An Investigation of the Dilute Solution Properties of the Block Copolymers of Styrene and Methyl Methacrylate

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SUMMARY.

An Investigation of the Dilute Solution Properties of the Block Copolymers of Styrene and Methyl Methacrylate.

The dilute solution properties of four well characterized, homogeneous block copolymer samples of styrene and methyl methacrylate were examined using the techniques of turbidimetric titration, viscosity, osmometry and light-scattering. The block copolymer samples had an increasing molecular weight corresponding to an increase in polystyrene content from 48 to 85% styrene by weight. The turbidimetric titration studies showed each sample to be uncontaminated by homopolymer and to possess a precipitation point somewhere between each homopolymer. In methyl ethyl ketone the four block copolymer samples were found to fractionate as some function of their overall molecular weight.

Viscosity measurements on each sample were carried out in toluene, methyl ethyl ketone, carbon tetrachloride and nitroethane. The measurements in toluene and methyl ethyl ketone showed a more expanded configuration for the block copolymers than would be expected from the averaged behaviour of the pure homopolymers. The determination of the Huggins viscosity slope constant gave a qualitative measure of the intermolecular interactions present in solution. The results indicated a greater repulsion between the block copolymer molecules than between polystyrene-polystyrene, polymethyl methacrylate-polymethyl methacrylate or polystyrene-polymethyl methacrylate molecules.

The osmotic pressure measurements in toluene showed a decrease in the second virial coefficient A_2, with increasing molecular weight of the block copolymer samples. The second virial coefficient A_2 was determined at several temperatures for one block copolymer sample and the Flory or θ-temperature obtained from the extrapolation of these varies to $A_2 = 0$. The entropy of dilution parameter ψ_1 and the heat of dilution parameter κ_1 were also calculated and found to be numerically greater than the corresponding homopolymer parameters. The Flory-Huggins interaction constant χ was calculated and found to be 0.445.

The light-scattering measurements were carried out in toluene. The second virial coefficient A_2 was found to be slightly lower than the corresponding values determined from osmometry. However, the trend of A_2 with molecular weight was in the same direction. The A_2 values for the block copolymer samples were found to be slightly higher than those of either homopolymer of similar molecular weight, suggesting a more expanded configuration for the block copolymers. The radius of gyration and the root mean square end-to-end distance were calculated for each block

copolymer sample and the values found to be larger than those calculated for homopolymers of similar molecular weight. The Flory universal parameter Φ was also calculated for the block copolymer samples and found to be 2.0×10^{21}.

The extension ratios and the configurational parameters $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\bar{r}_0^{\,2}/M)^{\frac{1}{2}}$ were also determined. The extension ratio α was found to increase with increasing molecular weight of the block copolymer samples. The unperturbed displacement length parameter $(\bar{r}_0^{\,2}/M)^{\frac{1}{2}}$ was larger for each block copolymer sample than the values for each homopolymer. The values of $(\bar{r}_0^{\,2}/M)^{\frac{1}{2}}$ showed no marked variation with block copolymer composition. The parameter $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ was almost constant and independent of block copolymer composition in toluene and in carbon tetrachloride. In methyl ethyl ketone the values of $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ did change gradually from the value for pure polymethyl methacrylate to that for polystyrene.

In many respects the dilute solution properties of the block copolymer samples were similar to the known behaviour of random copolymers.

To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma in any University, except where due reference is made in the text.

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CHAPTER I.

Introduction.

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In recent years, much work has been devoted to the synthesis of block copolymers. The various methods of preparation and attempts to examine the properties of these polymers have been reviewed several times during this period.[1-5] The need for a comprehensive coverage of the preparative work and techniques of characterization of block and graft copolymers has at last been met by Ceresa,[6] whose recent book includes the synthesis of some 1,400 block copolymers. However, even though this is a major contribution to the ever growing field of block and graft copolymer studies, there is still a dearth of information on the solution properties of copolymers with "long-ranged periodicities".[7,8]

Burnett and co-workers[9] have recently investigated the dilute solution properties of the block copolymers of styrene and methyl methacrylate. This recent study is the most comprehensive since the preliminary work of Woodward and Smets.[10] Several theoretical treatments predicting the dilute solution behaviour of block copolymers have appeared recently in the literature.[11-13] However, a more detailed study must be made on the dilute solution properties of block copolymers in order to test the theories which have been put forward.

The block copolymers of styrene and methyl methacrylate were chosen for this study because a) the solution behaviour of the two homopolymers has been well characterized in a variety of solvents, b) mixtures of both homopolymers have been studied[14,15] and c) the method of preparation governed the choice of the monomers used.

For a precise study of solution behaviour of block copolymers, well defined samples of polymer are required. These samples must be completely characterized as regards their composition and molecular weight. Solution behaviour of a polymer can be governed to a large extent by the degree of heterogeneity of the sample under investigation. It is therefore essential that the method of preparation yields a) polymer of narrow molecular weight distribution, or b) sufficient material to enable fractionation to be carried out.

The early syntheses of block copolymers did not produce high yields and in many cases the material produced was extremely heterogeneous, both in composition and molecular weight. Since the introduction of the synthesis of "living-polystyrene" by Szwarc and co-workers,[16-20] the possibility of producing block copolymers of predetermined molecular weight and composition has been greatly increased. This method of synthesis has been shown[16] to produce material virtually uncontaminated by homopolymer and furthermore under careful experimental conditions material of narrow molecular weight distribution is formed.[21-25] The preparation of the block copolymers investigated in this work was carried out using a modification of one of the above techniques.[21]

By definition,[6] a block copolymer results, when two homopolymers are linked together such that a macromolecule with two or more uninterrupted sequences of the homopolymeric species is formed. If A denotes the segment of one sequence and B denotes the segment of the other, then a linear block copolymer can be represented as in (1-I).

— AAAAAAAAAAAABBBBBBBBBB — (1-I)

Variations on this schematic structure can lead to a block copolymer of the 'sandwich' type as shown in (2-I).

— AAAAAAAABBBBB·····BBBBBAAAAAAAA — (2-I)

It is essential in the study of the solution behaviour of a particular block copolymer that the arrangement of specific sequences within the chain be completely known.

The linear block copolymers employed in this study were of the 'sandwich' type as represented schematically in (2-I). The reason for the use of the 'sandwich' type structure is due to the method of preparation, which will be discussed fully in Chapter III.

It was mentioned earlier that several authors[11-13] have attempted to predict some of the solution and fractionation behaviour of block copolymers. Lautout-Magat[13] has applied the Guggenheim[26-27] semi-chemical method to the study of the thermodynamic properties of block copolymers. The findings of this author[13] suggest that the approximations obtained by the Guggenheim method are no better than the more simple calculation based on the mean value of the solubility indexes of the constituent homopolymers. Kilb and Bueche[11] have used the Flory-Huggins[28-31] 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. These authors[11] suggest that the fractionation of block copolymers can not be a function of the overall molecular weight of the polymer. Evidence to support the theories of Kilb and Bueche[11] have been reported by several authors.[10,32] However, from an examination of the evidence presented, all that can be said is that the solubility of a block copolymer lies somewhere between that of the corresponding parent homopolymers. On the other hand, the recent work of Schlick and Levy[33] on the block copolymers of styrene and isoprene seems to contradict the theoretical calculations of Kilb and Bueche.[11] Schlick and Levy[33] prepared block copolymers of uniform molecular weight with variable distribution of sequences along the polymeric chain. Turbidimetric titration studies by these authors[33] showed that as the size of the blocks decreased, the solubility increased, even though the overall molecular weight of the block copolymer remained constant, in contrast to the behaviour predicted by Kilb and Bueche.[11]

Quite obviously a more detailed investigation is required before any definite conclusions can be reached. Furthermore, the nature of the monomers employed in the synthesis of block copolymers and the type of solvent employed in the study of their solution properties may affect the results obtained. A serious criticism of work in the field of block and graft copolymers is that very few workers carefully examine the nature of their 'end-product'. If progress is to be made in this field, then more emphasis should be placed on a study of solution behaviour, using well defined polymers, rather than the methods of synthesis.

If a detailed investigation of the thermodynamic behaviour of a dilute polymer solution is to be carried out then it is essential[28] that three main factors be determined: (1) the molecular weight, (2) the thermodynamic interaction parameters ψ_1 and κ_1, or ψ_1 and θ, which characterize the segment-solvent interaction, and (3) the configuration, or 'size' of the molecules in solution. The molecular weight of a block copolymer may be determined from either osmotic pressure or light-scattering studies. The entropy of dilution ψ_1 , the heat of dilution κ_1 and the Flory temperature θ , can be determined from detailed osmotic pressure studies over a range of temperatures. The configuration, or 'size' of the block copolymer molecules in solution may be determined by suitable measurements of the limiting viscosity number or more directly from light-scattering measurements. Thus for a detailed investigation on dilute solution behaviour it is essential that viscosity, osmometry and light-scattering studies be carried out on the block copolymer samples. In order to carry out an efficient and rapid fractionation on the block copolymer samples, the method of turbidimetric titration is by far the better technique.

The application of all four methods, osmometry, viscosity, light-scattering and turbidimetric titration, to the investigation of the dilute solution behaviour of block copolymers is discussed in the next chapter. It should be emphasized, however, that care should be taken when attempting to interpret the data obtained for block copolymers using the above techniques. Although certain thermodynamic parameters, which characterize intermolecular and intra molecular interaction, may be valid for homopolymers, the specific application of these quantities to block copolymers is at present doubtful.[9]

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CHAPTER II.

Theory of the Techniques Employed.

1. Approach to the Problem.

2. Turbidimetric Titrations.
   - a) Introduction.
   - b) Some theoretical aspects of turbidimetric titrations.
   - c) The relationship between turbidity and the concentration of the polymer suspension.
   - d) The relationship between solubility, molecular weight and concentration.
   - e) Calculation of molecular weight distribution functions from the turbidimetric titration data.
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3. Viscosity.
   - a) Introduction.
   - b) The significance of the limiting viscosity number and the Huggins constant.
   - c) The behaviour of the Huggins constant in mixed polymer systems.
   - d) Some aspects of the Flory-Fox treatment of viscosity.

1. Approach to the Problem.

Until recently[65] interest in block copolymers has centred around the problem of synthesis. Most of the early syntheses of block copolymers gave poor yields and produced material, polydisperse in molecular weight and composition. For this reason very little work has been done with the object of obtaining exact solution data. The isolation of the block from homopolymer requires a rapid method for analytical examination of the polymer. With this in mind, and with the idea of testing recent theories[31] on block copolymer fractionation, the turbidimetric titration technique was developed.

One of the objectives of a study of dilute solution properties must be to discover whether the experimental data can be fitted into the existing theories. All that can be done is to find suitable approximations to fit the data with a reasonable degree of accuracy, and where a particular model is used, to show that the behaviour is similar to that found experimentally.

In a study of this kind one must recognize intuitively that in a block copolymer, in which long sequences of two distinct homopolymers are linked together, the solution behaviour will be different from either a mechanical mixture or a random copolymer. In a mechanical mixture of homopolymers, intermolecular interaction between unlike segments will be reduced considerably on dilution. However, for a random copolymer the number of unlike polymer-polymer contacts will be large. It must therefore be expected that these differences will enable a solution of a block copolymer to be distinguished from a random copolymer or a simple mixture of equal composition.

2. Turbidimetric Titrations.

a) Introduction.

Since the introduction of the technique of turbidimetric titration by Morey and Tamblyn,[1] this method of analysis of polymer solutions has been widely used.[2-14] As a means of finding molecular weight distribution it has advantages over fraction techniques. The quantity of material necessary to carry out an analysis is small, and with careful standardization of the experimental conditions, reproducible results can be obtained easily and quickly.

The technique of turbidimetric titration has proved useful in the analysis of block and graft copolymers.[2,4-6] It is possible to detect small traces of homopolymer present as impurity with the block copolymer. The method is therefore valuable as a critical analytical check for the synthesis of block copolymers and can also provide useful information on the solution behaviour of such block copolymers.

b) Some theoretical aspects of turbidimetric titrations.

The development of the theory of turbidimetric titration was initiated by Oth and co-workers, who have applied the method with partial success to the analysis of polyvinyl chloride,[13] cellulose acetate[12] and nitrocellulose.[11] The method is in principle very simple;

however, in practice it is only with difficulty that the method can be applied quantitively.

The method involves the slow and continuous addition of a precipitant (non-solvent) to a dilute (ca.10 mg/litre) well-stirred solution of the polymer. The polymer is dissolved in a suitable solvent that is completely miscible with the precipitant and should have approximately the same refractive index. As the volume of precipitant is increased, polymer is precipitated from solution in the form of a gel strongly swollen by solvent, and remains in suspension. The turbidity at any stage during the titration is readily measured photometrically. This can be done by an examination of the loss in transmission, or an increase in scattering of light at some fixed angle. A combination of the measured scattered light and transmission is sometimes used.[13] It is usual to relate the measured turbidity to the amount of precipitant added γ, where

$$\gamma = \frac{\text{volume of precipitant}}{\text{volume of solvent + volume of precipitant}} \qquad (1\text{-II})$$

The turbidity, after correction for dilution of the polymer precipitate, is taken as a direct measure of the amount of polymer in suspension at any instant. It is therefore necessary to find a relationship between γ and the measured turbidity for a given polymeric species.

Furthermore, the value of γ, at which a given molecular species precipitates, is some function of its molecular weight M and the concentration C at the precipitation point. It has been shown[18] that this relationship is of the form,

$$\gamma = K \log C + f(M) \qquad (2\text{-II})$$

where K is a constant, characteristic of a given polymer solvent precipitant system, and f(M) a function of the molecular weight for the same polymer.

In order that the turbidimetric titration curve can be interpreted quantitatively, it is necessary to establish the relationships between the measured turbidity and the mass of polymer suspension m, and the relationship between the point of precipitation γ with the molecular weight M, and its concentration C at the precipitation point. Having established these relationships, it will be shown that it is possible to construct the molecular weight distribution curve of mass (m) = F(M). In order to establish these relationships it is necessary to carry out a series of turbidimetric titrations on polymers of known molecular weight and narrow distribution. The molecular weights of these samples must cover a reasonable range of values, and the titrations must also be conducted on each polymer species at several different concentrations. The validity of equation (2-II) can then be tested.

As mentioned above, the experimental application of turbidimetric titrations often proves to be difficult, and because of this, quantitative interpretation of the results is often of doubtful value. There are several factors which limit the general application of the turbidimetric titration technique, and attention has been drawn to the following points by Morey and Tamblyn.[1]

i) There will be a refractive index change for the solvent/precipitant medium unless both components have the same, or very nearly the same, refractive index. If there is a large change in refractive index, then a Rayleigh refractive index correction must be applied to the measured turbidities.

ii) The polymer must have a different refractive index from that of the solvent-precipitant medium.

iii) The scattering power of the polymer suspension could be some function of molecular weight due to a dependence of particle swelling on molecular weight.

iv) The effect of coagulation, aging or agglomeration of the precipitate will cause variations in the turbidity unrelated to the quantity of precipitate.

