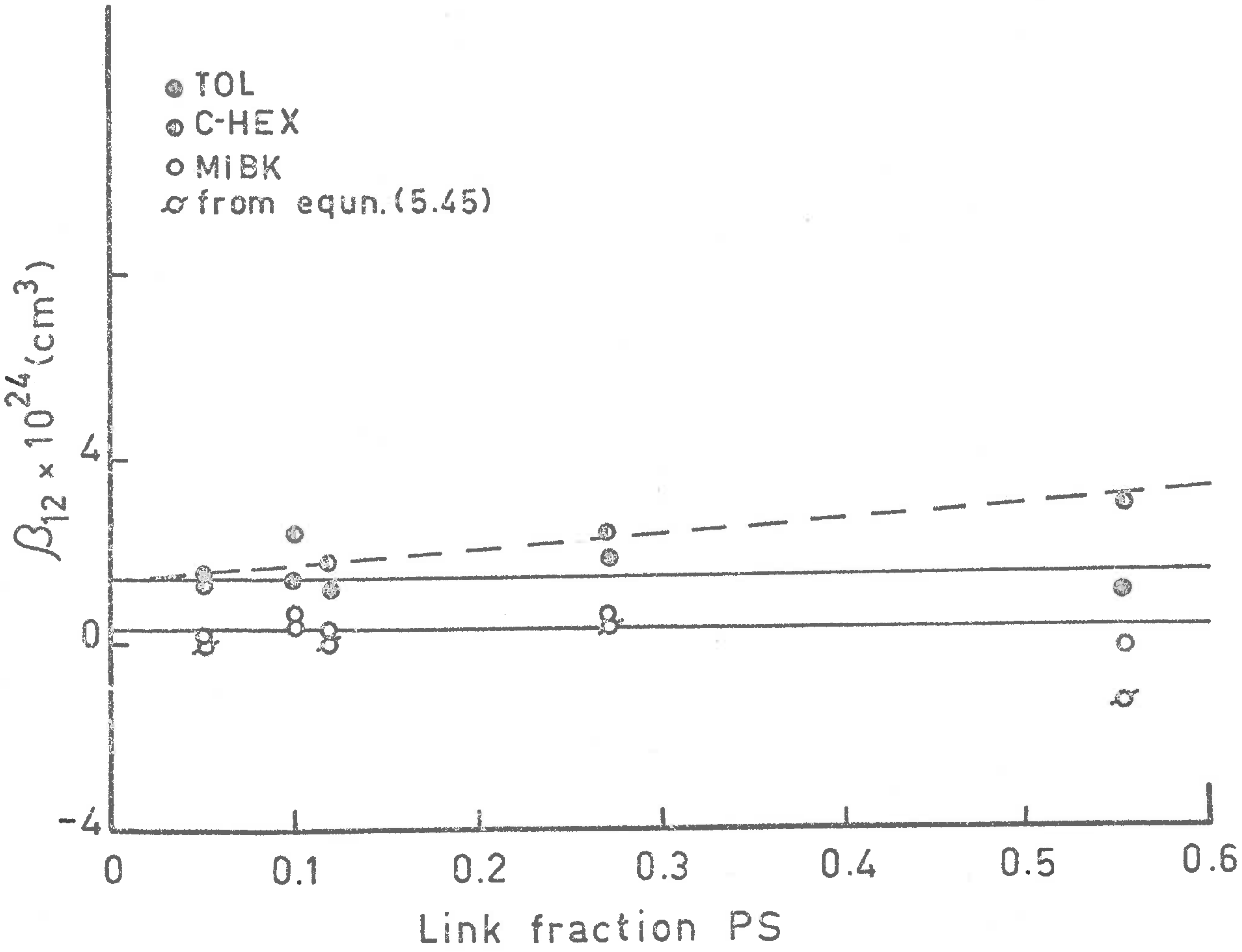

● TOL
◐ C-HEX
○ MiBK
ơ from equn.(5.45)
$\beta_{12} \times 10^{24}$ (cm^3)
4
0
-4
0
0.1
0.2
0.3
0.4
0.5
0.6
Link fraction PS

Fig. 5.7

cyclohexane the copolymers exhibit partial phase separation is correct, then the validity of equation 5.39 is questionable in this solvent.

In general terms equation 5.39 for the excluded volume may be written as

$$\bar{\beta} = \sum_{ij} \beta_{ij} \varepsilon_{ij}$$

where $\varepsilon_{ij} = \varepsilon_{ji}$ and is the fraction of i-j configurations characterized by a parameter $\beta_{ij} (\equiv \beta_{ji})$. For a two sequence block copolymer this equation would reduce to

$$\bar{\beta} = \beta_{11} \varepsilon_{11} + \beta_{22} \varepsilon_{22} + 2\beta_{12} \varepsilon_{12} \qquad 5.44$$

If the assumption is made that the probability of contacts is directly proportional to the number of segments, i.e., $\varepsilon_{ij} = x_i x_j$, then equation 5.44 reduces to equation 5.39 used in the previous section. A calculation of ε_{ij} would require a knowledge of the segment distribution function in the presence of long-range interactions and the assumption of an effective range for segment-segment interaction. Froelich and Benoit[70] have attempted this problem. They utilized the exact solution for the expansion factor, which strictly is only applicable when α tends to unity. Their equation takes the form:

$$\alpha^2 = 1 + (3/2\pi)^{3/2} a^{-3} Z^{1/2} [\beta_{11} X_1 + \beta_{22} X_2 + \beta_{12} (134/105 - X_1 - X_2)] \qquad 5.45$$

where the coefficients

$$X_1 = x^{5/2} (392 - 258x)/105$$

and $$X_2 = (1-x)^{5/2} (258 + 134)/105$$

From the previously measured values of α the values of β_{12} were calculated using the above equation. Equation 5.45 has limited use and is strictly applicable only under conditions for which α approaches unity. For this reason possibly only the values in MIBK should be considered to have any significance. These values are shown plotted in Fig. 5.7. As can be seen the values have a reasonable correlation with those calculated from equation 5.39.

In summary the results provide evidence and support that two-parameter semi-empirical theories, developed originally for flexible homopolymers, are also applicable to the block copolymers. The results in solvents equally good, or equally poor, for both homopolymers comprising the copolymer chain, indicate that the distribution of segments is similar to that in homopolymers: the copolymer chain can be considered as a random distribution of segments. In a preferential solvent such as cyclohexane a different behaviour is indicated.
In this solvent the results suggest that the segmental distribution

is not completely random, i.e., some intramolecular phase separation is indicated.

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Chapter 6

PHASE SEPARATION IN BLOCK COPOLYMERS

INTRODUCTION

In composite systems, such as block copolymers, there is always the possibility of phase separation occurring. Such a phenomenon causes the chemically different segments of the block to occupy different domains, thus giving rise to a heterophase system. The occurence of such a phenomenon has been the point of many discussions,[1-3] especially in attempting to explain the sometimes peculiar but interesting solution and physical properties of these type of systems. Most efforts in this area in the last few years have been concerned with the bulk state.[4-6] This has stemmed mainly from the recently recognized technological importance of the new thermoplastic elastomers.[7,8] It is now generally agreed and accepted that the interesting physical properties of these materials is due to the possibility of domain formation in the bulk polymer. Such properties are highly dependent on molecular weight, composition and molecular weight and composition distribution. However, as yet there is still no quantitative explanation of the conditions and factors contributing to this domain formation. The problem is no doubt complex and any information, from whatever source of study, which might aid in solving some of the problems must always be welcomed.

Due to the incompatibility of two chemically different polymers, the mixing of two such polymers will always be accompanied by a large positive enthalpy of mixing, but only a small gain in entropy. From this consideration it would be expected that in the bulk state, phase separation of two chemically different polymers would always occur. The problem of intramolecular phase separation in solution is even more complex than in the bulk phase. Here an extra parameter must be considered: the solvent. However, it might not be over optimistic to think that common problems exist in both the bulk and solution phase. This can be more easily appreciated if as a first approximation one is justified in considering the bulk state of a polymer as similar to the solution state when immersed in a theta environment. At least the unperturbed dimensions have been shown to be the same in both states.[9]

One of the easiest measurable property of a polymer solution is its intrinsic viscosity. The useful information which can be obtained from such measurements has been discussed in Chapter 5. The present chapter extends this study and adds to its to give information, on what we believe, the phenomenon of intramolecular phase separation in block copolymers. At least the results obtained can best be explained by assuming that such a phenomenon is taking place. At this stage it should be pointed out that the aims for embarking on such a detailed study were not completely clear and defined from the outset, but only became apparent as the study progressed. However, the circumstances which initiated the study were present from the beginning. These were that both the thermodynamic (Chapter 4) and hydrodynamic (Chapter 5) evidence indicated that the behaviour of the copolymers in preferential or selective solvents were somewhat different to these in non-selective solvents. Also the intrinsic viscosity $[\eta]$ and Huggins viscosity constant (k_H) seemed to show a different behaviour in cyclohexane as compared to toluene and MIBK as solvent systems. Since $[\eta]$ and k_H should be some measure of the intra- and intermolecular interactions respectively, it was decided that it might prove fruitful to extend the study of either of these parameters further. Because of the inaccuracy and the low sensitivity to environmental changes in the parameter k_H it was decided that the best course of action would be to follow changes in $[\eta]$ with changes in certain parameters. The most obvious and easiest parameter to change was the temperature. Changes in temperature should cause a change in $[\eta]$ and thus the effective hydrodynamic volume of the polymer.

In the first section of this chapter $[\eta]$-temperature studies in cyclohexane and other selective solvents will be discussed. Also some studies in solvent mixtures have been made. In the second section of the chapter glass transition studies on solvent cast films are discussed. Although at first sight these two sections might seem unrelated; it is hoped that from the study the relationship between the two will become evident: essentially both give complimentary evidence of the same phenomenon in different phases.