It is possible to control points i) and ii) by a careful choice of polymer and solvent-precipitant system. The degree of swelling of a polymer in a given solvent-precipitant mixture appears to be independent of its molecular weight, according to the work of Boyer.[22] The work of Schulz[23] and also Breitenbach and Frank[24] gives support to this claim. However, swelling may be influenced to a certain degree by variations in the solvent-precipitant composition. If this effect was prominent then the relationship between measured turbidity and the mass of the polymer suspension would be in error.

Perhaps the most serious defect in the technique of turbidimetric titration is the fact that in many systems the suspended polymer is not stable, and aggregation takes place. This is a serious defect in the system polystyrene-benzene-methanol, as has been shown recently by Hastings, Ovenall and Peaker.[25,26] Experimental results reported in Chapter V for polystyrene precipitated from butanone by the careful addition of isopropanol show that aggregation is not a problem in this system. However, a change in particle size was observed during the titration. Correction to the measured turbidity must be made in order that the data may receive quantitative interpretation. It is only possible to use the Rayleigh-Gans-Debye theory on turbidity measurements for determining the mass of the precipitated polymer, when the particles remain small. In Chapter V is has been shown that it is possible to obtain a quantitative relationship between the corrected turbidity and mass of suspended polymer.

c) The relationship between turbidity and the concentration of the polymer suspension.

In the determination of the mass of material suspended it is necessary to measure the intensity of both the transmitted light and of the scattered light at fixed angles.[13] The usual angles chosen are 45, 90 and 135°. The measurement of the intensity at 45 and 135° enables the dissymmetry function Z to be calculated. A knowledge of Z then allows correction for the change in size of the suspended polymer particles to be determined.

The turbidity τ, of a suspension of particles in a dispersing medium of refractive index n_o, may be expressed by the relation,[13]

$$\tau = 2.3/L \log (I_o/I_t) \qquad (3\text{-II})$$

where L is the length of the absorbing medium and I_o and I_t are the intensities of the incident and transmitted light respectively. The intensity of the scattered light is related to the turbidity, by

$$\tau = \frac{16\pi}{3} \frac{r^2}{V}\left(\frac{i^*_{90}}{I^*_o}\right) \qquad (4\text{-II})$$

where i^*_{90} is the intensity of the scattered light at 90° at a distance r from a volume of liquid V, receiving an intensity of non-polarized light I^*_o.

However, in a titration cell, in which the scattering volume is situated at the centre of the cell, the light intensity received by this element of volume is less than the incident intensity I_o, so that

$$I_o^* = I_o e^{-\tau L/2} \qquad (5\text{-II})$$

Similarly, the measured intensity at 90° is less than i_{90}^*, so that

$$(i_{90}) \text{ meas.} = i_{90}^* e^{-\tau L/2} \qquad (6\text{-II})$$

Thus, since $I_t = I_o e^{-\tau L}$

$$i_{90}^*/I_o^* = (i_{90}/I_t) \text{ meas.} \qquad (7\text{-II})$$

The measured turbidity τ is related to the intensities of the scattered light at 90° and the transmission, by

$$\tau = K(i_{90}/I_t) \text{ meas.} \qquad (8\text{-II})$$

where K is a constant to be determined (see Chapters IV and VII).

It is essential to ensure that the solvent and the precipitant have the same or very nearly the same refractive index. In the past it has been assumed[9,13] that the polymer particles remain spherical in shape, and that their dimensions are small compared to the wavelength of the light in the absorbing medium. Recent observations

[25,26] have shown that this situation does not always exist. The precipitation of polystyrene in the butanone-isopropanol system is accompanied by an increase in particle size as the titration proceeds, nevertheless it has been shown (Chapter V) that the particles are essentially spherical in shape. As a result of the size of the swollen polymer particles, the intensity of the scattered light is not symmetrical, but diminishes as a function of the angle of observation θ. To correct for this dissymmetry, Debye[15] has introduced the concept of a particle scattering factor $P(\theta)$, which can be used to correct the measured intensity at 90°. For spheres up to one wavelength in diameter and whose refractive index is equal to or very nearly equal to that of the surrounding medium,

$$P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2 \qquad (9\text{-II})$$

$$\text{where} \quad x = 2\pi(D/\lambda^1)\sin\theta/2 \qquad (10\text{-II})$$

and λ^1 is the wavelength of light in the medium. D is the diameter of the particle and θ is the angle between the direction of the incident beam and the direction of observation. Thus, from the measured dissymmetry Z, where $Z = (i_{45^\circ}/i_{135^\circ})$, the size of the precipitated particles can be obtained, and hence the observed intensity of scatter at 90° corrected by multiplying by the particle correction factor $^1/P(90)$. The corrected intensity is the intensity which would have been observed had internal interference due to particle size not been present. Tables of (D/λ^1) and the corresponding Z values and also values for $^1/P(\theta)$ have been published by Doty and Steiner[16] and also by Stacey.[17] It should be pointed out, however, that the requirement that the refractive index of the precipitated particles is very nearly equal to that of the medium does not apply, and corrections based on the Mie theory[17] should be used.

Consequently, as a result of the above corrections, the quantitative application of the turbidimetric titration technique has been further simplified by establishing the relationship between the corrected turbidity and the concentration of the polymer suspension.

d) The relationship between solubility, molecular weight and concentration.

The very early theoretical work on the fraction properties of high polymers was initiated by Schulz,[18,23] whose treatment considered the distribution of polymer between solution and precipitate to be governed by the relative energies in the two phases and the Boltzmann probability for such energies. Schulz, however, did not take into consideration the entropy of mixing of polymer and solvent molecules. A thermodynamic approach to fractional precipitation was thus developed by Flory,[27] Gee[28] and Huggins[28] based on the entropies and heats of mixing for the solution and precipitate phases. A third approach to this problem of fractional precipitation was initiated by Morey[30] and later developed by Morey and Tamblyn.[19] This approach was based on the kinetics of precipitation, in which the start of the aggregation of the polymer particles is considered as a reversible equilibrium reaction. Although open to criticism, the Schulz[18] treatment of fractional precipitation is extremely useful, particularly in turbidimetric titration studies, where extremely dilute solutions are used. The assumption by Schulz that the activities in the Bronsted-Boltzmann expression for the distribution of a substance in two immiscible solvents can be replaced by actual concentrations, is thus not greatly in error.

Schulz has shown that the saturation concentration C, of a polymer species, could be related to the point of precipitation γ , by an equation of the form

$$\log C = a - b\gamma \qquad (11\text{-II})$$

It was also shown[18] that at a constant concentration the relationship between the molecular weight M and the precipitation point γ, is an equation of the form

$$\gamma = x + \frac{y}{M^n} \qquad (12\text{-II})$$

where x, y and n are constants for a given polymer solvent-precipitant system. Other relationships between γ and the molecular weight M have been established by several authors[19,13] for various polymer solvent-precipitant systems. For a turbidimetric titration study to be quantitative, it is necessary for the relationships between the point of precipitation γ, and the concentration and the molecular weight to be determined for the system under investigation. For polystyrene precipitated from butanone by the slow and continuous addition of isopropanol, it has been shown (Chapter V) that the solubility relationship has the form,

$$\gamma = A + \frac{(B - D \log C)}{M^{\frac{1}{2}}} \qquad (13\text{-II})$$

where γ is the point of precipitation corresponding to half the weight of material suspended in solution, M is the molecular weight and C the concentration. The parameters B and D are constants characteristic of the polymer and the solvent-precipitant system. In the solubility laws for polymer solutions the parameters usually chosen are the saturation state values of concentration and point of precipitation. These parameters are chosen for convenience and because they are readily measurable. In equation (11-II) the concentration C is not the saturation state value, but the original concentration of the polymer solution before the addition of precipitant. In the constant volume type cell the polymer solution is being continually diluted and also removed from it as the process continues. This involves correcting at each stage of the titration for dilution and loss of polymer solution in order to obtain the concentration at any instant. The initial concentration is a readily determined quantity and thus correction factors are eliminated from the calculations. The solubility law was still found to hold and the results obtained were similar to those using the saturation concentration values.

e) Calculation of molecular weight distribution functions from the turbidimetric titration data.

Having established the solubility relationships in section (d), preferably using sharp fractions of the polymer whose molecular weights have been well established, it is then possible to construct the molecular weight distribution curve for any polymer of the same series. Two main methods for establishing molecular weight distribution curves have been developed independently by Morey and Tamblyn[1] and by Claesson.[20] The method shown in Chapter V is perhaps simpler than both of these techniques. The solubility curve obtained from the turbidimetry data is a curve of γ at the point of precipitation plotted against weight of material. The curve is corrected for loss of polymer precipitate (see Chapter V), and molecular weights at set intervals of γ are determined, using an equation established by the technique mentioned above (section d). An integral curve of weight versus molecular weight is then readily constructed. The units of weight are calculated assuming that at complete precipitation unit weight exists in the cell. The differential molecular weight distribution curve is then obtained by graphical differentiation. A curve fitting procedure using polynomials was attempted, but the calculation was found to be too tedious and did not warrant the effort required.

f) Application of turbidimetric titration to the examination of block copolymer solutions.

The application of the turbidimetric titration to the examination of block copolymers has so far been of a qualitative nature only. The main purpose of the analysis[2,4-6] is to detect traces of homopolymer present as impurity with the block copolymer. The basis of such analysis is the solubility difference between the block copolymer and either parent homopolymer. The fractionation behaviour of block copolymers has only recently been examined on a small scale by Schlick and Levy[21] with block copolymers of styrene and isoprene. Fractionation behaviour of block copolymers has, however, been treated theoretically by Kilb and Bueche.[31] These authors examined the solution and fractionation properties of block copolymers using the Flory-Huggins[32-35] lattice model. Kilb and Bueche[31] predicted that the solubility of a block copolymer was mainly dependent on the heat of interaction of the various polymer segments with the solvent. Furthermore, they showed that block copolymers do not fractionate as a function of overall molecular weight. By contrast, Schlick and Levy[21] found that as the size of their block copolymers decreased, the solubility increased, even though the overall molecular weight remained constant. It is evident that more experimental data is required before the theoretical predictions of Kilb and Bueche[31] can be substantiated.

It is obvious that the type of polymers and the solvents used in any investigation will affect markedly the results obtained. It seems difficult to predict a general type of behaviour for block copolymers without a more thorough investigation of both homopolymers used to synthesize the block copolymers. Results of a qualitative nature[36,37] indicate solution properties for block copolymers intermediate between each homopolymer, in agreement with the theoretical predictions of Kilb and Bueche.[31]

The technique of turbidimetric titration provides a fairly efficient method for carrying out a rapid fractionation of a polymer species. Its application to the examination of the block copolymers of styrene and methyl methacrylate was therefore investigated. It is essential, however, that the data obtained be correlated with that obtained from each parent homopolymer, and that the instrument used is capable of giving a quantitative interpretation for a homologous polymer series.

The fractionation data for four block copolymers of styrene and methyl methacrylate has been presented in Chapter V.

3. Viscosity.

a) Introduction.

The application of viscosity measurements for the determination of the molecular weight of block copolymers is not an established technique. However, for random copolymers of styrene and methyl methacrylate in methyl ethyl ketone, Stockmayer and co-workers[41] have shown that the log of the limiting viscosity number is linear with the log of molecular weight. The recent work of Schlick and Levy[21] on the block copolymers of styrene and isoprene in toluene and toluene-methanol mixtures, shows that as the size of the block copolymer decreases, the limiting viscosity number increases, although the overall molecular weight remains constant. It is evident that the solvent and the incompatibility of different polymeric species will affect the results obtained from viscosity measurements.

In order to explain the viscosity behaviour of polymer solutions it is necessary to find suitable approximations which will represent the experimental data with a reasonable degree of accuracy, and, where a theoretical model has been chosen, to show that the behaviour is similar to that found experimentally. In examining the block copolymers used in this work, the Flory-Fox[39,40] dilute solution theory of viscosity was used as a means of explaining the behaviour of the polymers. However, the calculations resulting from this investigation were carried out with some reservation, because although applicable to homopolymer solutions, the Flory-Fox treatment has yet to be established for the examination of block copolymers.

The main purpose of the viscosity study on the block copolymer solutions was to obtain information on the intramolecular and intermolecular forces governing dilute solution behaviour. For this purpose the limiting viscosity number and the Huggins constant were determined in a variety of solvents. The viscosity measurements were also carried out so that the data could be combined with that obtained from light-scattering and osmotic pressure measurements, in order to evaluate the thermodynamic parameters governing polymer-solvent interaction.

b) The significance of the limiting viscosity number and the Huggins constant.

The most general expression relating the viscosity of a polymer solution, η, the viscosity of the solvent, η_o, and the concentration c of the solution is given by the relation,[42,43]

$$\eta\ sp/c \;=\; \frac{\eta - \eta_o}{\eta_o c} \;=\; A + Bc + Cc^2 + Dc^3 + \ldots \quad (14\text{-II})$$

where $\eta sp/c$ is the viscosity number. This equation has been found to fit the experimental data remarkably well for a large number polymer-solvent systems. In dilute solution the c^3 term is negligible, and, except in the case of very high molecular weight polymers, measurements in dilute solution indicate a linear relationship between $\eta sp/c$ and c, indicating that the c^2 term is also negligible. Equation (14-II) now becomes,

$$\eta\ sp/c = A + Bc = [\eta] + Bc \qquad (15\text{-II})$$

where $[\eta] = \lim_{c \to 0} (\eta\ sp/c) = A$. Equation (15-II) is the familiar Huggins[29] equation, where $B = k_H [\eta]^2$.

Thus

$$\eta\ sp/c = [\eta] + k_H [\eta]^2 c \qquad (16\text{-II})$$

The Huggins viscosity slope constant k_H is a dimensionless parameter, which, according to Huggins, should be independent of the molecular weight of the polymer.

The determination of the limiting viscosity number and the calculation of the Huggins constant both serve as a measure of the solvent power of a particular solvent for a particular polymeric species. Flexible polymer molecules are usually extended in good solvents and will thus exhibit high limiting viscosity numbers. The Huggins empirical constant k_H serves as a measure of solvent power[44-46] by having high values in poor solvents and low values in good solvents.

The limiting viscosity number, $[\eta]$, has been the subject of many investigations in the last two or three decades; its value as a measure of molecular weight of polymer species, of solvent power, and of shape and structure of polymers is well established.[39,44,47,48] In recent years the Huggins slope constant, k_H, has been the subject of many investigations.[43,49-64] Essentially, the Huggins constant is dependent on polymer-polymer and polymer-solvent interactions; these in turn are affected by the nature of the polymeric species, the solvent and the temperature. The Huggins constant has been shown to be independent of the molecular weight in a variety of good solvents[39,49,50] and thus has many advantages over the limiting viscosity number. As has been pointed out previously,[43] the Huggins constant is sensitive to solvent power, whether the solvent be altered by changing from one solvent to another,[44,63] or by altering the composition of a mixed solvent[50,60,62] or by altering the temperature.[51] It is sensitive to changes in polymer structure, as in the case of branched polymers. For branched polyvinyl chloride, k_H has been found[54] to increase with increasing complexity of the polymer structure. However, k_H has been found[64] to be insensitive to small degrees of branching, and variations in k_H are only detected when the branching is of the 'bushy' type, particularly if it can lead to gel formation.[55,57,59,61]

The Huggins constant has also been found to be influenced by the composition of copolymers,[53] changing linearly from the k_H value for one pure homopolymer to the k_H value for the second homopolymer.

The behaviour of k_H in certain systems can be predicted by theoretical reasoning; however, there are cases where the behaviour of the Huggins constant can only be determined empirically. The interactions responsible for k_H are not completely understood and very little experimental work has been done with this in mind. Perhaps the most useful data regarding the behaviour of k_H has come from studies in ternary systems, where the polymer solvent interactions have been varied by changing the composition of a mixed solvent,[50,60,62] and where polymer-polymer interactions have been varied by introducing a second polymer.[43]

c) The behaviour of the Huggins constant in mixed polymer systems.

In an attempt to predict the behaviour of k_H in ternary systems composed of two different polymeric species in a common solvent, Cragg and Bigelow[43] have derived an equation which relates the k_H, the limiting viscosity number $[\eta]$, and the weight fraction, for each polymeric species. This equation has the form,

$$(k_H)m = \frac{(k_H)_A[\eta]_A^2 W_A^2 + (k_H)_B[\eta]_B^2 W_B^2 + 2(k_H)_A(k_H)_B[\eta]_A[\eta]_B W_A W_B}{([\eta]_A W_A + [\eta]_B W_B)^2} \tag{17-II}$$

where $(k_H)m$ is the Huggins constant for the mixture, and the subscripts A and B denote the different polymeric species.

This equation was derived[43] for the case where the only interaction between molecules in solution is purely hydrodynamic in nature. The thermodynamic interactions between molecules in solution have been ignored in the derivation of equation (17-II), hence the determination of $(k_H)m$ could provide information on the nature of such interactions. It is also possible to vary the number of polymer-polymer contacts by altering the weight fraction W, of one or both species.

The findings of Cragg and Bigelow[43] using a mixture of polystyrene and polymethyl methacrylate in m-xylene, indicate negative deviations of the (k_H) measured value of the mixture from that calculated by equation (17-II). These negative deviations have been explained as being due in part to repulsive forces existing between these two polymers in m-xylene. The fact that m-xylene is a bad solvent for polymethyl methacrylate would cause severe aggregation of this polymer. The true effect of this, however, on the calculated value of $(k_H)m$ will be masked somewhat by the presence of polystyrene. Although information can be obtained in this way concerning polymer-polymer interactions, the data should be correlated[43] with that obtained from other thermodynamic data obtained from osmotic pressure and light-scattering studies.

The application of equation (17-II) to the determination of a calculated $(k_H)m$ for a block copolymer is in itself informative. Knowing the molecular weight and weight fraction of each species present in the block copolymer provides a means of determining $(k_H)m$. This value, however, assumes a mechanical mixture of both homopolymers and an absence of thermodynamic interactions. It is possible then to obtain an arbitrary measure of the thermodynamic interactions resulting from the combination of two chemical distinct polymers. It must be realized, however, that the Huggins constant gives a measure of intermolecular interactions, as distinct from the intramolecular interactions, which affect the limiting viscosity number.

It is evident that it becomes increasingly difficult to apply the data from a mixed polymer system to the case of block copolymers where there is a permanent polymer-polymer contact. For a mixture of two homopolymers, A and B, dissolved in a common solvent, it is possible to predict the resulting limiting viscosity number by the equation[43]

$$[\eta]\text{mix.} = [\eta]_A W_A + [\eta]_B W_B \qquad (18\text{-II})$$

However, this equation assumes that combination, aggregation or association of the polymer molecules is broken down on dilution. The fact that in a block copolymer both chains cannot act independently of each other eliminates equation (18-II) as a means of predicting the limiting viscosity number. It is thus evident that the examination of a block copolymer using the technique of viscometry has certain restrictions. The evaluation of the limiting viscosity number and the Huggins constant can both serve as a measure of solubility in a particular solvent. The Huggins constant can give a measure of the intermolecular interactions present in solution and also acts as a guide in distinguishing the block copolymer from both homopolymers. The Huggins constant for both random and block copolymers appears to be lower[65] than that for either homopolymer.

d) Some aspects of the Flory-Fox treatment of viscosity.

The Flory-Fox[39,40] treatment of the molecular weight dependence on the viscosity of dilute polymer solutions is perhaps the most successful theory put forward to date. It is certainly a step forward in the establishment of the viscosity method as a means of determining absolute molecular weights. It is based on an earlier theoretical treatment put forward by Kirkwood and Riseman.[47]

The polymer molecules are represented as random coil structures with a Gaussian distribution of chain segments 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 interaction with the solvent molecules. The degree of extension is defined by a function α, where α is related to the polymer dimensions by the equation,

$$\alpha^2 = \frac{(\overline{r}^2)}{(\overline{r_o}^2)} \qquad (19\text{-II})$$

$(\overline{r}^2)$ is the mean square end-to-end distance for the polymer in a particular solvent at a particular temperature and $(\overline{r_o}^2)$ is the unperturbed end-to-end distance measured at the θ or Flory temperature. The Flory temperature represents the lowest temperature for complete miscibility in a given poor solvent at the limit of infinite molecular weight. The extension function α is critically dependent on the entropy of dilution parameter ψ_1 and the heat of dilution parameter κ_1. The extension factor α measured as a function of the above thermodynamic parameters is given by the equation,

$$\alpha^5 - \alpha^3 = 2Cm\,\psi_1(1 - \theta/T)M^{\frac{1}{2}} \qquad (20\text{-II})$$

where $\psi_1(1 - \theta/T) = \psi_1 - \kappa_1$ and Cm is a constant such that,

$$Cm = 1.4 \times 10^{-24}(\bar{v}^2/V1)\,\Phi/K \qquad (21\text{-II})$$

Here $\bar{v}$ is the partial specific volume of the polymer, $V1$ the molar volume of the solvent, Φ the Flory-Fox constant and K is a constant such that

$$K = \Phi\,(\bar{r}_o^{\,2}/M)^{3/2} \qquad (22\text{-II})$$

The Flory-Fox relationship between the limiting viscosity number $[\eta]$ and the molecular weight M is of the form,

$$[\eta] = K\,M^{\frac{1}{2}}\alpha^3 \qquad (23\text{-II})$$

Using equations (19-II) and (22-II) it is possible to write the Flory-Fox equation in equivalent forms such that,

$$[\eta] = \Phi\,\frac{(r^2)^{3/2}}{M} = \Phi\left(\frac{\bar{r}_o^{\,2}}{M}\right)^{3/2}\alpha^3 M^{\frac{1}{2}} \qquad (24\text{-II})$$

The Flory-Fox constant Φ is a universal constant having values from 1.95×10^{21} to 2.6×10^{21} with a weighted mean of 2.1×10^{21}.

From equation (24-II) it is possible to determine values for the limiting viscosity number from independent light-scattering measurements, where the molecular weight and dimensions of the linear randomly coiled chain can be determined. The method also provides a means of checking the Flory-Fox $\bar{\Phi}$ value for a particular polymer-solvent system; although evidence suggests that it is independent of polymer, solvent or temperature.

Perhaps the most convincing test of the Flory-Fox treatment has come from measurements of the limiting viscosity number at the θ or Flory temperature, where α is unity, and hence from equation (19-II) $(\bar{r}^2) = (\bar{r}_o^{\,2})$. This means that the limiting viscosity number will be proportional to the square root of the molecular weight of the solute at the θ-temperature. This fact has been substantiated[66-69] for a number of polymer-solvent systems over ranges of molecular weight from several million down to 10,000. Perhaps the critical factor in such measurements is an accurate evaluation of the θ-temperature. Accurate osmotic pressure or light-scattering studies in the particular solvent over a range of temperatures is a method usually employed.

The application of the Flory-Fox theory to dilute solutions of block copolymers must, however, be carried out with some reservation. 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 theory developed for homopolymers.

4. Osmotic Pressure.

a) Introduction.

The determination of osmotic pressure data for a polymeric species is essential, if complete characterization of the material under investigation is to be carried out. The measurement of the osmotic pressure provides a relatively simple technique for molecular weight determination, provided suitable semi-permeable membranes can be obtained for the system to be studied. The osmotic pressure is generally determined for two main reasons, a) to obtain the number average molecular weight of a polymer, and b) to obtain information on the thermodynamic properties of the polymer solution.

If M is the molecular weight of the solute and c the concentration of the solute in g/cm^3 of solution, then at infinite dilute the relationship between the number average molecular weight and the osmotic pressure is given by,

$$(\pi/c)_{c=0} = RT/M \qquad (25\text{-II})$$

The reduced osmotic pressure in dilute solution is generally expanded into a power series in concentration, c. Three equivalent forms of this expansion are commonly employed:

$$\pi/c = RT/M + Bc + Cc^2 + \ldots \qquad (26\text{-II})$$

$$\Pi/c = RT(1/M + A_2c + A_3c^2 + \ldots\ldots) \qquad (27\text{-II})$$

and $$\Pi/c = (\Pi/c)_0\ (1 + \Gamma_2c + \Gamma_3c^2 + \ldots) \qquad (28\text{-II})$$

McMillan and Mayer[70] have given evidence to show that such a virial expansion is always possible. The coefficients of the above expansions B, A_2 and Γ_2 are all commonly referred to as second virial coefficients. The theories of polymer solutions are concerned with attempts to derive values for these various coefficients and to establish the interrelationships existing between them. The two most promising theoretical approaches to the treatment of osmotic pressure measurements are the lattice theory of Huggins[71] and Flory[72] and the more recent dilute solution theory of Flory and Krigbaum.[73]

b) Some aspects of the Flory-Huggins lattice theory and the Flory-Krigbaum dilute solution theory of osmotic pressure.

The lattice theory has been proposed as a means of calculating the configurational entropy. The theory assumes that in a polymer solution the chain segments of the polymer occupy the same volume as a solvent molecule, and that solvent and polymer chains are arranged in such a regular manner as to be able to represent their spatial arrangements by a lattice. The total configurational entropy of the polymer solution is calculated considering the number of different ways of arranging the solvent and polymer molecules. The heat of mixing is obtained from consideration of the various types of interaction possible between a polymer segment and its solvent or segment neighbours. The free energy of mixing can be obtained once the configurational entropy and heat of mixing have been estimated.

From the Flory-Huggins expression for the free energy of mixing one can obtain an expression for the change of chemical potential of the solvent on mixing as follows,

$$\frac{\Delta\mu_1}{RT} = \ln\phi_1 + (1 - \tfrac{1}{m})\phi_2 + \chi\phi_2^2 \qquad (29\text{-II})$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and solute, m is the ratio of the molar volumes of polymer and solvent, and χ is a dimensionless parameter, the Flory-Huggins interaction constant. By expanding the logarithmic term in powers of ϕ_2 ($\phi_1 = 1 - \phi_2$) and knowing that $\Delta\mu_1 = -\pi V_1$, where V_1 is the molar volume of the solvent, then

$$\frac{\pi V_1}{RT} = \frac{\phi_2}{m} + (\tfrac{1}{2} - \chi)\phi_2^2 + \tfrac{1}{3}\phi_2^3 + \ldots. \qquad (30\text{-II})$$

Writing equation (30-II) in terms of the concentration of the solute c (g/cm^3), we have

$$\frac{\pi}{c} = \frac{RT}{M} + \frac{RT}{V_1\rho_2^2}(\tfrac{1}{2} - \chi)c + \frac{RT}{3V_1\rho_2^3}c^2 + \ldots. \qquad (31\text{-II})$$

where ρ_2 is the density of the solute. The equation was originally written in this form by Huggins.

The lattice theory assumes a uniform concentration of polymer segments throughout a dilute polymer solution. In very dilute solutions, however, it seems reasonable to expect individual polymer molecules to become separated from each other by regions of pure solvent. If this is the case, then the concentration of polymer segments must then become non-uniform in the solution. Flory and Krigbaum[73] have treated such dilute solutions as a dispersion of approximately spherical clusters of polymer segments, separated by regions of pure solvent. Each spherical cluster may be considered to have an average density, which has its maximum at the centre, but decreases as the solvent region is approached. This concept has been used to derive an expression for the chemical potential of mixing of the solvent. At high dilution the osmotic pressure can be expressed by a virial expansion of the form,

$$\pi/c = RT/M\left[1 + \Gamma_2 c + g\Gamma_2^2 c^2 + \ldots.\right] \qquad (32\text{-II})$$

where Γ_2 is a parameter, which depends on polymer-solvent interaction and contains the Flory-Huggins constant χ. Γ_2 is related to Γ_3 of equation (28-II) by the expression

$$\Gamma_3 = g\Gamma_2^2 \qquad (33\text{-II})$$

where g for non-interpenetrating spheres is numerically equal to $\frac{5}{8}$. However, Stockmayer and Casassa[74] have shown that this value of g is too high, and for polymers in a good solvent g is closer to $\frac{1}{4}$. If osmotic pressure measurements are carried out in poor solvents, then the second virial coefficient will decrease, as the solvent is made progressively poorer. This means that the contribution of the third virial coefficient will decrease as a consequence of equation (33-II) and the osmotic pressure plots will be characterized by a rapid decrease in curvature. However, in good solvents and in the normal concentration range usually employed, curvature might still be expected from equation (32-II), even if g is $\frac{1}{4}$. However, if g is $\frac{1}{4}$ and if higher terms in equation (32-II) are ignored,[80] then

$$\left(\frac{\overline{\Pi}}{cRT}\right)^{\frac{1}{2}} = M^{-\frac{1}{2}}(1 + \Gamma_2 c) \qquad (34\text{-II})$$

It has been shown[65,75,76,78,79] that if $(\overline{\Pi}/cRT)^{\frac{1}{2}}$ is plotted against c straight lines result, the intercept is $M^{-\frac{1}{2}}$ and the slope $\frac{1}{2}\Gamma_2 M^{-\frac{1}{2}}$.

It is possible to obtain much relevant data from the Flory-Krigbaum dilute solution theory of osmotic pressure. This treatment overcomes the severe shortcomings of the lattice theory when applied to regions of low polymer concentration. However, there are still some discrepancies to be cleared up, particularly as regards the numerical magnitude of g in equations (32-II) and (33-II).

c) Information that can be obtained from osmotic pressure measurements.

The osmotic pressure of a polymer solution at infinite dilution is proportional to the number of molecules of polymer and is independent of their weight. Thus an important reason for carrying out osmotic pressure measurements is to obtain information on the homogeneity of a polymer sample, that is from the ratio of the weight average molecular weight to the number average molecular weight.