EVIDENCE OF INTRAMOLECULAR PHASE TRANSITION IN DILUTE SOLUTION

Viscosity Studies

The experimental set up for viscometry has been described in Chapter 5. In this study the intrinsic viscosity $[\eta]$ was measured as a function of temperature. At each particular temperature $[\eta]$ was determined as described in Chapter 5: by plotting simultaneously both the Huggins and Kraemer viscosity relations as a function of concentration, for at least four different concentrations. Extrapolation of these plots to zero concentration gave a value for $[\eta]$.

The results obtained in cyclohexane are shown graphically in Figs. 6.1 and 6.2. The graphs show $[\eta]$ as a function of temperature. Care was taken to fully characterize the curve by obtaining as many points as possible. These plots are unique in that a sharp well defined maximum occurs in all of them. Because of the nature and reproducibility of this point we have defined the temperature at which it occurs as a temperature T_p. Similar studies on the homopolymers, polystyrene and polyisoprene, showed no such anomaly and exhibited normal behaviour when [η] was plotted as a function of temperature. Preliminary results on the copolymers in non-selective solvents, such as toluene and MIBK, also exhibited normal behaviour.

Figure 6.1 shows the plots of [η] versus temperature for the three block copolymers of constant molecular weight (2.5×10^5). The general features of the curves are common to all. They show an initial increase in [η] with temperature followed by a discontinuity in [η] at a particular temperature, which we have called T_p. 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 value of T_p was found to depend on the composition of the copolymer. The difference in temperature between T_p and the point at which the minimum occurs can be seen to also depend on composition: it increases with increasing polystyrene content.

To determine the effect of molecular weight on the position of T_p, copolymers having the same composition but different molecular weight were also studied. Fig. 6.2. shows the plots of two such polymers. The complete data is summarized in Table 6.1.

Fig. 6.1. Plots of intrinsic viscosity versus temperature for copolymers IS6, IS7 and IS8 in cyclohexane.

Fig. 6.2. Plots of intrinsic viscosity versus temperature for copolymers IS9 and IS10 in cyclohexane.

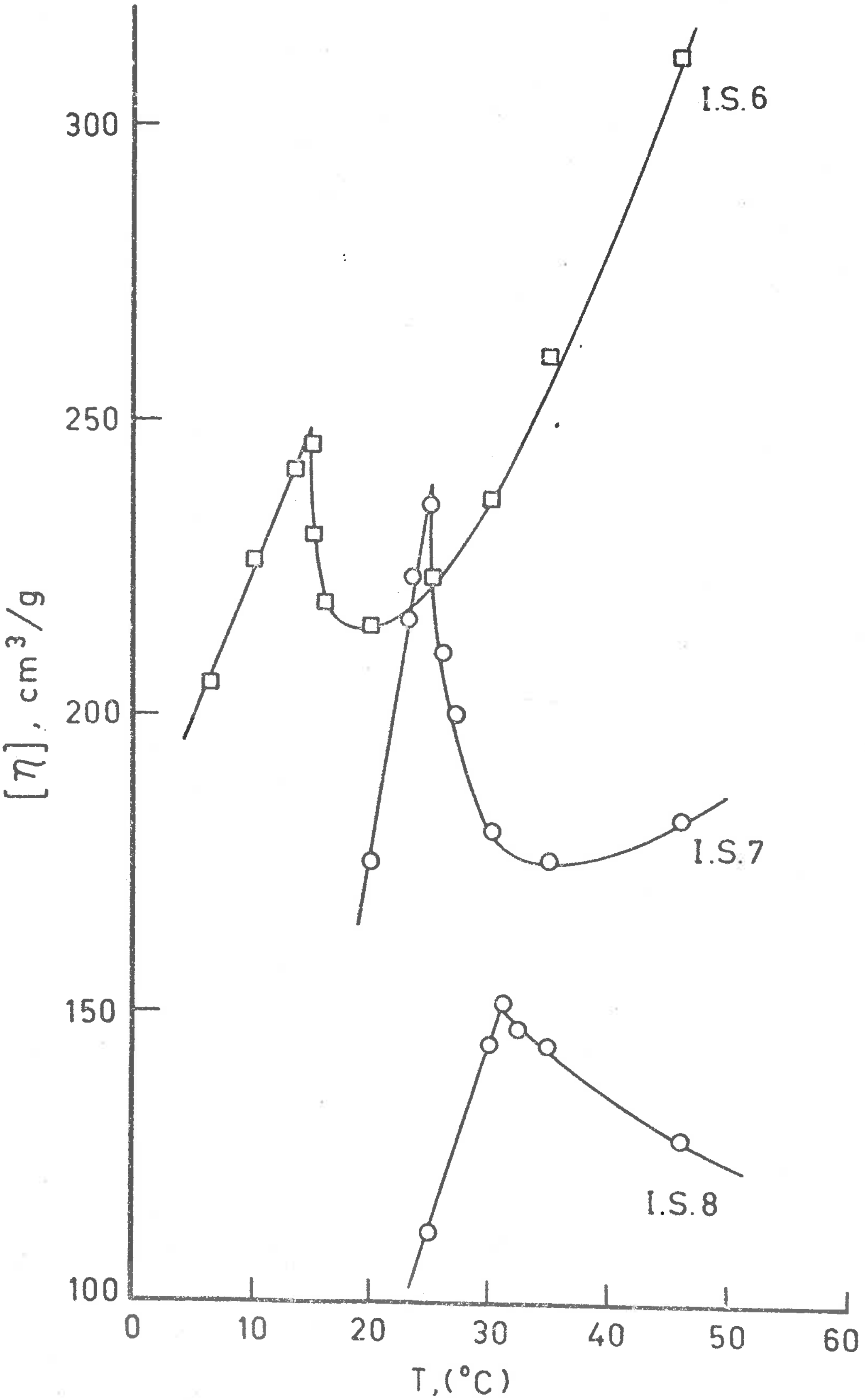


Fig.6.1

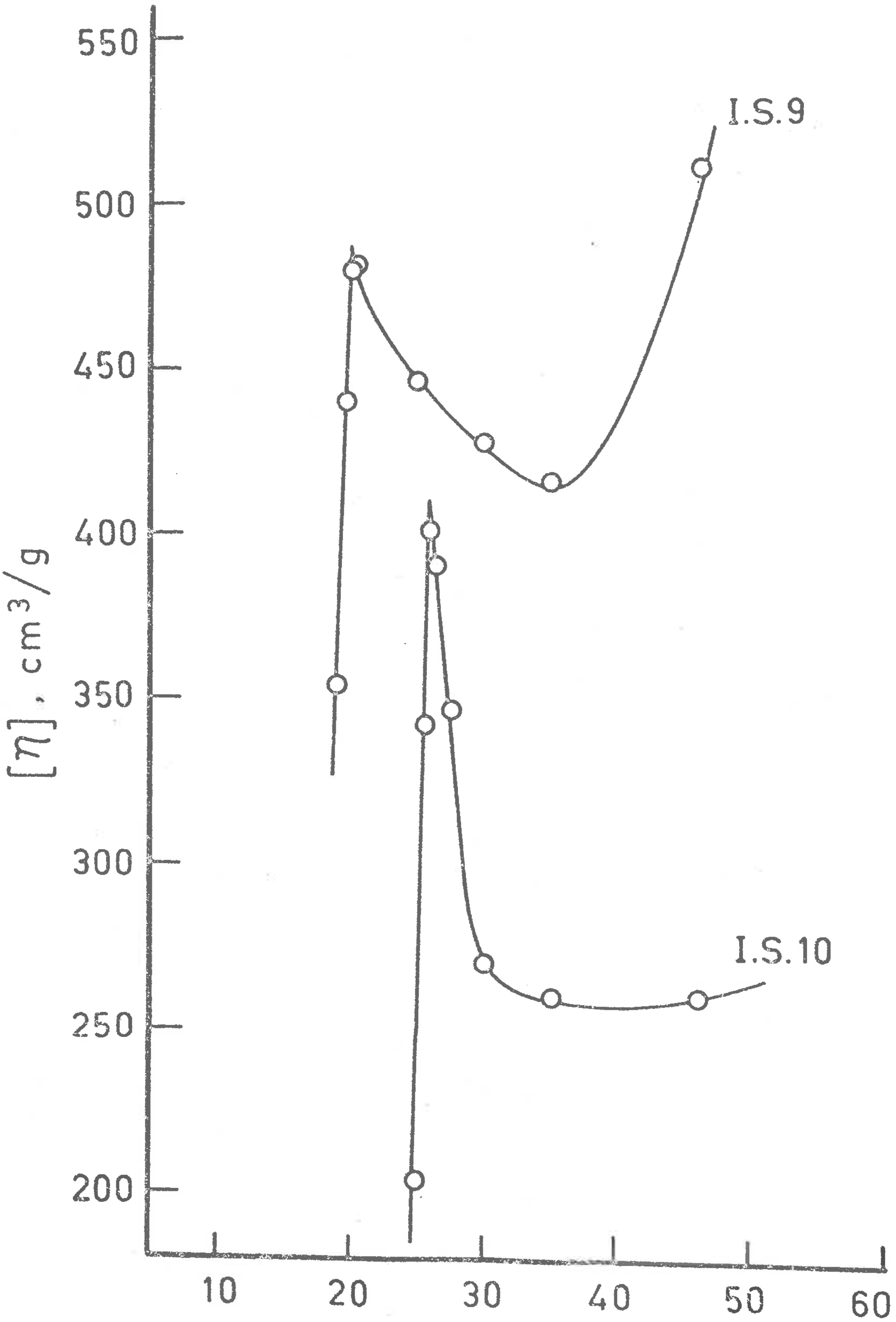

550
500
450
400
350
300
250
200
[η] , cm³/g
10
20
30
40
50
60
T, (°C)
I.S.9
I.S.10

Fig.6.2

Table 6.1. The Transition Temperature T_p for the Copolymers with Various Compositions and Molecular Weight in Cyclohexane

Polymer	Composition Wt.% PS	$10^{-5}\bar{M}n$	T_p (°C)
IS4	52.2	1.04	32
IS6	11.8	2.54	15
IS7	25.5	2.49	24.5
IS8	48.5	2.48	31
IS9	25.1	4.97	20
IS10	49.7	4.97	26

Inspection of the T_p values in Table 6.1 shows that they are a function of the composition of the copolymer as well as the molecular weight. T_p is seen to increase with increasing polystyrene content. Also T_p decreases with increasing molecular weight. These observations has led us to the belief that the peak in the [η] versus T curve is characteristic of the curve. Because of its well defined nature, reproducibility and dependence on certain molecular parameters we have defined the temperature at which it occurs T_p as corresponding to a transition temperature. The most likely transition occurring is an intramolecular phase transition which actually marks the change from a phase separated form to a phase mixed form. Below T_p the copolymer exists in a phase separated form in which the polystyrene and polyisoprene domains have minimum interpenetration. At temperatures sufficiently above T_p the copolymer chain exists in a random configuration in which the chemically different segments of the chain are mixed.