Flory[32] has shown from the thermodynamic treatment of dilute polymer solutions that the temperature dependence of the second virial coefficient A_2 may be expressed by the equation,

$$A_2 = (\bar{v}^2/V_1)\,\psi_1(1 - \theta/T)\,F(x) \qquad (35\text{-II})$$

where $\bar{v}$ is the specific volume of the polymer, V_1 the molar volume of the solvent, ψ_1 the entropy of dilution parameter and F(x) a function of the degree of expansion of the coiled polymer molecules. The function F(x) decreases slowly with decreasing molecular weight and at the Flory or θ-temperature $F(x) \cong 1$. The function F(x) is related to the excluded volume (u) by the relation,

$$\mu = \frac{\bar{v}^2}{NV_1} (\psi_1 - \kappa_1) M^2 F(x) \qquad (36\text{-II})$$

where N is Avogadros number, κ_1 the heat of dilution parameter and M the molecular weight of the solute. The function F(x) is expressed by the relation,

$$F(x) = 1 - x/2!2^{3/2} + x^2/3!3^{3/2} - \ldots (37\text{-II})$$

where x is related to the expansion factor α , by the equations,

$$x = 2(\alpha^2 - 1) = \frac{2\bar{v}^2 M^2}{V_1 N} \psi_1 (1 - \theta/T) (\cancel{\tfrac{3}{4}} \pi R_G{}^2)^{3/2} \qquad (38\text{-II})$$

where (R_G) is the radius of gyration of the polymer molecules. Thus, if ψ_1 and θ or ψ_1 and κ_1 are known, and if (R_G) can be determined, then it is possible to calculate the expansion factor α . The factor α is the ratio of the root mean square end-to-end dimensions $(\bar{r}^2)^{\frac{1}{2}}$ for the polymer coil to the unperturbed dimensions $(\bar{r}_0^2)^{\frac{1}{2}}$, characteristic of a polymer coil at the θ-temperature.

The Flory or θ-temperature may be determined from the temperature dependence of the osmotic pressure. The determination of the second virial coefficient A_2 at several temperatures and the extrapolation of these results to $A_2 = 0$, allows θ to be determined. The function $\psi_1 \theta (\bar{v}^2/V_1)$ may then be determined from the slope of the A_2 versus T plot. If $\bar{v}$ can be reliably estimated and V is known, then ψ_1 can be determined.

Having determined the entropy of dilution parameter ψ_1, the heat of dilution parameter κ_1 may be calculated from,

$$\kappa_1 = \theta\psi_1/T \tag{39-II}$$

Having determined κ_1, the heat of dilution $\Delta\overline{H}_1$ may be determined experimentally from the relation,

$$\Delta\overline{H}_1 = RT\,\kappa_1\overline{v}^2 \tag{40-II}$$

The osmotic pressure data alone can give detailed information on the thermodynamic parameters characterizing polymer-solvent interactions. In fact, it is not necessary to resort to light-scattering measurements in order to determine the expansion factor α. From equation (20-II),

$$\alpha^5 - \alpha^3 = 2\mathrm{Cm}\,\psi_1(1 - \theta/T)M^{\frac{1}{2}}$$

$$\text{where Cm} = \left(\frac{27}{2^{5/2}\,\pi^{3/2}}\right)\left(\frac{\overline{v}^2}{NV_1}\right)\left(\frac{\overline{r}_0^2}{M}\right)^{-3/2} \tag{41-II}$$

Since the limiting viscosity number is given by equation (24-II), where

$$[\eta] = \Phi\left(\frac{\overline{r}_0^2}{M}\right)^{3/2}\alpha^3 M^{\frac{1}{2}}$$

it is possible to combine equations (20-II), (41-II) and (24-II) to obtain

$$\alpha^2 - 1 = \frac{27\psi_1(1 - \theta/T)M\Phi\overline{v}^2}{2^{3/2}\,\pi^{3/2}NV_1\,[\eta]} \tag{42-II)a$$

Thus α may be calculated from the thermodynamic data determined from osmotic pressure measurements and the measurement of the limiting viscosity number. However, the method relies on the fact that the Flory-Fox universal parameter Φ is a constant, whereas this parameter may be determined from light-scattering measurements. The calculation of α allows the functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\bar{r}_0^{\,2}/M)^{\frac{1}{2}}$ to be readily determined. The function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ should be independent of the molecular weight for a particular polymer-solvent system, and the function $(\bar{r}_0^{\,2}/M)^{\frac{1}{2}}$ a constant independent of solvent or temperature, but characteristic of the unperturbed dimensions of the particular polymer.

d) Application of osmotic pressure measurements to the examination of block copolymers.

Until recently[65] very little experimental work on the dilute solution behaviour of block copolymers has appeared in the literature. Although the proper objective of a physicochemical investigation of block copolymers should be to explain the properties of the system in terms of the properties of the pure components, there has been little experimental work done, to do more than speculate on the behaviour of block copolymers in solution. Flory and Krigbaum[87] have, however, derived a theoretical value for the second virial coefficient A_2, for multicomponent systems composed of a single solvent and several polymer homologs differing in molecular weight. For mixtures containing two separate polymers and one solvent the equation is,

$$A_2 = W_a{}^2A_{2a}+W_b{}^2A_{2b}+W_aW_b\,\frac{\bar{v}_a\bar{v}_b}{V_1}(\psi_{1a}-\kappa_{1a}+\psi_{1b}-\kappa_{1b}+\chi_{ab})F(X_{ab}) \qquad \text{(42-II)b}$$

where the two polymers are represented by subscripts a and b; χ_{ab} is the Huggins interaction parameter for the pair of polymers, and $F(X_{ab})$ a function of the excluded volume of the polymer pair. Recent application[65] of this equation to a mixture of polystyrene and polymethyl methacrylate in toluene at 25°C suggests that A_2 reaches a maximum at about the middle of the composition scale. This contrasts with the near constant A_2 found by Burnett and co-workers[65] for their block copolymers of varying composition but near constant molecular weight. For block copolymers of varying molecular weight and varying composition it was found (Chapter VI) that A_2 decreased with increasing molecular weight.

The determination of the osmotic pressure in the examination of block copolymers is essential if characterization of the polymer is to be carried out. It was possible to examine the parent polystyrene prepared in the first stage of the block copolymer synthesis (Chapters III and VI) to check on the homogeneity of this material.

The homogeneity of the resulting block copolymer is dependent on that of the parent polystyrene. The examination of the block copolymer by osmotic pressure measurements combined with light-scattering determinations, allows the homogeneity of the block copolymer to be established.

Considerable intramolecular and intermolecular interactions have been shown to exist in both random and block copolymer[41,65] solutions; such behaviour should be evident in the second virial coefficient and the expansion factor α, both obtainable from osmotic pressure measurements.

The most important information regarding thermodynamic solution behaviour is to be obtained from osmotic pressure studies. The application to solutions of block copolymers must, however, be done with some reservation. The dilute solution theory of Flory and Krigbaum[72,73], although applicable to dilute homopolymer solutions, may not, in its present form, be applicable to block copolymer solutions. The dilute solution theory is based upon a Gaussian distribution of chain segments about the centre of mass, and this does not appear to be the case with block copolymers. However, in order to compare the results obtained for block copolymer solution behaviour with homopolymers and their mixtures, it seems reasonable to assume Gaussian statistics. Recent observations[65] show that such an assumption may not be greatly in error.

5. Light-scattering.

a) Introduction.

The application of the light-scattering technique to the determination of the molecular weight of macromolecules has become standard procedure in many polymer laboratories. Since the very early development[81] of light-scattering, the applications to different polymer-solvent systems has greatly increased. However, its application to copolymers, both random and block, has only recently[41,82-84] been given serious consideration. The work of Tremblay and co-workers[82] on a butadiene-styrene copolymer seemed to suggest that the intensity of the light scattered by the copolymer in dilute solution depended on the weight average molecular weight of the copolymer and on the heterogeneity of composition of the various polymer segments in the chain. The accuracy of these statements was later confirmed by Stockmayer and co-workers,[41] who were able to derive an equation which demonstrated how the intensity of the light scattered by a copolymer, after extrapolation to infinite dilution and zero scattering angle, varied with the composition of the sample. The work of Stockmayer and co-workers[41] has now been confirmed by the more recent investigations of Bushuk and Benoit[83] and Krause.[84]

b) Some theoretical considerations of the light-scattering equation applied to block copolymers.

It must be realized that when considering the scattering of light from a block copolymer sample, there will be two or more types of scattering elements, depending, of course, on how many monomer types make up the copolymer. It is also necessary to determine the refractive index increment, which for block and random copolymers is a function of the composition. On the assumption that the refractive index increment of a copolymer chain is proportional to its composition, Stockmayer and coworkers[41] derived the following expression,

$$\left(\frac{I_\theta}{K'c}\right)_{\substack{c \to o \\ \theta \to o}} = \left(\frac{dn}{dc}\right)_o^2 \overline{M_w} + 2b\left(\frac{dn}{dc}\right)_o (M\Delta x) + b^2(M(\Delta x)^2) \qquad (43\text{-II})$$

where I_θ 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 $(dn/dc)_o$ is the measured refractive index of the copolymer-solvent system; $K' = 2\pi^2 n_o^2 K/\lambda_o^4 N$ where n_o is the refractive index of the solvent for light of wavelength λ_o in vacuo, N is Avogadros number and K is a function of θ, which includes the instrument calibration constant.

The function b in equation (43-II) is related to the difference in refractive index increment between the polymer segments comprising the copolymer chain, such that,

$$b = \left(\frac{dn}{dc}\right)_A - \left(\frac{dn}{dc}\right)_B \qquad (44\text{-II})$$

where the subscripts A and B refer to the two homopolymers of the copolymer chain. It can also be seen from equation (43-II) that the scattering is also dependent on the composition distribution of the copolymer sample, where

$$(M \Delta x) = \sum w_i M_i (\Delta x)_i \qquad (45\text{-II})$$

and

$$(M(\Delta x)^2) = w_i M_i (\Delta x)_i^{\,2} \qquad (46\text{-II})$$

where w_i is the weight fraction of molecules in the sample having molecular weight M_i and composition x_i, with $(\Delta x)_i = (x_i - x_o)$, where x_o is the average composition of the copolymer sample.

The above equations have been investigated separately by the authors Bushuk and Benoit[83] and Krause[84], and their results are in agreement with the original theory.[41]

It thus seems that the determination of the molecular weight of a block copolymer in a single solvent will only yield an apparent molecular weight Mapp. in accordance with the equation,[84]

$$\left(\frac{I\theta}{K'c}\right) = \text{Mapp.}\left(\frac{dn}{dc}\right)^2 \qquad (47\text{-II})$$

To obtain the true molecular weight $\overline{Mw}$ it is necessary to carry out light scattering measurements in at least three solvents in order to determine the values of $\overline{Mw}$, $(M\Delta x)$ and $(M(\Delta x)^2)$ of equation (43-II). The recent work of Krause[84] has been aimed at determining these three functions. The results indicate that $(M\Delta x)$ and $(M(\Delta x)^2)$ are valuable parameters in the investigation of the composition distribution of copolymer samples.

Detailed studies by Bushuk and Benoit[83] for block copolymers in a variety of solvents of differing refractive indices, indicate that block copolymers prepared by the Szwarc[85] technique are characterized by uniform chain composition. It was also found[83] that in solvents, where the refractive index increment is reasonably high, there was close agreement between the true $(\overline{Mw})$ and apparent (Mapp.) molecular weights for block copolymers.

Thus, if it can be shown that a block copolymer is reasonably homogeneous both in molecular weight and composition, then the light-scattering behaviour will be identical with that for a homogeneous homopolymer and the experimental results may be treated in a similar manner.

c) Information obtainable from light-scattering studies.

Light-scattering data, when combined with osmotic pressure measurements, make it possible to obtain information on the homogeneity of the block copolymer from the ratio of the weight average and number average molecular weights. Having established the homogeneity, one can proceed to accurately appraise the remaining light-scattering measurements.

The second virial coefficients A_2 and Γ_2 may be obtained from Zimm[86] plots and compared with the values determined from osmotic pressure measurements. The second virial coefficient A_2 may also provide information on extra intramolecular and intermolecular forces present.

Perhaps the most important result to be obtained from light-scattering measurements is the size and shape of macromolecules in solution. From the Zimm plot the z-average radius of gyration (R_G) can be obtained and subsequently the expansion factor α may be evaluated from equation (48-II), provided the thermodynamic parameters ψ_1 and κ_1 or ψ_1 and θ are known.

$$x = 2(\alpha^2-1) = \frac{2\bar{v}^2 M}{V_1 N}\psi_1(1-\theta/T)\left(3/4\pi R_G^2\right)^{3/2} \qquad (48\text{-II})$$

where x is related to the excluded volume of the polymer segments. Having determined α, the functions $(\alpha^5-\alpha^3)/M^{\frac{1}{2}}$ and $(\bar{r}_o^2/M)^{\frac{1}{2}}$ can be determined by application of the equations listed in sections 2 and 3 of this Chapter.

Both block and random copolymers are characterized by intrachain repulsions, which lead to a more expanded configuration[41] for the polymer chain. From the radius of gyration the mean square end-to-end distance may be determined for random coils thus,

$$(R_G)^2 = \frac{(\overline{r})^2}{6} \qquad (49\text{-II})$$

where $(\overline{r})^2$ is the mean square end-to-end distance. Comparison with homopolymers of the same molecular weight, shows that the block copolymer is characterized by a greater value of $(\overline{r})^2$.

As has been pointed out by Flory,[39] the thermodynamic behaviour of dilute polymer solutions is characterized by 1) the molecular weight, 2) the thermodynamic interaction parameters ψ_1 and κ_1 and ψ_1 and θ, which characterize segment-solvent interaction, and 3) the configuration or 'size' of the molecules in solution.

It is obvious that in order to achieve a more complete characterization of a block copolymer it is necessary to resort to an independent method, other than osmotic pressure, to determine the size of the polymer molecule. A value for the Flory-Fox constant Φ can be assumed and $(\overline{r})^2$ determined by application of equation (24-II). However, light-scattering measurements enable Φ to be determined without resort to assumptions. The calculation of Φ for block copolymers is in itself instructive, since it should be a constant, independent of the type of polymeric species being examined.

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CHAPTER III.

The Preparation, Isolation and Characterization of the Block Copolymers of Styrene and Methyl Methacrylate.

1. Introduction.
    - a) Some aspects of the preparation of monodisperse polystyrene.
    - b) The effect of impurity and the method of monomer addition on the resulting anionic polymer.
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References.

CHAPTER III.

1. Introduction.

a) Some aspects of the preparation of monodisperse polystyrene.

In the investigation of the dilute solution behaviour of a polymeric species it is essential that the material has a narrow molecular weight distribution and has been completely characterized as regards number and arrangement of different chemical groups and polymeric species along its chain length.

Many of the early syntheses of block copolymers produced material which was extremely heterogeneous, both in molecular weight and chemical composition. The yields of these early syntheses were poor and hence fractionation was impossible.

In his recent book, Ceresa[1] has listed the synthesis of some 1,400 block copolymers. The general methods of synthesis are listed under: Transfer and Addition, Chemical, Radical and Irradiation, Mechanico-chemical, Condensation and Ionic synthesis. For the controlled preparation of the block copolymers of styrene and methyl methacrylate, the anionic synthesis introduced by Szwarc[2] is by far the best technique. This method of preparation, in which unterminated polystyrene ('living polystyrene') is formed, offers the best method of preparing block copolymers of predetermined molecular weight and composition. The yields of this anionic synthesis are quantitative, and if certain critical precautions are observed, such as the rigid purification of both monomers and solvent, it is then possible to prepare polymers of extremely narrow molecular weight distribution.