A qualitative explanation for this phenomenon, which explains the characteristics of the $[\eta]$ versus T curve and is consistent with an intramolecular phase transition, can be given in the following manner. Cyclohexane is a good solvent for polyisoprene so that this sequence of the block will exist in a random and expanded configuration in this solvent. On the other hand cyclohexane is a theta solvent for polystyrene at 34°C. As the temperature decreases below this value the polystyrene segment of the chain will be collapsed below unperturbed dimensions. This collapsion will also be aggravated due to the presence of the expanded polyisoprene domain in its vicinity. Under these conditions one might visualize the configuration of the copolymer as consisting of two separate domains, one containing the expanded polyisoprene sequence and the other the collapsed polystyrene sequence of the chain. Interpenetration of these domains is prohibited due to the incompatible nature of the two homopolymers.

As the temperature increases the polystyrene domain swells rapidly, in turn causing increased probability of heterocontacts between the two domains. These heterocontacts cause an increase in the dimension of the molecule as a whole which is reflected in a corresponding increase in viscosity. This gives rise to the first section of the $[\eta]$-T curve. As the expansion of the molecule [illegible] continuous with temperature, eventually a point is reached where the repulsive forces between the two domains are no longer sufficient to keep them from mixing. This point is actually T_p on the curve. As the temperature is increased just above T_p the domains which were previously segregated undergo mixing causing an initial contraction of the molecule. This is reflected by a decrease in viscosity in the second section of the curve. As the temperature is further increased the different segments of the chain become more randomly mixed and at the same time causing expansion of the molecule. This is reflected in the third stage of the $[\eta]$ versus T curve.

Alternatively the phenomenon can be given a qualitative thermodynamic explanation based on models used to discuss intramolecular interactions. 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 phase change, favours the transition from one form to the other. The enthalpies of mixing, at temperatures well below T_p, 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 - giving rise to the first section of the $[\eta]$-T curve. At the transition point, contribution 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 IS6 this difference is about 20% while for IS7 it is doubled. That is the minimum occurs at a lower $[\eta]$ and higher T with increasing concentration of polystyrene.

To study the dependence of T_p on the nature and selectivity of the solvent the study was extended to solvent mixtures and to two other preferential solvents. The selectivity of a given solvent can be changed by adding a co-solvent. In this section of the study a mixed solvent containing cyclohexane and n-heptane was employed. The latter is a good solvent for polyisoprene but a non-solvent for polystyrene. With this system the solvent could be made progressively poorer for the polystyrene sequence in the copolymer. The contention in mind when embarking on this section of the study was based on the following argument. If T_p actually represents a transition temperature as proposed, then a similar effect should be observed when plotting $[\eta]$ as a function of the composition of the solvent (γ).

Plots of $[\eta]$ versus the solvent composition γ, expressed as a percentage of cyclohexane by volume are shown in Figs. 6.3 and 6.4. Figure 6.3 shows the plots for IS10 at two temperatures above and below the T_p found in pure cyclohexane. As can be seen the curve obtained above T_p is similar to that obtained when plotting $[\eta]$ versus T for pure cyclohexane: it exhibits the characteristic peak at 86% cyclohexane, showing that the same phenomenon is occurring. However, the curve determined at a temperature below T_p shows no peak in the region of interest, i.e., the region between 86% cyclohexane and pure cyclohexane. Figure 6.4 shows similar plots for three other block copolymers. All these plots are similar and show the characteristic peak when operating above T_p and the absence of such a peak below T_p. At temperatures below T_p the plots all show a smooth increase of $[\eta]$ with solvent composition up to the value for the pure solvent. The results are summarized in Table 6.2. Here γ_c represents the critical composition of the solvent at which the peak in the curve appears for the given temperature T. The values of T_p in cyclohexane are also listed for reference.

Table 6.2. Critical Composition of the Mixed Solvent (Cyclohexane + n-Heptane) γ_c for the Copolymers at the Stated Temperature

Polymer	T(°C)	% C-HEX γ_c	T_p(°C)
IS6	30	83	15
IS7	30	95	24.5
	20	No peak	-
IS8	20	No peak	31
IS10	35	86	26
	20	No peak	-

Fig. 6.3. Plots of intrinsic viscosity versus solvent composition (cyclohexane + n-heptane) for copolymer IS10 at two temperatures above and below T_p.

Fig. 6.4. Similar plots for three other copolymers.

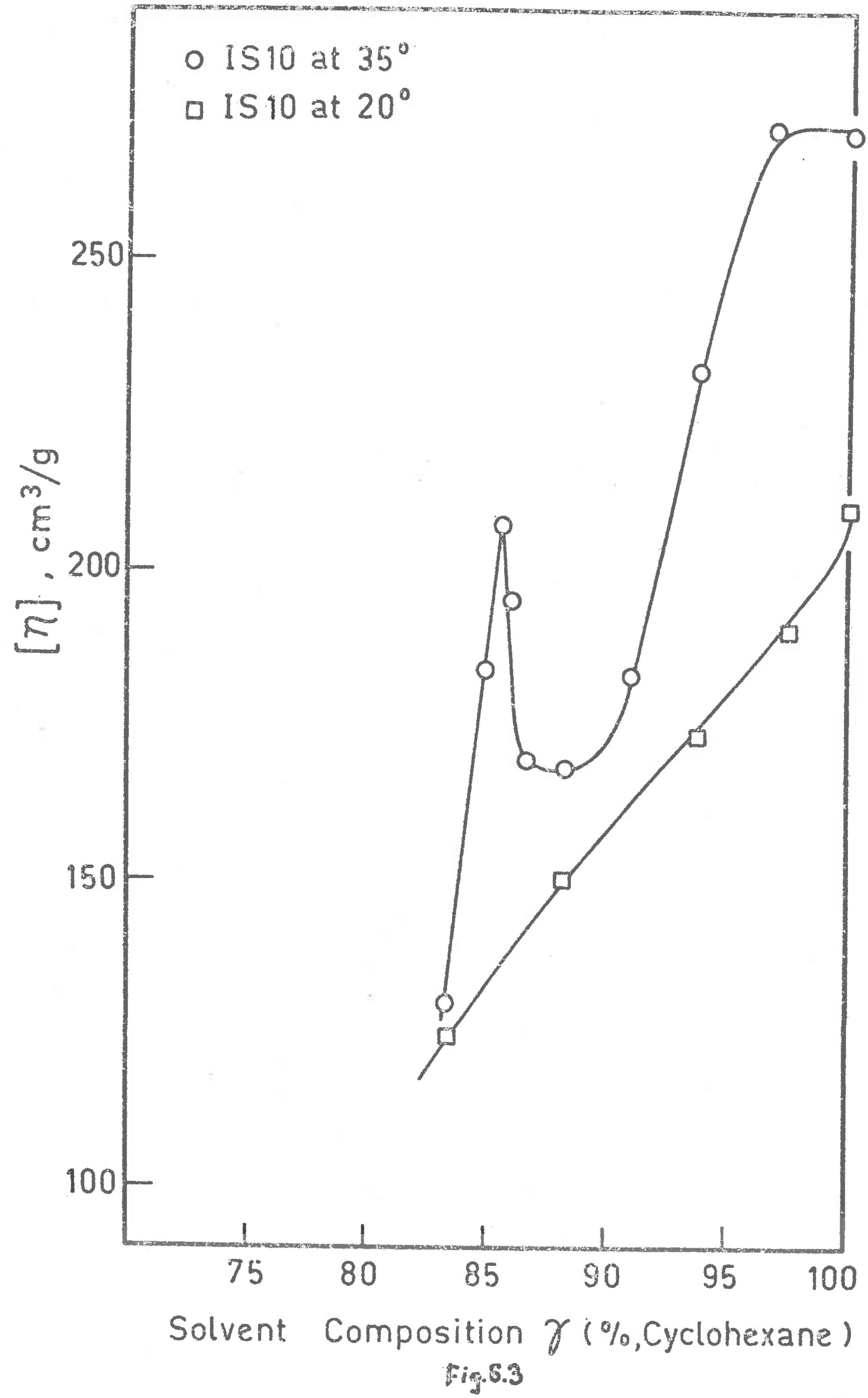
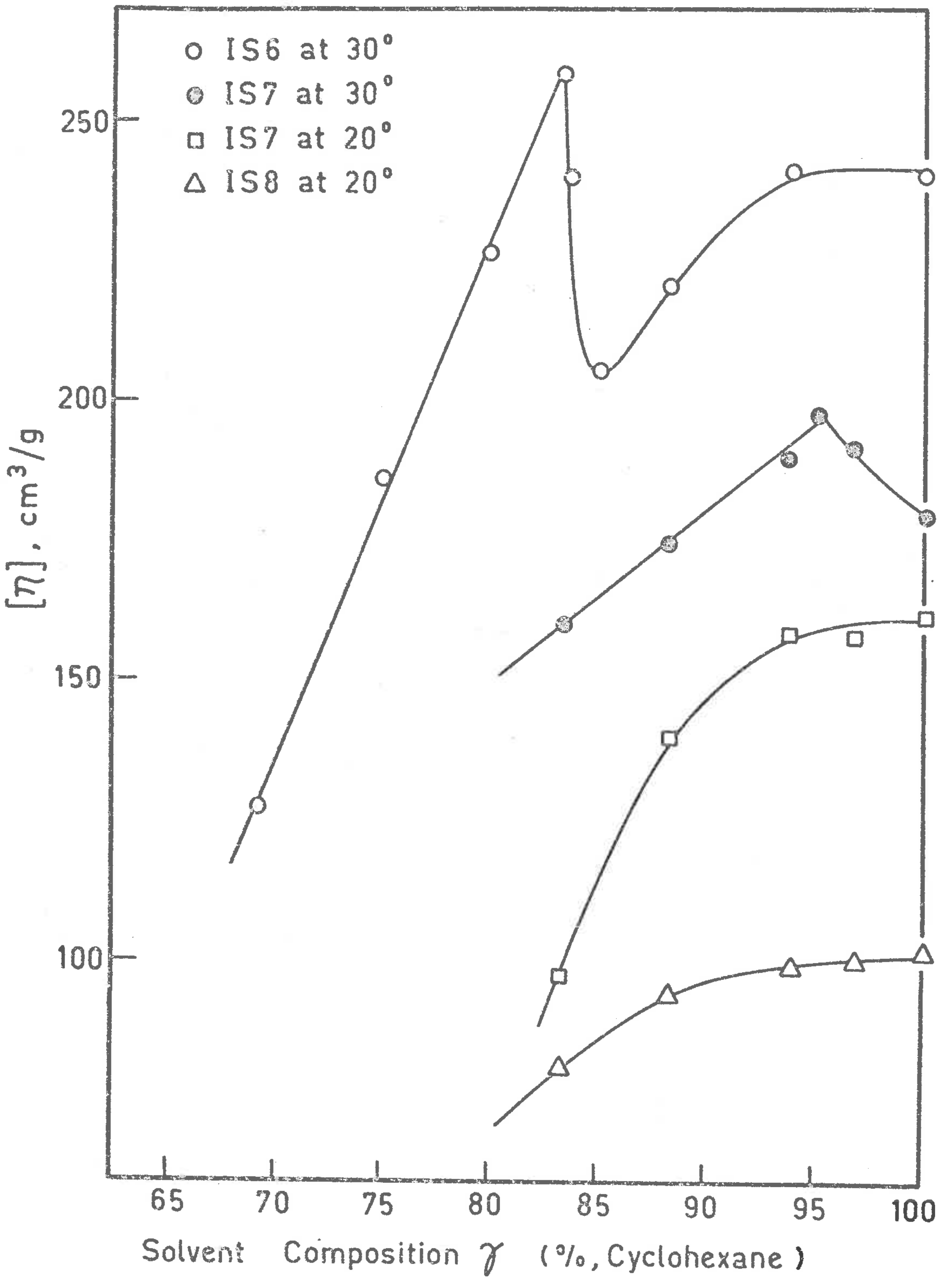

○ IS10 at 35°
□ IS10 at 20°
250
200
150
100
[η] , cm³/g
75
80
85
90
95
100
Solvent Composition γ (%,Cyclohexane)

Fig.6.3



○ IS6 at 30°
● IS7 at 30°
□ IS7 at 20°
△ IS8 at 20°
250
200
150
100
[η], cm³/g
65
70
75
80
85
90
95
100
Solvent Composition γ (%, Cyclohexane)

Fig.6.4

These results confirm the belief that the phenomenon being observed is a configurational transition from phase-mixed to phase-separated of the block copolymer. The plots of $[\eta]$ versus γ at temperatures above T_p show a transition point characterized by γ_c, which represents the composition of the mixed solvent for which T_p is the same as the experimental temperature. This shows that the transition phenomenon 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. A qualitative expalnation of the features of the $[\eta]$ versus solvent composition plots would resemble that given for the $[\eta]$ versus T plots in pure cyclohexane. When operating at a temperature below T_p, because the molecule is already in a phase-separated form in pure cyclohexane, all that can happen with the addition of non-solvent is that $[\eta]$ decreases smoothly from the value in pure cyclohexane due to desolvation. Here the characteristic curve is not observed because no transition phenomenon is occurring.

To investigate further the dependence of T_p on the nature of the solvent, two other solvents having different selectivity towards the polystyrene sequence of the copolymer chain were used. The two solvents chosen were decalin and methyl-cyclohexane (Me-C-HEX). The theta temperature for polystyrene in these solvents is 31°C in decalin and 71°C in methyl-cyclohexane;

i.e., on either side of the value in cyclohexane (34°C). Methyl-cyclohexane is thus the poorest solvent for polystyrene. The plots of [η] versus temperature are shown in Fig. 6.5 for IS6, IS7 and IS8 in methyl-cyclohexane and in Fig. 6.6 for IS7 and IS8 in decalin. These plots show that the typical discontinuity observed in cyclohexane (and the solvent Mixture), resulting in a peak in the curve, is also observed for these two solvents. Comparison of the characteristics of the plots show that they are similar in all three solvents - showing that the phenomenon being observed is general for all preferential solvents. The results are summarized in Table 6.3.

Table 6.3. Comparison of the Configurational Transition Temperature T_p for the Copolymers in Three Solvents

Polymer	T_p (°C) Decalin	 C-HEX	 Me-C-HEX
IS6	-	15	21
IS7	21.5	24.5	34
IS8	30	31	39

Fig. 6.5. Plots of intrinsic viscosity versus temperature for the copolymers in methyl-cyclohexane.

Fig. 6.6. Plots of intrinsic viscosity versus temperature for the copolymers in decalin.

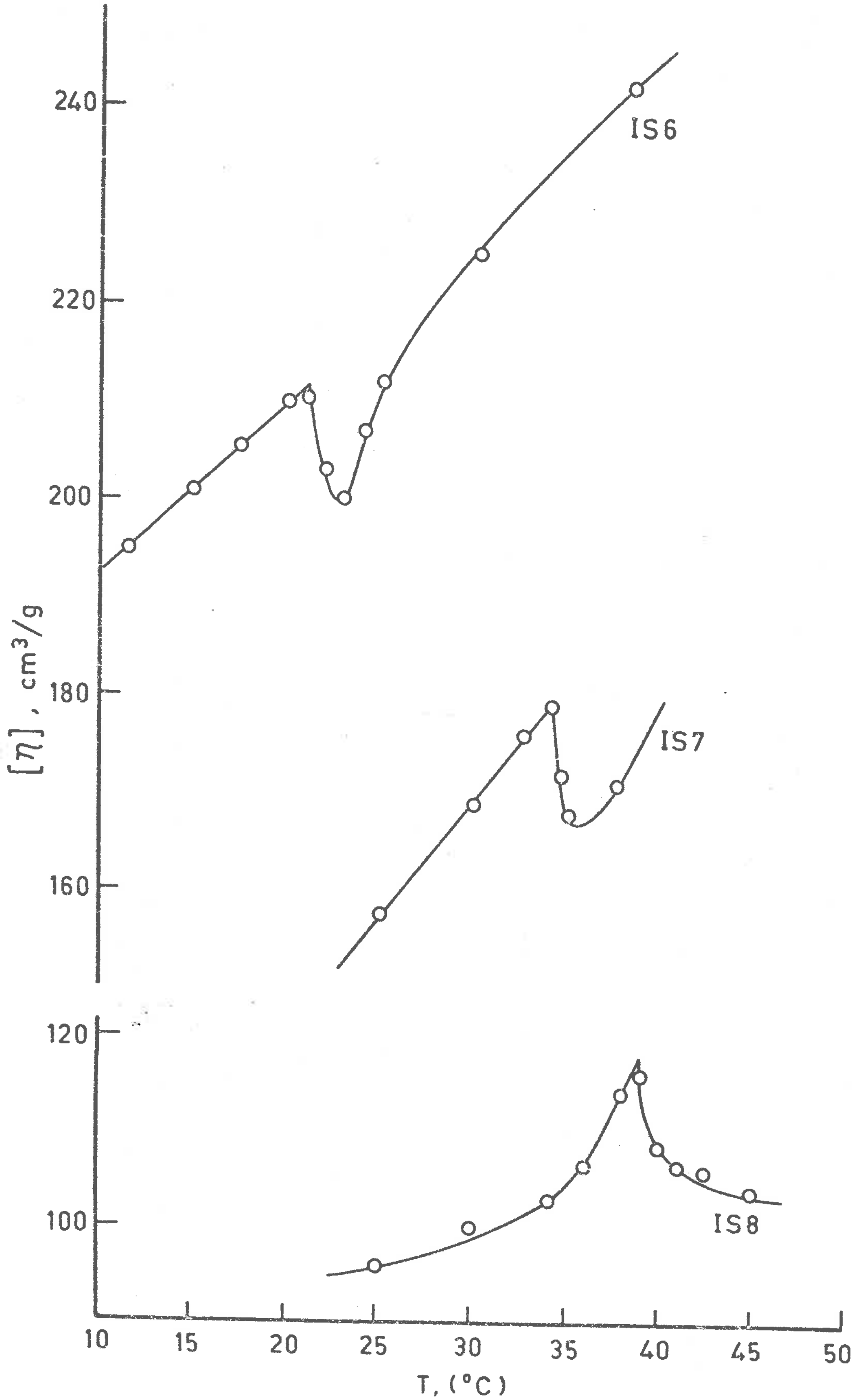

240
220
200
180
160
120
100
[η] , cm³/g
IS6
IS7
IS8
10
15
20
25
30
35
40
45
50
T, (°C)