Chain length distribution of the Poisson type for termination free polymerization in the case of ethylene oxide, was first recognised in 1940 by Flory[3]. The application to monomers of the styrene type was carried out in 1956 by Szwarc[2], using the initiator sodium naphthalene. Many of the properties of sodium naphthalene had been investigated some years before by Scott,[4,5] who found that coloured complexes of sodium and aromatic hydrocarbons in suitable solvents could initiate the polymerization of conjugated hydrocarbons like styrene, butadiene and cyclopentadiene.

Szwarc[2] postulated an electron transfer process for this unique polymerization process. In the case of styrene monomer and sodium naphthalene initiator, this has been represented as,

$$\text{Naphthalene}^- + \text{Styrene} \longrightarrow \text{Styrene}^- + \text{Naphthalene} \quad (1\text{-III})$$

The negative monomer ions, however, may be represented by two equivalent forms,

$$:CHX - CH_2\cdot \qquad (2\text{-}III) \qquad \cdot CHX - CH_2: \qquad (3\text{-}III)$$

where X is the aryl group.

Thus both ends of (2-III) or (3-III) can cause the propagation of polymerization; one by a radical mechanism, the other by a carbanion process. Szwarc[2] postulated that after the addition of the first monomer unit to either end, structures (2-III) and (3-III) become true ion radicals; an actual separation of electrons takes place and a new species (4-III) is formed.

$$:CHX - CH_2 - CHX - CH_2\cdot \quad \text{or} \quad :CHX - CH_2 - CH_2 - CHX\cdot \qquad (4\text{-}III)$$

At low temperatures the radical ends dimerize, forming the species (5-III).

$$:CHX - CH_2 - CH_2 - CHX: \qquad (5\text{-}III)$$

Since there is little likelihood of termination under the conditions of the propagation, polymerization continues until all the monomer is consumed and a 'living polymer' is produced.

Szwarc[6] showed that the number average molecular weight of the 'living polymers' could be determined by the equation,

$$\overline{M_N} = \frac{\text{Monomer (in grams)}}{\frac{1}{2}[\text{Initiator}]} \qquad (6\text{-}III)$$

Equation (6-III) has subsequently been verified by several authors.[7,8]

The preparation of polymers with a predetermined molecular weight is therefore feasible using this technique. The fact that the polymer remains unterminated under the appropriate experimental conditions, introduces the possibility of being able to polymerize a second monomer. Block copolymers of styrene and isoprene, styrene and butadiene, styrene and methyl methacrylate, and styrene and acrylonitrile have been prepared[9-11] using this technique. Although the preparation of monodisperse polymer using the above technique is feasible, in practice, the realization is often extremely difficult.

The original work of Szwarc[2,6] has recently been criticized by Wenger,[7,12] the main basis of Wenger's criticism being that on detailed analysis it was found that on the slow addition of styrene monomer to sodium naphthalene in tetrahydrofuran at -78°C, the initiator was found to be consumed only gradually over an extended monomer addition time. This behaviour of the initiator violates one of the requirements for the synthesis of a monodisperse polymer. Polymers prepared by Wenger[7] under these conditions had $\overline{M_W}/\overline{M_N}$ ratios of between 2.5 and 4, and thus claims that the $\overline{M_W}/\overline{M_N}$ ratios of 1.06, 1.12 and 1.06 for three samples of polystyrene prepared by Szwarc[6], are inconsistent with the presented data. Szwarc[13] has pointed out, however, that sodium naphthalene is not completely soluble in tetrahydrofuran at -78°C and hence polymers of extremely narrow molecular weight distribution would be difficult to prepare at this temperature. As a result of his findings, Wenger[7] has suggested a two stage polymerization synthesis for sodium naphthalene and styrene. The sodium naphthalene is reacted completely with a small amount of monomer at an elevated temperature, 0°C. The system is then cooled to the polymerization temperature, -78°C, and the rest of the monomer added. The choice of a polymerization temperature being such that the depropagation reaction is negligible. Wenger[7] claims to have prepared polymer of narrow molecular weight distribution employing this technique.

The two stage polymerization technique can be avoided if, as Wenger[7] has shown, a more electronegative initiator is used. Sodium biphenyl was thus chosen by Wenger[7], and in a one step polymerization process found to produce polystyrene of very narrow molecular weight distribution. Wenger[7] argued that in order to produce a system that would yield homogeneous polymers of predictable molecular weight, then the equilibrium of the initiation step, which is assumed to be an electron transfer reaction, must be shifted to the right quickly and completely. If $\bar{I}$ denotes a negative aromatic hydrocarbon and $\bar{S}$ a styrene radical ion, then the initiation step is represented by (7-III) of Wengers[12] scheme.

$$\bar{I} + S \rightleftharpoons I + \bar{S} \tag{7-III}$$

$$\bar{S} + S \rightleftharpoons {}^{\bullet}S - \bar{S} \tag{8-III}$$

$$\bar{S} + \bar{S} \rightarrow \bar{S} - \bar{S} \tag{9-III}$$

$$2\,{}^{\bullet}S - \bar{S} \rightarrow \bar{S} - S_2 - S \tag{10-III}$$

$$\bar{S} + {}^{\bullet}S - \bar{S} \rightarrow \bar{S} - \bar{S} + S \tag{11-III}$$

$$I + {}^{\bullet}S - \bar{S} \rightarrow \bar{S} - \bar{S} + I \tag{12-III}$$

$$\bar{S} - Sn - \bar{S} + S \rightarrow \bar{S} - Sn{+}1 - \bar{S} \tag{13-III}$$

The radical anions are assumed to disappear either by recombination (9-III) and (10-III) or by an electron transfer step (11-III) and (12-III), after at least one monomer unit has been added to give dianions (8-III). The propagation step is the addition of monomer to dianions (13-III).

In order to simplify the reaction scheme Wenger[12] has assumed that recombination as well as electron transfer involves the dimeric radical anion only. It is also assumed that at least some of the radical anions will grow anionically before either of the radical termination reactions occur. The original reaction scheme proposed by Wenger[7] has been altered as a result of Szwarcs[13] criticism. In view of Wengers findings it was decided that sodium biphenyl was the better initiator both from a point of view of solubility and electronegativity.

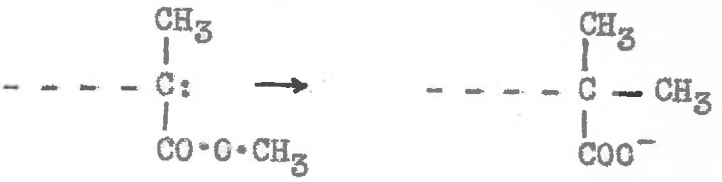
b) The effect of impurity and the method of monomer addition on the homogeneity of the resulting anionic polymer.

It was essential that the polystyrene prepared in the first stage of the block copolymer synthesis should be monodisperse. If the 'living polystyrene' is heterogeneous then the resulting block copolymer will show wide dispersity of molecular weight and composition. Two important factors control the heterogeneity of the polystyrene, (a) the level of impurity in both solvent and monomer, and (b) the method of monomer addition. The effect of impurities on the molecular weight distribution of anionic polymers has been exhaustively treated by several authors.[14-17] Orofino and Wenger[16] point out that in the case of mono- and bifunctional anionic polymers the molecular weight distribution will broaden with increasing impurity in the monomer supply. The molecular weight distribution for the monofunctional anionic polymer will be narrower than the bifunctional polymer, for corresponding levels of impurity content. Orofino and Wenger[16] distinguish between batch polymerisations, where initiator and monomer are mixed in a single operation and continuous monomer addition polymerizations, in which monomer is added gradually (e.g. from the gas phase[7]) to the initiator solution. On the basis of these findings,[16] it appears that it is extremely critical to reduce the level of impurities in both monomer and solvent to a minimum. If the reaction is fast, then a bifunctional initiator should be used and the monomer should be added to the initiator slowly and preferably from the gas phase.

c) The addition of methyl methacrylate to 'living polystyrene'.

Although the attainment of monodisperse polystyrene in the first stage of the synthesis is possible, it is important that the addition of the methyl methacrylate to the 'living polystyrene' be similarly controlled, so that a block copolymer of uniform molecular weight and composition is formed. The precautions taken for the purification of styrene monomer must be applied to the methyl methacrylate monomer.

It was originally[9] postulated that when methyl methacrylate was added to 'living polystyrene', the termination of the reaction was brought about by a rapid self-terminating mechanism of the methyl methacrylate. The termination mechanism was assumed to be,



$$---- \overset{CH_3}{\underset{CO \cdot O \cdot CH_3}{C:}} \longrightarrow ---- \overset{CH_3}{\underset{COO^-}{C}} - CH_3 \qquad (14\text{-}III)$$

where an intermolecular reaction for polymethyl methacrylate is assumed to take place.

Careful investigation by Wenger[18] into the polymerization of methyl methacrylate by sodium naphthalene failed to confirm the postulated,[9] rapid, self-terminating reaction. If particular care is taken in the purification of monomer and solvent, then 'living polymethyl methacrylate' can be prepared. Evidence to support this claim[18] has been reported by several authors,[19-21] who have obtained results to show that self-termination of polymethyl methacrylate is slow at low temperatures. Rempp and co-workers[20] suggest that when the reaction is carried out at a low temperature (-60 to -78°C) and subsequently warmed to room temperature, polymethyl methacrylate can be obtained without deactivation taking place. Rempp and co-workers[20] found no evidence for deactivation, but if rearrangement of methyl methacrylate were to take place, as suggested by Szwarc,[9] then it would be dependent on the temperature and the concentration of carbanions present in solution. Perhaps the main difficulty in preparing 'active' polymethyl methacrylate lies in the preliminary purification of the monomer. It has been pointed out previously,[20] that methyl methacrylate is an extremely difficult monomer to obtain free from moisture. Care in purification and in particular careful drying is thus required.

d) Discussion.

Consequently to prepare a block copolymer of styrene and methyl methacrylate, which is uniform in molecular weight and composition, using the anionic method of synthesis, requires skilful handling and rigorous control of impurities in both solvent and monomers. The purging process, originally introduced by Wenger,[22] in which a small amount of initiator is reacted with the styrene monomer until the red colour of the styryl ions is noted to slowly disappear, is perhaps the best way of reducing the impurity level in the monomer to a minimum.

The addition of the styrene monomer to the initiator must then be carefully controlled to ensure that the right conditions exist. If the reaction is fast, as is the case with sodium biphenyl in tetrahydrofuran, then the monomer should be added slowly and continuously, preferably from the vapour phase.

The addition of the methyl methacrylate monomer to the 'living polystyrene' must also be carefully controlled. After rigorous purification, the addition of methyl methacrylate should be carried out at a low temperature (-60 to -78°C). After allowing sufficient time for chain growth, the polymer should then be allowed to warm to room temperature and left for approximately an hour. This technique[20] then ensures that deactivation of the methyl methacrylate does not occur and hence greater control of chain growth is attained.

2. Preparation of the Block Copolymers used in this Work.

a) Purification of the solvent (Tetrahydrofuran).

Tetrahydrofuran was used as the solvent and this was obtained as a laboratory grade (B.D.H.) reagent. The solvent was first passed through a column of activated chromatographic alumina (B.D.H. grade), which acted as a preliminary drying agent and also helped remove any peroxides present as impurities. The tetrahydrofuran was then refluxed for several hours over sodium wire and finally distilled onto calcium hydride (B.D.H. grade). The solvent was then left over calcium hydride for 24 hours and then distilled onto freshly prepared sodium wire and biphenyl (B.D.H. grade). Refluxing of the solvent was then continued over the sodium wire and biphenyl until the blue colour characteristic of sodium biphenyl appeared. The tetrahydrofuran was then distilled from the sodium biphenyl under dry nitrogen pressure into storage bulbs of 500 ml. capacity, which were transferred to the vacuum line, where the solvent was degassed, and evacuated to approximately 1 x 10^{-5} mm. pressure of mercury. Before use, all storage bulbs were thoroughly 'baked' on the vacuum line.

The biphenyl (B.D.H. grade) was carefully recrystallized from purified diethyl ether and dried in a vacuum dessicator over phosphorus pentoxide before use. Freshly cut sodium and the dried, recrystallized biphenyl were placed in storage bulbs on the vacuum line and evacuated to approximately 1 x 10^{-5} mm. Hg. It was found necessary to cool the storage bulb to stop sublimation of the biphenyl. The purified tetrahydrofuran was then distilled onto the sodium and biphenyl on the vacuum line and left until the blue colour appeared. In some cases the storage flasks were heated in order to melt the sodium and vaporize the biphenyl and hence expose a larger surface area for the action of the solvent. The formation of the blue colour characteristic of the complex occurred almost immediately. The tetrahydrofuran was stored over sodium biphenyl on the vacuum line.

b) Purification of the monomers.

The styrene monomer was obtained from Colonial Sugar Refineries Ltd., and the methyl methacrylate from Imperial Chemical Industries. Both monomers contained a small amount of an inhibitor which was removed by washing with a solution of 10% caustic soda in the ratio 5 monomer to 1 of caustic soda. After removal of the inhibitor, the monomers were thoroughly washed with distilled water to remove excess alkali. Preliminary drying of both monomers was effected by storage over anhydrous sodium sulphate (B.D.H. grade) for 24 hours.

The styrene monomer was then carefully filtered from the sodium sulphate and dried over calcium hydride for a further 24 hours. The styrene was then fractionated under dry nitrogen through an efficient column. The fraction distilling in the range 145.9 - 146.1°C at 760 mm.pressure, was collected in a storage bulb fitted with a vacuum tap and transferred to the vacuum line, where it was degassed three times by alternate freezing and melting. The styrene monomer was finally evacuated to 1 x 10^{-5} mm. Hg. The styrene was then distilled into a second storage bulb on the vacuum line, which contained calcium hydride and left for several hours. The styrene was again distilled from the calcium hydride to a third storage bulb, also containing calcium hydride. This storage bulb, which was fitted with a vacuum tap, was removed from the vacuum line and the styrene stored in the dark at -20°C. Before being used in the preparation to be described the styrene was distilled from the storage bulb on the vacuum line onto freshly activated Linde molecular sieves, type 5 A (B.D.H. grade). The molecular sieves were activated by heating to approximately 150°C in a round bottom flask under continuous pumping from the vacuum line pump. After leaving over molecular sieves for several hours the styrene was finally distilled onto calcium hydride once more, ready to be distilled into the reaction vessel.

The methyl methacrylate monomer was also carefully filtered from the preliminary drying agent (sodium sulphate) and dried for 24 hours over calcium hydride. On fractionation, the portion distilling in the range 99.8 - 100.1°C at 760 mm. Hg was collected and dried in the same manner as the styrene monomer above.

c) Preparation of the initiator.

The apparatus for preparing the initiator (sodium biphenyl) for the polymerization is shown in Fig.(1-III). Before assembly, the complete apparatus was thoroughly cleaned in chromic acid solution, rinsed with distilled water several times, and finally dried in a vacuum oven at 80°C for 24 hours. On assembly, the apparatus was baked on the vacuum line by heating, together with continuous pumping of the vacuum pump. A stock solution of purified biphenyl (section a) this Chapter) was prepared in purified tetrahydrofuran (T.H.F.). This solution contained 0.0860 grams of biphenyl in 100 mls. of T.H.F. 20 mls. of this solution (0.0172 grams of biphenyl) were then introduced into section A of the apparatus Fig.(1-III). Section C of Fig.(1-III) was actually attached to section A at B - B^1, but has been separated for convenience in Fig.(1-III). The complete apparatus was sealed off to the atmosphere and the T.H.F. very carefully distilled from the biphenyl contained in

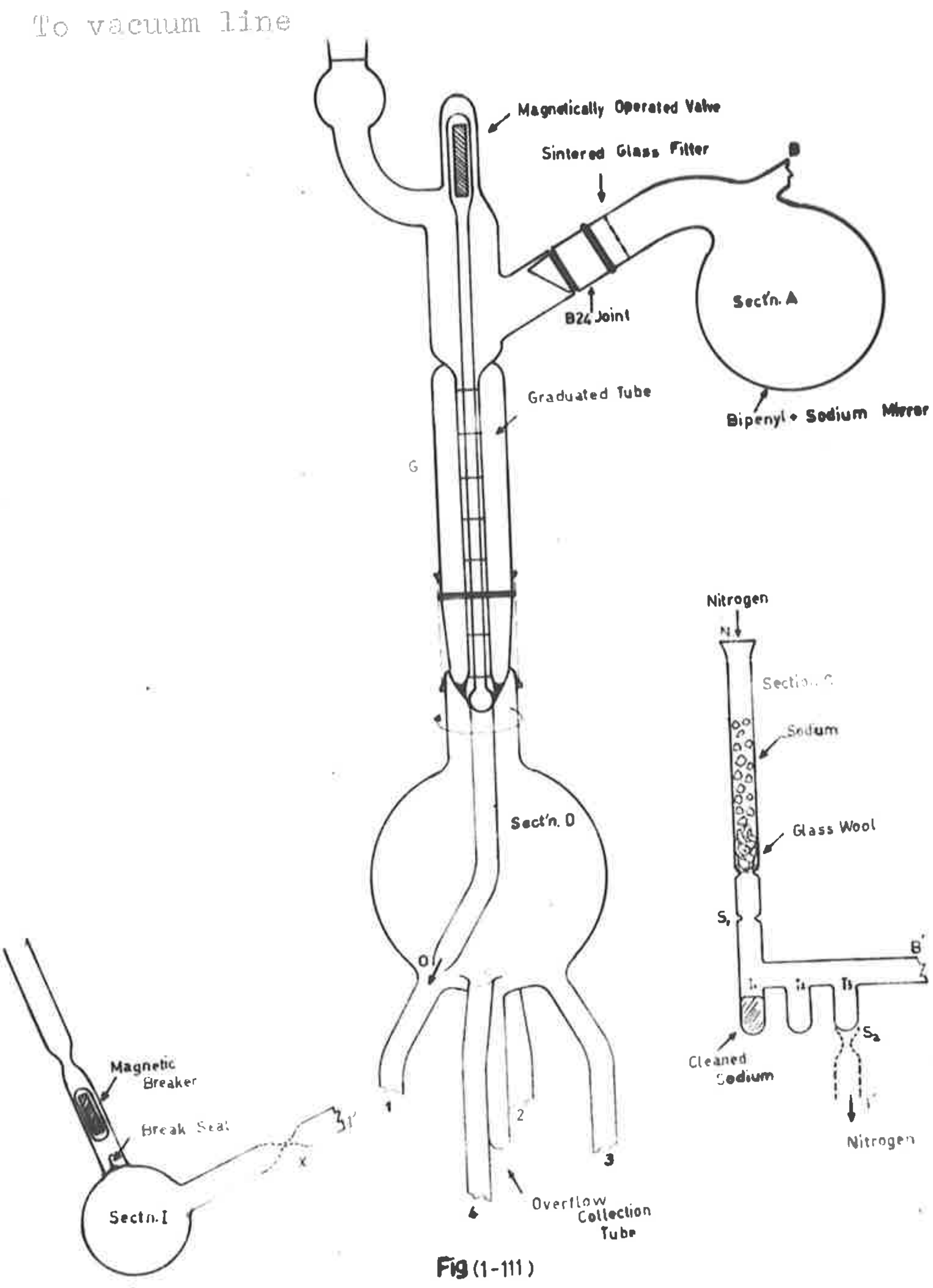


Fig (1-111)

Fig.(1-III). The apparatus for preparing the initiator samples.

section A. Section A was cooled in an ice-water bath and the air ballast pump used to remove the T.H.F. Dry, oxygen free nitrogen was then introduced into the apparatus at N, of section C. Sodium was then added to section C through N, under a continuous stream of nitrogen. Before being added to the apparatus the sodium (B.D.H. grade) was carefully purified. It was heated in toluene (B.D.H. grade) for several hours at 95°C to help remove the oxide film and any excess paraffin absorbed during storage. The sodium was filtered under toluene and quickly removed to the vacuum line, where the air ballast pump removed the last traces of solvent. The sodium was stored on the line under high vacuum. Approximately 1 to 2 grams of sodium were introduced through N into section C. The tube containing the sodium in section C was then heated. When the sodium melted, the nitrogen pressure was slightly increased and the molten sodium forced through the glass wool insert in C. The glass wool acted as a filter and helped remove any oxide formed on the sodium during previous handling processes. Having forced the cleaned sodium into tube T_1 of section C, the nitrogen pressure was stopped and section C sealed off at S1 and S2. S2 acted as a by-pass for the nitrogen.

The whole apparatus was then evacuated, care being taken not to sublime the biphenyl in section A. This was achieved by cooling. Having evacuated the whole apparatus to approximately 1×10^{-5} mm Hg the sodium in T_1 of section C was carefully distilled into section A. This was accomplished by cooling section A to liquid air temperature and heating the sodium to above its melting point. The sodium slowly distilled into the tubes T1, T2 and T3 and finally into section A, where a bright mirror formed on the walls of the vessel. The traps T1, T2 and T3 were included in the apparatus to help control the distilling of the sodium, and trap oxide film not completely removed by the filtering process. When excess sodium had been distilled into section A, the section C assembly was sealed off at B under vacuum.

Purified tetrahydrofuran, which had been standing over sodium biphenyl under high vacuum, was then slowly distilled into section A. The blue colour characteristic of sodium biphenyl immediately appeared. After the addition of 120 mls. of T.H.F. the distillation was stopped. The initiator was then left at 0°C for approximately an hour, then gradually allowed to rise to room temperature. The apparatus was continually kept under high vacuum. After allowing sufficient time for the sodium and biphenyl to react completely, section A was slowly rotated and initiator allowed to slowly filter through a coarse sintered glass frit into the graduated tube, G. The graduated tube G was fitted with a magnetically operated glass valve and had a capacity of 20 ml (with the valve in position). On opening the valve, initiator solution slowly ran through the opening O, into a storage bulb, as shown in section I of Fig. (1-III). The initiator storage bulb was fitted with a break-seal and magnetic breaker at one end and was attached to section D at the other. Three similar vessels were attached to section D at the remaining positions, 2, 3 and 4. After the addition of 30 mls of the initiator solution, section I was carefully sealed off and removed from section D. The sealing off process was achieved under high vacuum, whilst cooling section A and section I to liquid air temperature to stop distillation of the solvent. Section D was then rotated, so that the opening at O was now over a second initiator storage bulb at position 2. The above process was repeated and a second 30 ml. of initiator solution obtained. This process was repeated for all four storage bulbs. The advantage of this technique was that four identical samples of initiator could be prepared and removed from the reaction vessel, without fear of contamination from the atmosphere. It was thus possible to keep the initiator concentration constant and vary the quantity of monomer, to obtain samples of differing molecular weight in accordance with equation (6-III)

d) Preparation of the block copolymers from the unterminated polystyrene.

i) <u>The apparatus</u> for preparing the block copolymers is shown diagrammatically in Fig.(2-III). The design was such that it was possible to prepare the parent 'living polystyrene' and also carry out the addition of the methyl methacrylate, without having to remove any of the reactants from the vessel. The apparatus was so constructed that it was possible to carry out all phases of the preparation under high vacuum and therefore without fear of contamination from the atmosphere. The apparatus was carefully 'baked' out on the vacuum line before the addition of the reactants and the use of break-seals in the main body of the apparatus avoided the possible contamination from vacuum tap grease.

ii) <u>The preparation procedure</u>. Section I (Fig.(1-III)) containing the initiator sodium biphenyl, was carefully sealed onto the apparatus at I^1 (Fig.(2-III)). Prepurified methyl methacrylate, which had been standing over calcium hydride on the vacuum line, was distilled into a preparation storage bulb, section MMA Fig. (2-III). Purified T.H.F., which had been standing over sodium biphenyl, was also distilled into section MMA and the bulb removed from the vacuum line at X. Section MMA, containing the methyl methacrylate and T.H.F., was then

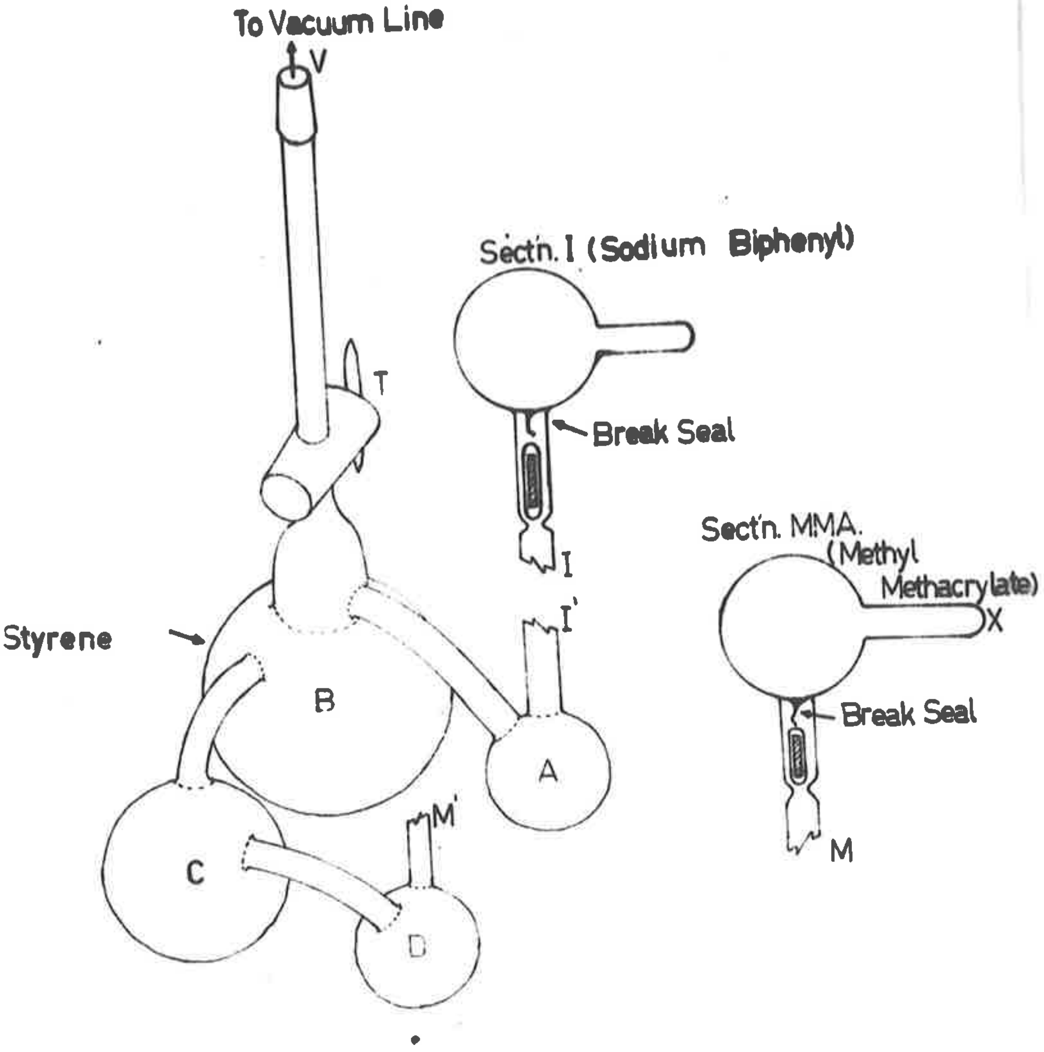


Fig.(2-III). Apparatus for preparing the parent polystyrene and block copolymer samples.

carefully sealed onto the preparation apparatus at M^1 Fig.(2-III). The whole apparatus was then evacuated to high vacuum (1×10^{-5} mm. Hg) and carefully 'baked' on the vacuum line for 15 minutes. Purified styrene, which had been stored over calcium hydride on the vacuum line, together with T.H.F., was then distilled into bulb B. After thorough evacuation to 1×10^{-5} mm. Hg the apparatus (Fig.2-III) was removed from the vacuum line, after closing stopcock T. The bulbs B and A were cooled to 0°C and when temperature equilibrium had been attained, the break-seal of section I was broken and the initiator carefully run into bulb A. The styrene monomer was then purged with a very small amount of the sodium biphenyl from A. This was done by adding very small increments of the initiator to the styrene monomer, until the red colour due to the styryl ions was noted to disappear very slowly. At this stage it was deemed that the impurity level in the monomer had been reduced to a minimum. After allowing sufficient time for all the impurities to be used up, a small amount of the purged styrene monomer was distilled into bulb A. The initiator immediately changed colour from blue to the red colour characteristic of the styrene anions. Having initiated the polymerization, the solution of short chain polystyryl ions in bulb A was left at 0°C for approximately 15 minutes. The bulbs A and B were then cooled to -78°C in an alcohol dry ice bath and the styrene monomer added slowly to bulb A. The apparatus was continually swirled to ensure mixing of initiated solution and monomer. The styrene monomer was added slowly and continuously over a period of about 1 hour.

After completion of the polymerization the newly formed 'living polystyrene' was divided into two sections. Half of the active polymer was carefully run into bulb C and the remainder left in bulb A. Bulbs A, C and D were all cooled to -78°C. After cooling the methyl methacrylate and T.H.F. in section MMA to -78°C, the break-seal was opened and the contents carefully added to bulb D. The methyl methacrylate in T.H.F. from D was then added to the active polystyrene in bulb C, at -78°C. Swirling of the apparatus ensured mixing of the 'living polystyrene' and the added methyl methacrylate. On addition of the methyl methacrylate, the red colour due to the polystyryl ions disappeared. The contents of bulb C were left at -78°C for approximately 30 minutes and then allowed to warm to room temperature. The apparatus containing the polymers was left under vacuum at room temperature for a further 30 minutes. The above process was carried out to ensure that chain end deactivation of the polymethyl methacrylate did not occur. During this period the parent polystyrene in bulb A remained active. Termination of the polymeric species in the apparatus was effected by allowing the entry of air. Both polymer samples were then carefully removed and added separately to a large excess of methanol.