Fig. 6.5

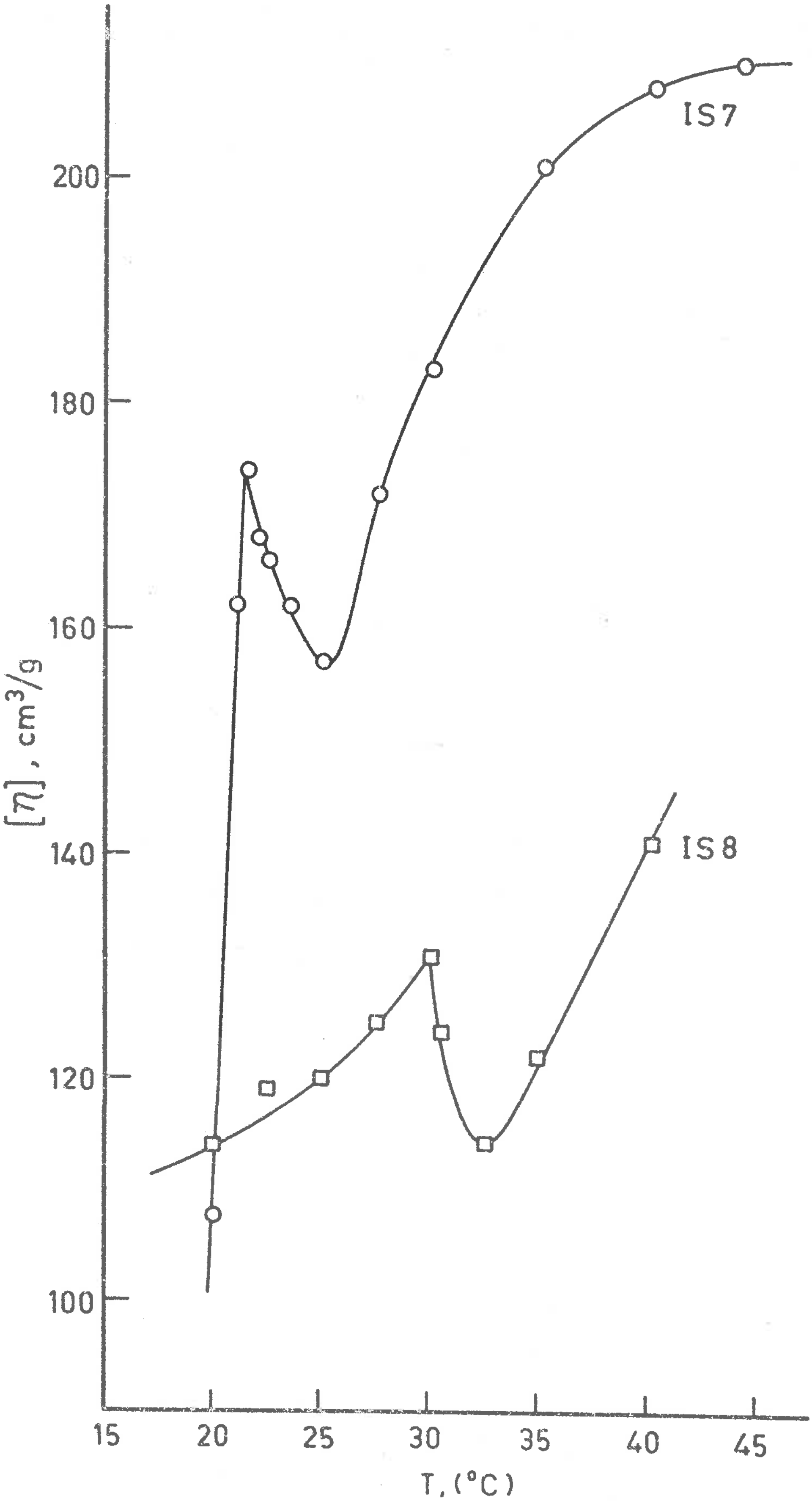


Fig.6.6

Inspection of Table 6.3 shows that T_p exhibits the same trend with composition in all three solvents, i.e., it increases with increasing polystyrene content. Also the values of T_p in a particular solvent increase with increasing theta temperature of the polystyrene in that particular solvent. The value of θ for polystyrene therefore seems to be another factor affecting T_p.

To sum up, the configurational transition temperature T_p has been shown to be a function of molecular weight, composition and the θ temperature of the least soluble homopolymer sequence of the copolymer in the particular solvent. In fact these parameters would be the ones one might expect such a phenomenon as phase separation to be dependent on. As an extension of this work it might be of interest to repeat the above studies with solvents which have a reverse selectivity for the copolymer, i.e., solvents which are selective towards the polystyrene sequence of the chain.

Light Scattering Studies

The intrinsic viscosity against temperature plots must reflect the change in hydrodynamic volume or, at least qualitatively, the changes in the representative parameter of the end-to-end distance of the polymer chain, with respect to temperature. If this is correct then a similar effect should be detected from measurements of radius of gyration (which is also a measure of the effective hydrodynamic volume of the polymer molecule) by light scattering techniques. It must be recalled that light scattering measurements on block copolymers in a single solvent will only yield apparent values. Nevertheless the change in apparent radius of gyration should be useful as a measure of the change in the effective hydrodynamic volume.

The radius of gyration was measured for four of the block copolymers in cyclohexane as a function of the temperature. Plots of the apparent radius of gyration as a function of temperature are shown in Fig. 6.7. The marked similarity of these plots with the corresponding [η] versus temperature plots can be easily seen. More important still is that the discontinuity peak was found at a temperature corresponding to the value of T_p found from the viscosity studies. The viscosity results probably reflect the changes in the hydrodynamic volume, brought about by the phase transition, much more accurately but the light scattering data adds weight to the argument.

Further Evidence From Two-Parameter Solution Theories

In view of the above results it must be accepted that what is being observed is a change in hydrodynamic volume brought about by a change of configuration of the copolymer molecule in solution. It is interesting to speculate on the possible radial distribution of the segments in the copolymer molecule. In the phase-separated form the polystyrene domain

Fig. 6.7. Variation of the apparent radius of gyration with temperature for the copolymers in cyclohexane.

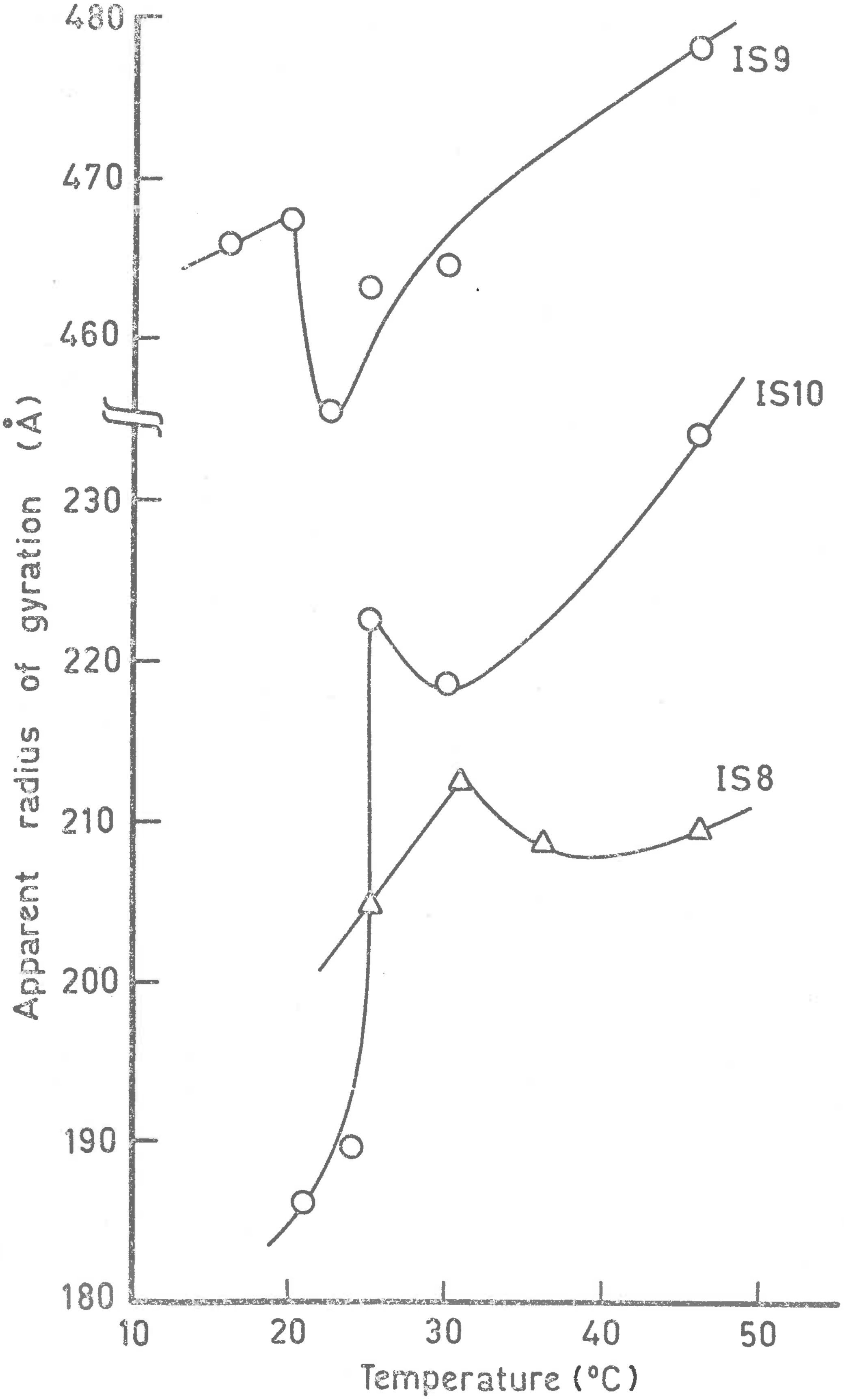

480
470
460
230
220
210
200
190
180
Apparent radius of gyration (Å)
10
20
30
40
50
Temperature (°C)
IS9
IS10
IS8

Fig.6.7

would have a high segment density and the polyisoprene domain a much lower segment density. Due to the incompatibility of these two domains there would exist an interface region of almost zero segment density: corresponding to a void. On phase mixing a pseudo-Gaussian distribution of segments might be expected. This change of segmental distribution might be expected to give rise to some anomalies in results derived from the application of various solution theories which are sensitive to such configurational changes.