The preparation procedure described above allowed not only the preparation and isolation of a block copolymer sample, but also the parent polystyrene used in its synthesis. The preparation of four such block copolymers was carried out using the above technique. In each case the concentration of the initiator was kept constant, but the quantity of monomer was varied in order to obtain species of differing molecular weight and composition. The various monomer and initiator concentrations for each preparation are listed in Table (1-III).

Table (1-III). The initiator concentration and the concentration of monomers, expressed in grams/litre, together with the total polymer yield for the preparation of block copolymer samples B1, B2, B3 and B4.

Sample	Moles of Initiator	(Styrene) g/l	(MMA) g/l	(Yield)%
B1	0.280×10^{-4}	13.3	13.3	93
B2	"	15.0	10.0	94
B3	"	23.5	13.3	93
B4	"	22.5	10.0	94

The total polymer yield for each preparation was not quite quantitative as shown in Table (1-III). All polymer samples were thoroughly washed in a large excess of methanol and finally dried in a vacuum oven at 60°C. The samples of polystyrene (PS1, PS2, PS3 and PS4) together with the block copolymer samples (B1, B2, B3 and B4) were then dissolved in benzene (A.R. grade) filtered through a No. 3 sintered glass filter and finally recovered by freeze-drying.[23] The polymer samples were again dried in a vacuum oven for 5 hours at 60°C.

3. Removal of Homopolymer Impurity from the Block Copolymer.

a) Selective Extraction.

The removal of homopolymer from a block copolymer may be carried out using a number of varying techniques, a summary of which has recently been published by Ceresa.[24,25] Perhaps the most widely used of these techniques is selective extraction. Selective extraction of a block copolymer is only possible when two solvents are available, such that each solvent dissolves only one of the polymeric species, being a non-solvent for the other. Both solvents must be non-solvents for the block copolymer. Szwarc[6] has suggested that homopolymer can be removed from the block copolymer of styrene and methyl methacrylate by extraction, firstly with cyclohexane and then followed by acetonitrile. Cyclohexane is a solvent for polystyrene and acetonitrile a solvent for polymethyl methacrylate. This method of extraction was adopted in this work using a soxhlet extraction apparatus. The finely divided polymer, obtained by freeze-drying from benzene, was first extracted with cyclohexane (B.D.H. grade), to remove the polystyrene. The extraction was carried out continuously for approximately 96 hours, fresh solvent being used after 48 hours. The polymer remaining in the extraction thimble was then extracted with hot benzene (B.D.H. grade) and the polymer recovered by freeze-drying. The finely divided polymer was then extracted for a further 96 hours with acetonitrile (B.D.H. grade) to remove the free polymethyl methacrylate. The polymer remaining in the thimble was again extracted with hot benzene (B.D.H. grade) and recovered by freeze-drying. To test the efficiency of the extraction technique the block copolymer samples were subjected to a turbidimetric titration. A description of the principles involved, the apparatus and the information obtainable from this technique are described in Chapters IV and V. Very briefly, the method is based on the fact that the solubility of the block copolymer lies somewhere between that of the parent homopolymers. Non solvent is added to a solution of the block copolymer and scattered light used to 'weigh' the species precipitated from solution. The method offers an excellent means of detecting not only homopolymer present in a block copolymer, but also the amount of each species present. The turbidimetric titration curve of block copolymer sample B4 is shown in Fig.(3-III). The ratio of the scattered light at 90° and the transmitted light has been plotted against the volume of non-solvent added, γ. The actual value of (i_{90}/I_t) meas. has been normalized to the extent that at complete precipitation the value of (i_{90}/I_t) meas. has been put equal to unity. From the titration curve it can

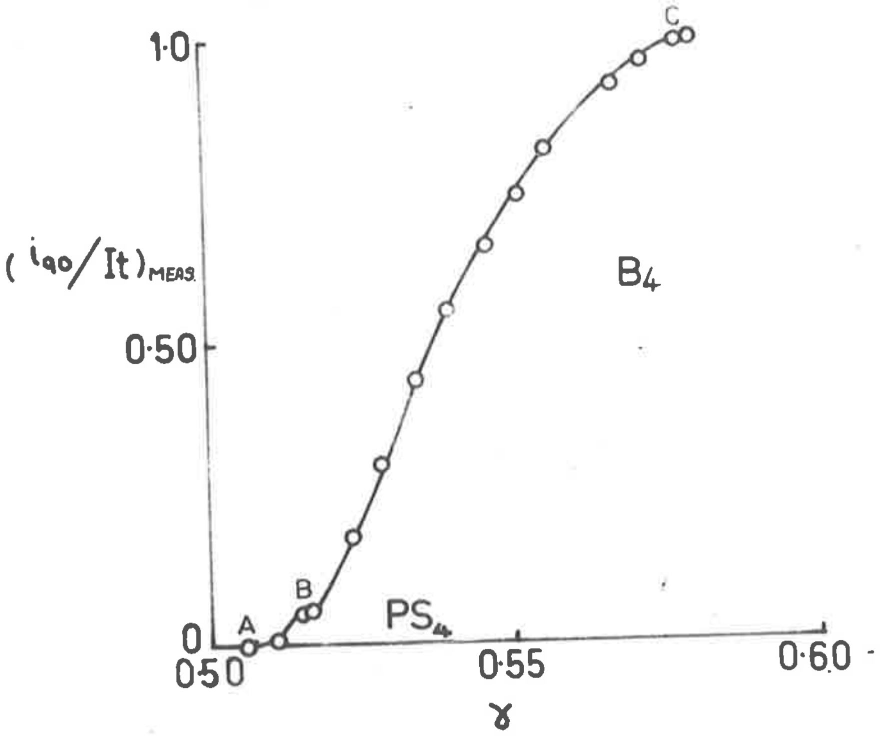


Fig.(3-III). Turbidimetric titration curve for block copolymer B4 in the butanone-isopropanol system. Curve shows the presence of a small amount of homopolymer PS4.

be seen that a small amount of polystyrene is still present with the block copolymer. The polystyrene is precipitated in the region A - B and the block copolymer in the region B - C. The amount of polystyrene present is approximately 5%. Thus the extraction technique did not completely remove the free polystyrene. Polymethyl methacrylate was not detected.

It has been suggested[26] that dimethyl sulphoxide and carbon disulphide are better extraction solvents for removing free polymethyl methacrylate and polystyrene respectively from the block copolymer. Unfortunately, dimethyl sulphoxide can only be used in the cold as it decomposes on heating. Graham, Dunkelberger and Cohn[19] suggest cyclohexane containing 10% benzene for efficient removal of free polystyrene from the block copolymer. However, it seems essential to combine selective extraction with an independent method, in order to obtain efficient removal of all homopolymer impurity from the block copolymer. Selective precipitation seems by far the better technique.

b) Selective precipitation.

The technique is very similar to fractional precipitation and the method has been described in detail by Ceresa.[24,25] The block copolymer samples were dissolved in benzene (A.R. grade) to give a 2% solution, which was diluted with an equal volume of acetone (A.R. grade). Petroleum ether (B.D.H. grade b.p. 60 - 80°C) was then added slowly to the solution with continuous stirring. Care was needed in the control of the stirring rate to ensure a minimum of turbulence. As the ratio of volume of precipitant to volume of solution approached 0.80 the rate of addition of the petroleum ether was controlled, such that after 2 ml. addition intervals the precipitation was stopped, and the contents of the titration flask centrifuged for 15 minutes at 5,000 g. All fractions were centrifuged in a Servall SS-1 angle head centrifuge, using stainless steel tubes. The supernatant solution was removed from the centrifuge tubes, and the titration continued at 1 ml. intervals until a point was reached such that further addition of petroleum ether produced no further precipitation of polymer. At this stage free polymethyl methacrylate had been removed from the block copolymer, leaving free polystyrene and block copolymer in solution. This point corresponded to a ratio of precipitant to solvent of 0.98. The precipitated polymer was extracted from the centrifuge tubes with benzene and recovered by freeze-drying. After drying for 3 hours in a vacuum oven at 60°C, the recovered polymer was examined for purity, using the ultra-violet spectrographic method (to be described in this Chapter). The amount of polymer recovered was only of the order of 2% of the total and showed an average purity of about 98% in the four samples examined.

The free polystyrene and block copolymer mixture was recovered from the solution by freeze-drying. After drying in a vacuum oven at 60°C for two hours the polymer mixture was dissolved in benzene (A.R. grade) to give a 2% solution and diluted with an equal volume of chlorobenzene (B.D.H. grade). Methanol (B.D.H. grade), which had been dried over calcium chloride and fractionally distilled, was then added slowly with careful stirring to the polymer solution. As the ratio of precipitant to solution approached 0.80 the methanol was added in 2 ml. and finally 1 ml. intervals, centrifuging the solution after each addition. The centrifugate was left in the centrifuge tube each time and the supernatant carefully removed with a dry, clean pipette. The titration was continued until a point was reached where no further precipitation took place. The free polystyrene was recovered from the centrifuge cells by extraction with benzene and finally recovered by freeze-drying. Examination of the recovered polystyrene, after drying in a vacuum oven for 2 hours at 60°C, showed a purity of approximately 97% in the four samples examined. The amount of polystyrene recovered showed a maximum of 5% in the case of block copolymer sample B4. The amount of free polymethyl methacrylate and free polystyrene recovered from each block copolymer sample was very small and only enough material was available for one examination in each case.

The block copolymer samples were recovered from the benzene-chlorobenzene-methanol mixture by slow evaporation, then finally precipitation into a large excess of a water-methanol mixture. After recovery, the block copolymer samples were dried in a vacuum oven for 3 hours at 60°C. The samples were then dissolved in benzene and recovered by freeze-drying, and again dried in the vacuum oven for 3 hours at 60°C.

4. Characterization of the Block Copolymer Samples.

a) After removal of the homopolymer the block copolymers were again subjected to the turbidimetric titration analysis. The detailed investigation is discussed in Chapter V. Analysis showed the block copolymers to be free from polystyrene and polymethyl methacrylate. The block copolymer samples were also shown not to be purely mechanical mixtures of polystyrene and polymethyl methacrylate. This was achieved by the titration of a mixture of polystyrene, block copolymer and polymethyl methacrylate. The examination of the titration curve showed the precipitation of three distinct species, whose precipitation point could be located by examination of each species separately. The detailed analysis of this investigation is also discussed in Chapter V.

b) The analysis of the block copolymer samples for percentage polystyrene and polymethyl methacrylate was carried out using: i) ultra-violet absorptiometry, ii) direct oxygen determination, and iii) the ratio of the number-average molecular weights for polystyrene and the block copolymer.

The ultra-violet absorptiometry method is perhaps the most reliable and the most convenient of the above techniques.

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

$$K = xK_S + (1 - x)K_M \qquad (15\text{-III})$$

For a mixture of polystyrene and polymethyl methacrylate

$$K = \frac{\text{Optical density at 2620 Å}}{\text{cell length (cm) x conc.(g/l)}} \qquad (16\text{-III})$$

K_S is the specific extinction coefficient for polystyrene, K_M for polymethyl methacrylate, and x is the weight fraction of polystyrene. Chloroform (A.R. grade) was used as solvent and the optical density readings were measured in a Unicam SP 500 spectrophotometer.

The use of the direct oxygen determination for the analysis of the block copolymer samples was used as a check on the U.V. technique. Polystyrene does not contain oxygen, whereas polymethyl methacrylate contains 32%. Thus the percentage oxygen in the copolymer is given by,

$$O\% = 32(1 - x) \qquad (17\text{-III})$$

where x is the weight fraction of polystyrene in equation (15-III) above. The oxygen determination of the block copolymer samples was carried out by Dr. K. W. Zimmermann of the Chemistry Department of the University of Melbourne.

The number average molecular weights can also be used to determine the percentage polystyrene present in the block copolymer. The method of preparation allowed the isolation of the polystyrene prepared in the first stage of the synthesis. Thus the ratio of the number average molecular weight for the polystyrene to that measured for the block copolymer gives the percentage polystyrene present. The analysis by all three methods is given in Table (2-III) below.

Table (2-III). The analysis of the block copolymer samples expressed as a percentage of polystyrene present.

Sample	U.V.analysis	O-determination	Osmotic pressure
B1	15.1	16.7	13.0
B2	30.2	32.8	29.8
B3	38.1	39.4	37.8
B4	52.1	54.1	51.9

The percentage polystyrene determined by the U.V. method was used in all subsequent calculations. The method is convenient and quick and does not suffer from some of the disadvantages connected with combustion analysis and the extrapolation of osmotic pressure readings.

Discussion.

Four block copolymer samples (B1, B2, B3 and B4) were prepared by a technique designed to give control of the heterogeneity of chain length and composition. The technique of preparation also allowed for the isolation of the four polystyrene samples (PS1, PS2, PS3 and PS4) used in the synthesis of each block copolymer. The four block copolymer samples were found to be contaminated by small amounts of homopolymer impurity, the removal of which was carefully controlled by the technique of turbidimetric titration.

The block copolymers were shown to be pure polymers and not mechanical mixtures of the parent homopolymers (Chapter V). The analysis of each sample was carried out using three separate techniques to determine the percentage polystyrene and polymethyl methacrylate present. The three methods gave results, which within experimental error, compared favourably with each other. It was concluded that the preparation and analysis were completely satisfactory and that four well characterized samples of polystyrene-polymethyl methacrylate block copolymer had been prepared.

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CHAPTER IV.

The Automatic Turbidimetric Titration Apparatus.

CHAPTER IV.

1. Introduction.

The turbidimetric titration apparatus was designed and built, firstly to act as a critical analytical check on the homogeneity of the block copolymer samples and of the parent polystyrenes used in the first stage of the block copolymer synthesis. Secondly, the instrument was developed to determine quantitatively the molecular weight and molecular weight distribution.

The method of turbidimetric titration offers an excellent means of detecting small traces of homopolymer[1,2] present as an impurity with the block copolymer. The complete removal of all homopolymer from the block copolymers is essential before making a detailed study of dilute solution behaviour. The method of turbidimetric titration also offers a quick and reliable means of effecting the fractionation of a polymeric species. Kilb and Bueche[3] have suggested that the fractionation of a block copolymer will not be a function of the overall molecular weight of the polymer. Kilb and Bueche[3] have based their predictions on an extension of the Flory-Huggins[4-7] lattice model to the dilute solution behaviour of block and graft copolymers. Turbidimetric titration offers an efficient and rapid technique for testing the above predictions.

The method has proved to be effective in giving a qualitative guide to the molecular weight distribution of a polymeric species. Careful calibration with polymers of known molecular weight and narrow distribution can lead to the construction of a quantitative molecular weight distribution curve for a polymer of the same species. In practice however, the quantitative application of the turbidimetric titration method is often extremely difficult. The polymer and the nature of the solvent-precipitant system can affect markedly the interpretation of the data obtained. The quantitative application is discussed more fully in Chapter V.

Turbidimetric titrations have been used previously to determine the molecular weight distribution of high polymers,[8-14] and for the characterization of block and graft copolymers.[1,2,15]

For the latter purpose the measurement of the intensity of the transmitted light is usually employed and instruments designed specifically for this determination do not give the scattering pattern. For the determination of molecular weight distribution, however, it is necessary to measure the intensity of both the transmitted light and the scattered light at fixed angles.[11,16] Such instruments have the wider application to polymer systems, and are thus to be preferred. The instrument to be described was therefore modelled on the usual principles of light-scattering apparatus for the determination of molecular weight and molecular weight distribution. The instrument employs a photomultiplier, coupled with a suitable mirror optical system, for the measurement of the scattered light at three fixed angles.