The Mark-Houwink-Sakurada equation relating the intrinsic viscosity to molecular weight is given by the equation:

$$[\eta] = KM^a$$

In order to discover just how far the Mark-Houwink-Sakurada equation is obeyed the copolymer series coded 50/50 was examined over a range of temperatures in cyclohexane. The MHS exponent a was approximately 0.8 for all temperatures except at 20°C when the exponent rose to 1.0. The theory of viscosity for various models of homopolymers predicts that the semi-permeable coil should have an exponent in the MHS equation from 0.5 to 0.8 and for a free-draining coil an exponent of 1.0 or greater. It seems plausible, therefore, that the rise in the exponent from about 0.8 to 1.0 at 20°C may be real and perhaps due to the configurational change from a semi-permeable coil, which would be expected for the pseudo-Gaussian segmental distribution at temperatures above T_p, to the separated configuration which may approach the free-draining structure at temperatures below T_p. This is of course a purely speculative and qualitative approach.

To investigate the matter further an attempt was made to estimate the unperturbed dimensions using the current two-parameter theories applicable to flexible homopolymers (as discussed in Chapter 5). Provided the hydrodynamic drainage effect is negligible the short- and long-range interactions have been estimated for homopolymers by using the Stockmayer-Fixman equation

$$[\eta] = K_\theta M^{1/2} + 0.51\Phi_o BM$$

In Chapter 5 it was shown that when used for the copolymers this equation gave good estimates for the unperturbed dimension in both good and poor solvents. The results in cyclohexane, for the copolymer series 50/50, were analysed by this method at various temperatures both above and below T_p. The results obtained are shown in Table 6.4.

Table 6.4. Values of K_θ and B of the Stockmayer-Fixman Relation at Various Temperatures and the Characteristic Ratio C_∞ for the Copolymer Series 50/50 in Cyclohexane

Temp.(°C)	$10^2 K_\theta$	$10^{11}(\bar{r}_o^2/M)^{1/2}$	C_∞	$10^{28}B$
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^+	11.63	757	6.6	

$^+$ Direct measurements in θ solvent

As discussed in Chapter 5 the value of the unperturbed dimension $(\bar{r}_o^2/M)$ obtained for the copolymers in both toluene and MIBK at 30°C, using the Stockmayer-Fixman relation, was in good agreement with the value measured directly in a θ solvent. As also mentioned in Chapter 5 and as can be seen from Table 6.4 the same good agreement of the unperturbed dimension is obtained in cyclohexane at a temperature of 46°C. This temperature is well above the T_p found for this copolymer series. At temperatures near T_p the estimated unperturbed dimension is lower than the value at 46°C by a factor of 10-20%. However, at a temperature well below T_p (i.e. at 20°C) the unperturbed dimension obtained is less than 50% of the value at 46°C. Of course this decrease cannot be due to the temperature alone: it was shown in Chapter 5 that the temperature coefficient of the unperturbed dimension is negligible for these copolymers. The explanation must be that what is being observed is a change in configuration with temperature, as previously postulated.

The results seem to indicate that at 46°C, which is well above T_p for the copolymers, the two-parameter theories of dilute polymer solutions (originally derived for flexible homopolymers assuming a Gaussian distribution of segments) are also applicable to these copolymers in preferential solvents such as cyclohexane. This must be indicative that above T_p the behaviour of the copolymer is that of a random distribution of segments - in accordance with what was postulated from the $[\eta]$-T studies. The drop in the estimated unperturbed dimension with temperature decrease may well indicate a change in distribution which should influence the value of the viscosity constant Φ_o. The sudden drop in the unperturbed dimension at 20°C would therefore indicate an even greater change in distribution. Such a change is consistent with the proposed configurational change from phase-mixed to phase-separated forms on either side of T_p.

The viscosity constant Φ_o is a function of bond lengths, angles and rotational potentials which would not be expected to change greatly over a small temperature range. However, Φ_o is also dependent on the actual distribution of segments which in the phase-separated structure would be quite different from the pseudo-Gaussian distribution expected for the mixed phase configuration. Under these circumstances the calculated long-range interaction parameter B may also be expected to change with change in Φ_o, i.e., change in the distribution of the segments of the copolymer. The value at 46°C is probably the most reliable estimate of this parameter; here contributions from segment-segment contacts of like nature and unlike nature would all be present. Values of B at temperatures near T_p are less reliable and at 20°C the result might be ambiguous, for here contribution from heterocontacts should be reduced to negligible proportions.

In summary, the unique character of the $[\eta]$ versus temperature plots in preferential solvents defines a temperature T_p which we have called a transition temperature. This marks the change from a phase-separated to a phase-mixed form of the copolymer. The dimensions of the copolymers, using viscosity relations derived from two-parameter theories, may be calculated with reasonable accuracy from the viscosity data at temperatures well above T_p in these preferential solvents, but results at temperatures near or below T_p are not so readily interpreted. All the evidence obtained points to a configurational change, the most likely is an intramolecular phase transition.

MORPHOLOGY OF SOLVENT CAST FILMS

Introduction

Glass transition temperatures have been of considerable interest in describing the mechanical behaviour of copolymer systems. Measurements of Tg's offer a probe into the multiphase nature of the polymer in the bulk state. For amorphous random copolymers the situation is understood and well documented.[10,11] Such polymers behave in a similar manner to mixtures of compatible homopolymers[12] in forming a single thermodynamic phase and consequently exhibit a single glass transition. The transition temperatures for such polymers vary with composition and the variations can often be predicted. Wood[13] has reviewed the relation between the glass temperature and composition for a number of copolymers. There is less complete understanding of glass transition phenomena for block copolymers. If the homopolymer segments form a single thermodynamic phase, then the block copolymer should behave like a random copolymer and show a single glass transition, whose temperature should be composition dependent. However, if homopolymer segments form separate phases then the copolymer should exhibit two transitions each characteristic of a given homopolymer phase. Multiple main glass transitions have been reported in the literature.[14-16]

The purpose of this section of the work was to study the transition behaviour of the block copolymers cast from dilute solution. Measurements were done on films carefully cast under controlled conditions at two different temperatures above and below the proposed transition temperature T_p, found from solution viscosity. If there exists any relation between the configuration of the block copolymers in solution and the ultimate configuration assumed in the solid, after the simple process of extracting the solvent, then studying the glass transition behaviour of films cast from solution might prove fruitful.

Experimental

Preparation of films. Polymer films were formed by casting them from 0.5 percent solutions in cyclohexane. One polymer IS8 was also cast from toluene and another IS10 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°C) were formed by placing the glass pans in a vacuum oven, thermostated at 50°C, and then allowing slow evaporation of the solvent. After the films had formed, they were kept under high vacuum for a further 48 hours at 50°C. The films prepared at the low temperature (8°C) 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°C under high vacuum (10^{-5}mm) for a further 24 hours.

Instrumental. The instrument used to detect glass transitions was a Perkin-Elmer differential scanning calorimeter, Type DSC.1B. This instrument consists of sample and reference holders which are insulated from each other but always maintained at the same temperature by closed loop control of the electrical power provided to heaters in each of the holders. In this differential temperature control loop, signals representing the sample and reference temperatures, measured by platinum thermometers permanently embedded in the sample and reference holders, are fed to a circuit which determines whether the reference or sample temperature is greater. The differential temperature amplifier output will then proportionate a small amount of power between the reference and sample heaters in such a way as to correct any temperature difference between them. This is done by increasing the power to one while decreasing the power to the other. A signal proportional to the differential power is also transmitted to the main recorder pen.

The direction of the pen excursion indicates whether the change occurring in the sample is exothermic or endothermic. The operator can raise or lower (using the liquid nitrogen assembly) the average temperature of the sample holders to a desired initial temperature, select one of eight temperature program rates (64°/min to 0.5°/min) and program the desired change in average temperature of the sample holders. Any transition phenomena occuring in the sample is easily noted from the trace of the thermogram made by the dual pen recorder. The rate of heat flow (dq/dt mcal sec^{-1}) is followed as a function of temperature. A comprehensive description of the theory and operating principles of such an instrument have been given by Watson and coworkers[17] and O'Neill.[18]

Calibration of the temperature scale of the DSC instrument was affected 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 20mg weight were cut from the polymer films and encapsulated in aluminium pans. The temperature was lowered to the operating limit (-80°) by cooling with liquid nitrogen in a dewar flask and the sample was scanned at a selected heating rate under a nitrogen atmosphere. The reference holder contained only an empty aluminium pan.

Results

Thermograms showing the rate of heat flow dq/dt versus temperature (°C) for the block copolymer films cast under set conditions of temperature and solvent are shown in Fig. 6.8. The multiple transitions shown refer to the main glass transition temperature Tg, in conforming to the nomenclature proposed by Boyer.[19] The value of Tg was the temperature taken at the beginning of the change in slope for each transition. It has been noted[20] that the value of Tg depends on the heating rate as measured by DSC and can result in some error, depending on how the instrument has been calibrated. This rate dependence is a result of a) a time lag in the sample, b) a time lag in the heat path through the sample, and c) the free volume effect. For precise comparison of Tg data, measurements should be made for at least three different heating rates and the log of Tg's obtained plotted against heating rate. Then extrapolated of this plot to zero rate gives the correct Tg. The data on the copolymers was treated in the above manner and all the Tg's shown in the thermograms represent the corrected Tg's at zero rate. Two samples of each homopolymer, polyisoprene and polystyrene, were also measured to check the operation of the instrument. Tg's for these homopolymers fall within the acceptable range of published values.[21-23] Tg for polyisoprene was found to be -64°C, in good agreement with values for natural rubber or polyisoprene. The measured value for polystyrene was 94°C. The reported Tg's for polystyrene range from 70° to 100°C depending, to some extent, on the method of synthesis, the molecular weight[21] and the method of measurement. The experimental value 94°C therefore seems a reasonable value for the polymer measured.

Table 6.5 lists the glass transition temperatures determined for the block copolymers. Tg_1 is the value assigned to polyisoprene, Tg_2 the value for polystyrene and Tg the glass transition temperature of the third or intermediate species which appears at temperatures between the other two. The polymer IS8 was cast from toluene and IS10 from a mixed solvent (84:16 by volumes of cyclohexane + n-heptane) as well as from pure cyclohexane. In each case, the film cast at the higher temperature shows Tg_1 and Tg only; the films cast from the lower temperature exhibit Tg_1 and Tg_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 Tg_1 and Tg_2 are observed.

Fig. 6.8. (DSC) Thermograms of the block copolymer films cast from solution under the specified conditions: The glass transition temperatures (Tg) observed are shown by the arrows.

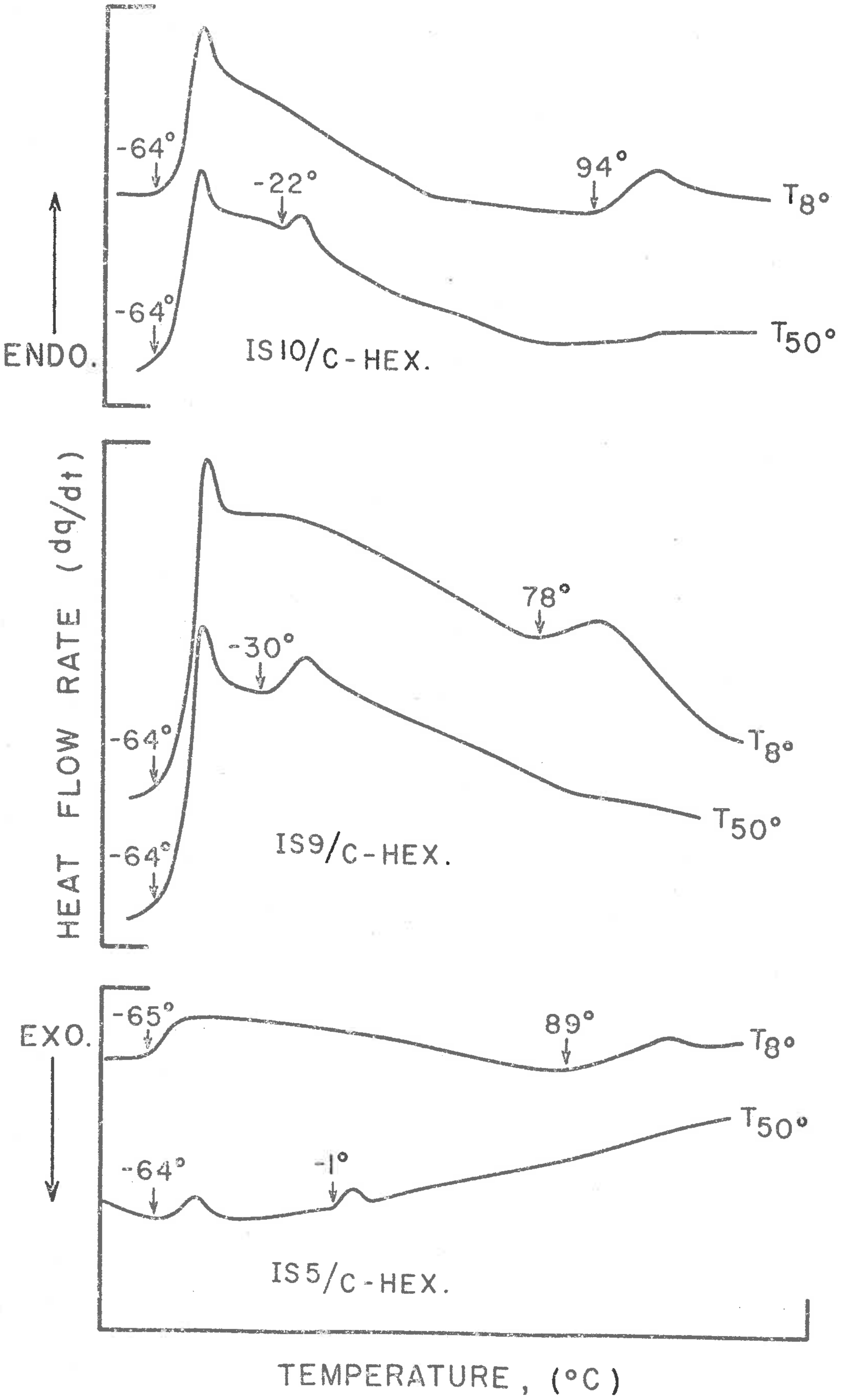
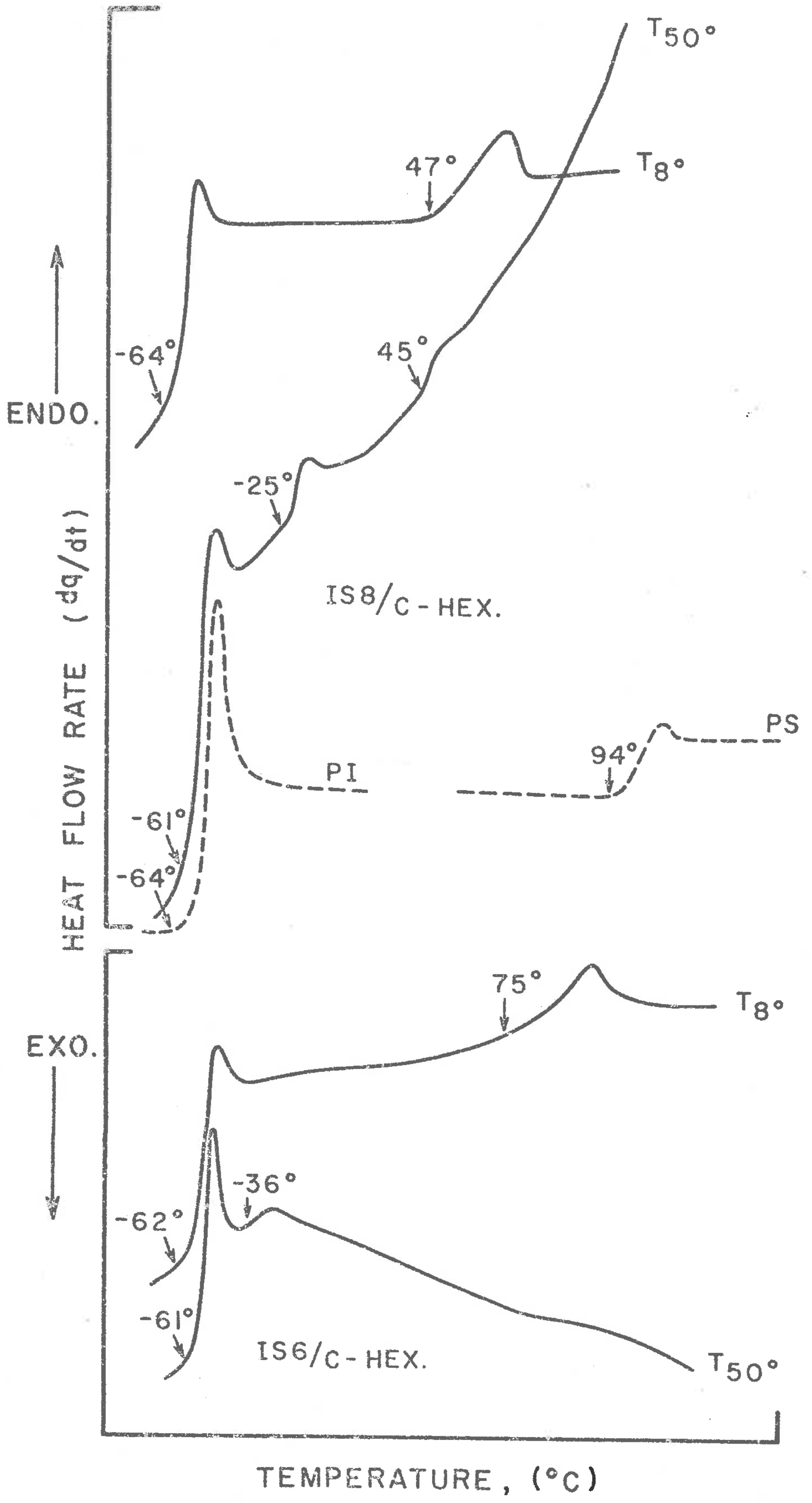

ENDO.
EXO.
HEAT FLOW RATE (dq/dt)
-64°
-22°
94°
T8°
-64°
T50°
IS10/C-HEX.
78°
-30°
-64°
T8°
-64°
T50°
IS9/C-HEX.
-65°
89°
T8°
T50°
-64°
-1°
IS5/C-HEX.
TEMPERATURE, (°C)

Fig.6.8


T50°
T8°
47°
-64°
45°
ENDO.
-25°
HEAT FLOW RATE (dq/dt)
IS8/C-HEX.
PS
94°
PI
-61°
-64°
75°
T8°
EXO.
-36°
-62°
-61°
IS6/C-HEX.
T50°
TEMPERATURE, (°C)

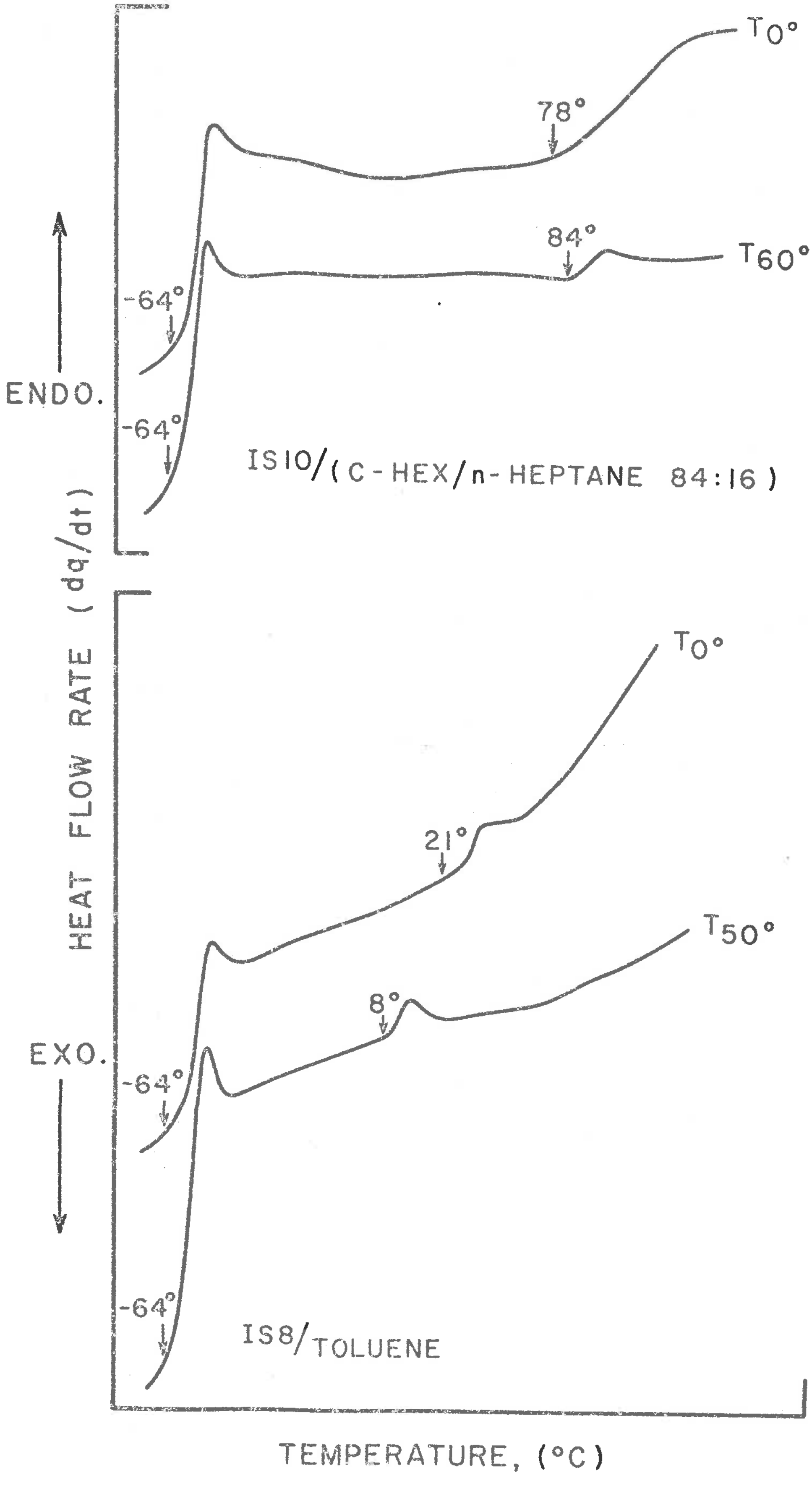

T0°
78°
84°
T60°
-64°
-64°
ENDO.
IS10/(C-HEX/n-HEPTANE 84:16)
HEAT FLOW RATE (dq/dt)
T0°
21°
T50°
8°
EXO.
-64°
-64°
IS8/TOLUENE
TEMPERATURE, (°C)

Table 6.5. Glass Transition Temperatures of the Copolymers Cast from Cyclohexane at 8° and 50°C

Polymer	Composition Wt.% PS	Casting Temp.(°C)	Tg_1 (°C)	Tg (°C)	Tg_2 (°C)
IS5	78.2	8	-65		89
		50	-64	-1	
IS6	11.8	8	-62		75
		50	-61	-36	
IS7	25.5	8	-63		76
		50	-64	-29	
IS8	48.5	8	-63		47
		50	-61	-25	
IS9	25.1	8	-64		78
		50	-64	-30	
IS10	49.7	8	-64		
		50	-64	-22	94
IS8 +	48.5	0	-64	21	
		50	-64	8	
IS10 ✚	49.7	0	-64		78
		60	-64		84

\+ Cast from toluene

✚ Cast from a mixture of cyclohexane + n-heptane 84:16 by volumes.

Discussion

The most significant point emerging from these results is the appearance of a new species characterised by Tg and the absence of Tg_2 in all films cast from the higher temperatures in cyclohexane; this contrasts with the films cast at the lower temperature in which only Tg_1 and Tg_2 appear. The simplest conclusion we can draw is that, at temperatures of casting well below the configurational transition temperature Tp derived from $[\eta]$ versus T plots in the same solvent, there exists phase separation in which polystyrene and polyisoprene are confined to separate domains. On the other hand, the polystyrene domain has disappeared in films cast at temperatures well above Tp and instead, a mixed phase has formed in its place. The continued existence of polyisoprene means that not all of the polyisoprene 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.[13] It was found that a relation having the form:

$$Tg = K(Tg_2 - Tg)\frac{w_2}{1 - w_2} + Tg_1 \qquad 6.1$$

is generally obeyed, where Tg_1 and Tg_2 are the glass transition temperatures of the two homopolymers and Tg the glass temperature of the mixed phase. Here, w_2 is the weight fraction of polymer 2. A plot of $(Tg_2 - T_g)w_2/(1-w_2)$ versus Tg 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 polyisoprene (Tg_1) and polystyrene (Tg_2) then the relation is obeyed to the extent that the plot is linear (Fig.6.9) but in this case, extrapolation to $w_2 = 0$ does not yield the expected glass transition temperature of polyisoprene. However, as has already been observed, the polyisoprene is still present in sufficient quantity to show a glass temperature Tg_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 Tg_1 calculated by application of equation 6.1. In plotting Fig. 6.9 the value of Tg_2 used to calculate $(Tg_2 - Tg)$ was assumed to be that found experimentally for the homopolymer, i.e., 94°.

It seems clear that, at temperatures above Tp in cyclohexane, the two sequences in the block copolymer are mixed forming a single phase. In the process of casting the film, some polyisoprene, which is present in excess in all except IS5,

Fig. 6.9. Dependence of the glass transition temperature (Tg) upon composition of the copolymer.

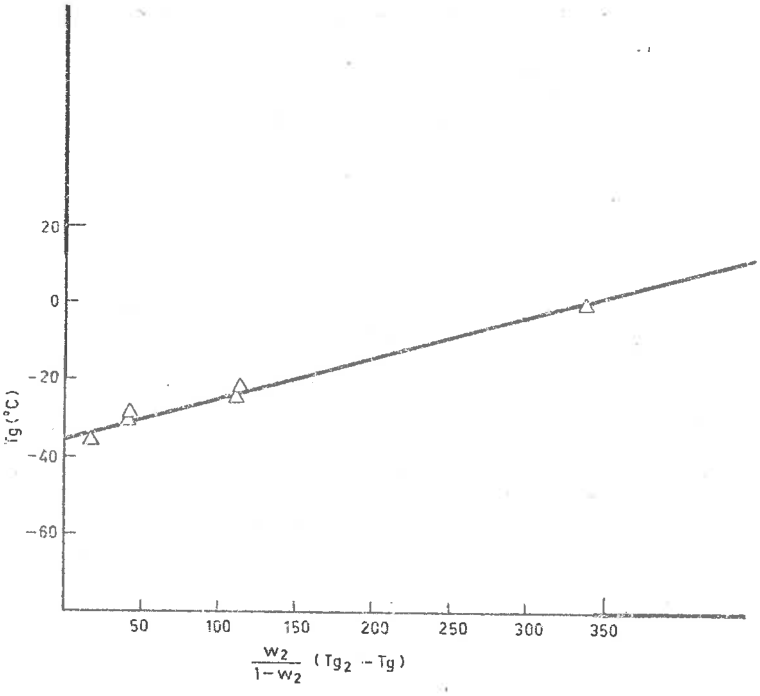


Fig.69

remains in the very concentrated solution which is associated with the gelled mixed phase. In IS5 the typical sharp endotherm observed with thermograms of polyisoprene, which is due to the lag in the equilibrium free volume with scanning rate,[24] 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 polyisoprene transitions were always sharper than the polystyrene. If we can specualte that the sharpness is in some way related to the purity of the phase then we may assume that mixing of the polyisoprene 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 percent by weight or equimolar composition, there must surely be the greatest inter-mixing, which would account for the unusually low value for Tg_2 found for IS8. On the basis of this argument and evidence presented earlier from the viscosity studies, 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 Tg's for this particular solvent shown in Table 6.5 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 Tp 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 Tp, only the two transitions Tg_1 and Tg_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 polyisoprene.

The data presented provide substantial confirmatory evidence for the original contention that the transition temperature Tp observed in plots of $[\eta]$ versus T in cyclohexane and similar liquids which are good solvents for one polymer sequence but poor for the other, marks a configurational 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 under strictly controlled conditions.

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