It has recently been pointed out[17] that it is essential, when determining the intensities of the scattered light, that experimentally reproducible results be obtained and that resort is not made to a normalizing procedure, which may reduce the apparent error. To achieve reproducibility it is essential to correct for optical effects, dilution and changes in the scattering pattern. Furthermore, it is necessary to control accurately the rate of addition of the non-solvent, the temperature and the rate of stirring, and to be able to observe the scattering pattern during titration.

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

2. Description of the Turbidimeter.

The layout of the instrument is shown diagrammatically in Fig.(1-IV). The original[18] light source was a 250 watt ME/D box-type mercury arc lamp (British Thomson Houston), which operated on 250 volts A.C. mains supply. This lamp has been replaced by a Philips S.P. 500 watt water-cooled mercury arc lamp, which also operates on 250 volts A.C. mains supply. The reason for replacing the original lamp was to eliminate as far as possible fluctuations in light intensity, a characteristic of the Mazda box-type mercury arc lamp. The Philips S.P. 500 mercury arc lamp shows negligible variation in light intensity, although the life-time is considerably less than the Mazda box-type lamp.

To overcome any fluctuations which may occur in the light intensity, a beam-splitter is employed in which a portion of the incident beam is deflected and allowed to fall onto a reference photocell, the output from which controls the slide-wire voltage of the recorder. The efficiency of this system was checked by rapidly varying the voltage applied to the lamp and observing the output voltage from the transmission photocell. It was found that there was no observable change with fluctuations in voltage up to 10%.

Collimation is achieved by adjusting the condenser lens C, so that the image of the mercury arc is in the

Figure (1-IV). Diagrammatic layout of the instrument. L, light source; C, condenser lens; P, pin-hole; A, Achromat lens; F, ZEISS Monochromatic filter; S, S_1, S_2, slits; B.S., beamsplitter; R.P.C., reference photocell; T.P.C., transmission photocell; M, mirrors for deflecting the scattered light at 45, and 135° to photomultiplier; P.M., photomultiplier (11 stage E.M.I. 6097B); L.S., electrically operated light stops.

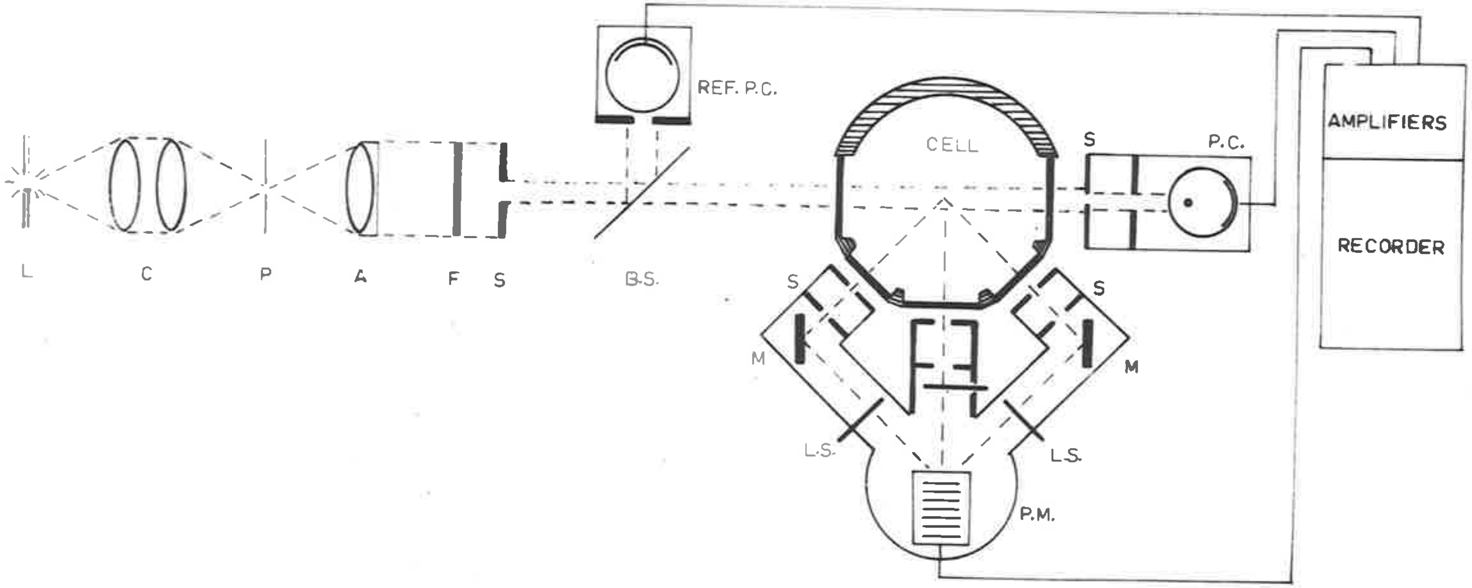


Fig. (1-IV). Diagrammatic layout of the instrument.

plane of the pin-hole P. A mirror is placed in front of the achromat lens A and the lens adjusted to bring the reflected image into the plane of the pin-hole. It was found that a good parallel beam resulted. The beam is then cut to 2.5 mm. x 12 mm. by the slit S_1. The dimensions of the accepted transmission beam are 2.0 mm.x 10 mm. and the accepted scattered beam is 1.5 mm.x 10 mm. The filters F are Zeiss monochromat glass filters for use with mercury and helium light. They are made from several optically constant glasses cemented together with Canada balsam. They transmit a particular wavelength with negligible amounts of unwanted radiation. Gelatine filters were found to be unsatisfactory.

The open type of cell has several disadvantages, notably its large capacity and the difficulty of maintaining proper temperature equilibrium. The totally enclosed constant volume cell described by Oth and Desreux[11] was therefore adopted.

The cell has been fabricated from brass, with optically flat quartz windows set in Woods metal. The inner surface is finished in matt black nickel to avoid stray reflected radiation. A water jacket is included in the walls and base of the cell, and also in the glass-head, as shown in Fig. (2-IV). The metal cell ensures rapid temperature adjustment, and the thermostat maintains the temperature of

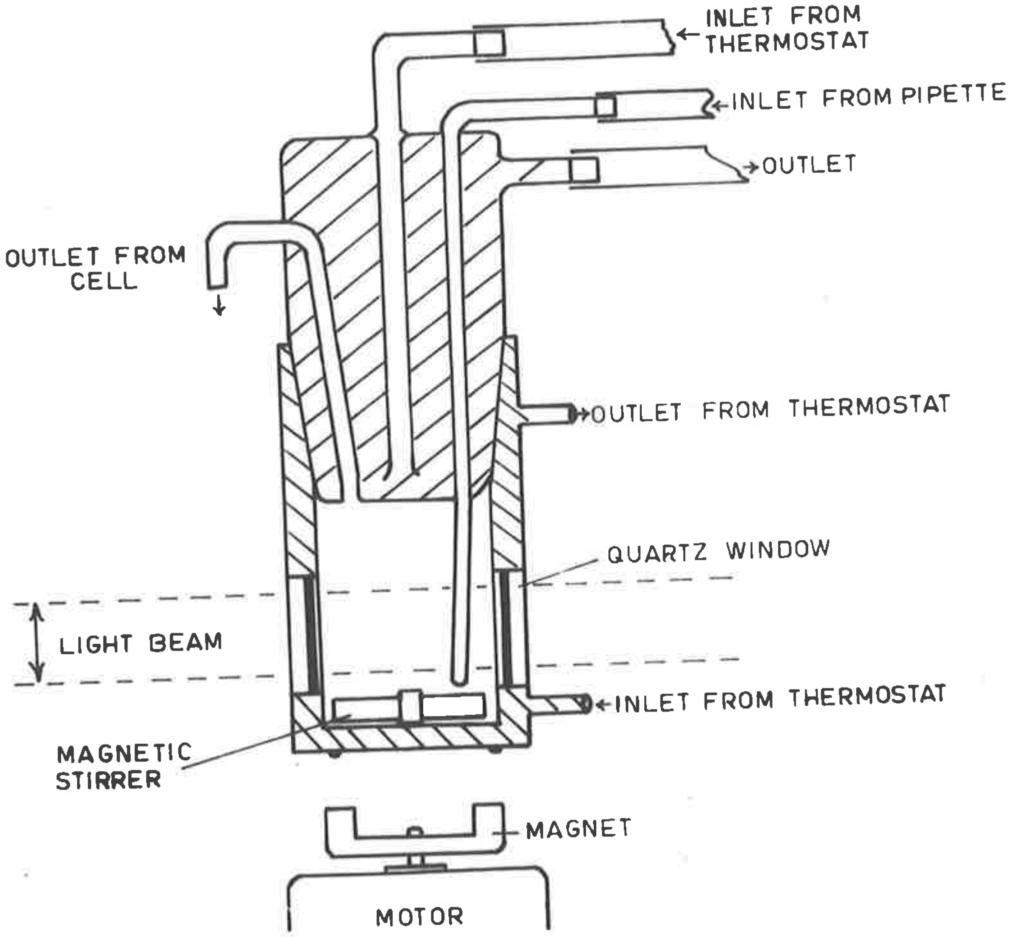


Fig.(2-IV). The constant volume cell fitted with thermostated glass-head.

the cell to within ± 0.02°C during a run. For ease of centralization, three hardened steel pins have been set in the base of the cell, and these pins fit into holes in a plate mounted above the magnetic stirrer motor. The outside of the cell is also fitted with a black polythene jacket for insulation. The cell is insulated from the plate above the stirrer motor by means of a perspex disc. The volume of the cell was taken as the volume with the magnetic stirrer in position, the capillary of the delivery tube sealed off and liquid up to the outlet opening in the glass-head. The volumes of the two cells used in the apparatus were 55.90 ml. and 53.86 ml. These volumes were obtained by direct weighing, using water as the solvent medium. The magnetic stirrer is covered with a Teflon jacket to reduce friction to a minimum and to avoid scratching the inside surface of the cell.

The intensity of the transmitted beam is measured by the photocell, T.P.C. (Fig.(1-IV)). The scattered intensities at the fixed angles, 45, 90 and 135° are measured by the photomultiplier, P.M. (Fig.(1-IV)). Rotation of the cathode about the vertical axis produced no change in the output voltage. A Cambridge multipoint model D.E. recorder, which was modified to suit the amplifiers, records the data. Chart speeds from ½" to 12" per hour can be used. The A.C. amplifiers were designed and built by the Electronics Instrument and Lighting Co., Adelaide, South Australia.

The injection pipette (Fig.(3-IV)) was constructed from 1" diameter precision bore glass tubing. The plunger forces mercury into the vessel containing non-solvent and since it is important that there should be no back-leakage the plunger is fitted with two rubber "O" rings.

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

A variable speed motor mounted below the scattering cell (Fig.(2-IV)) allows a choice of the rate of stirring of the polymer solution. Speeds from 0 to 500 r.p.m. are possible. However, experimentation showed that speeds of 370 r.p.m. could not be exceeded without aggregation of the polymer suspension taking place. The complete instrument is shown in Photo.(1-IV).

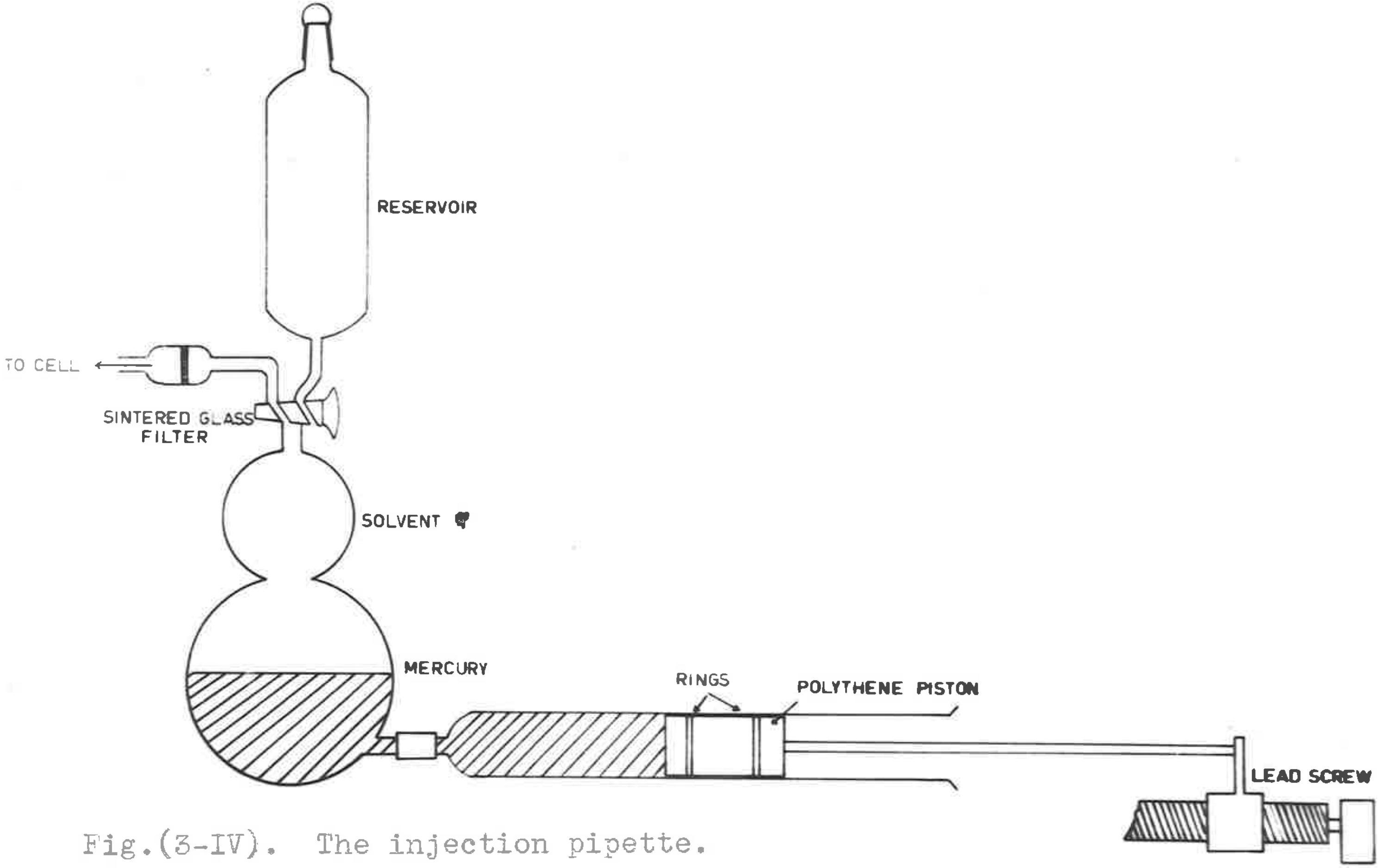
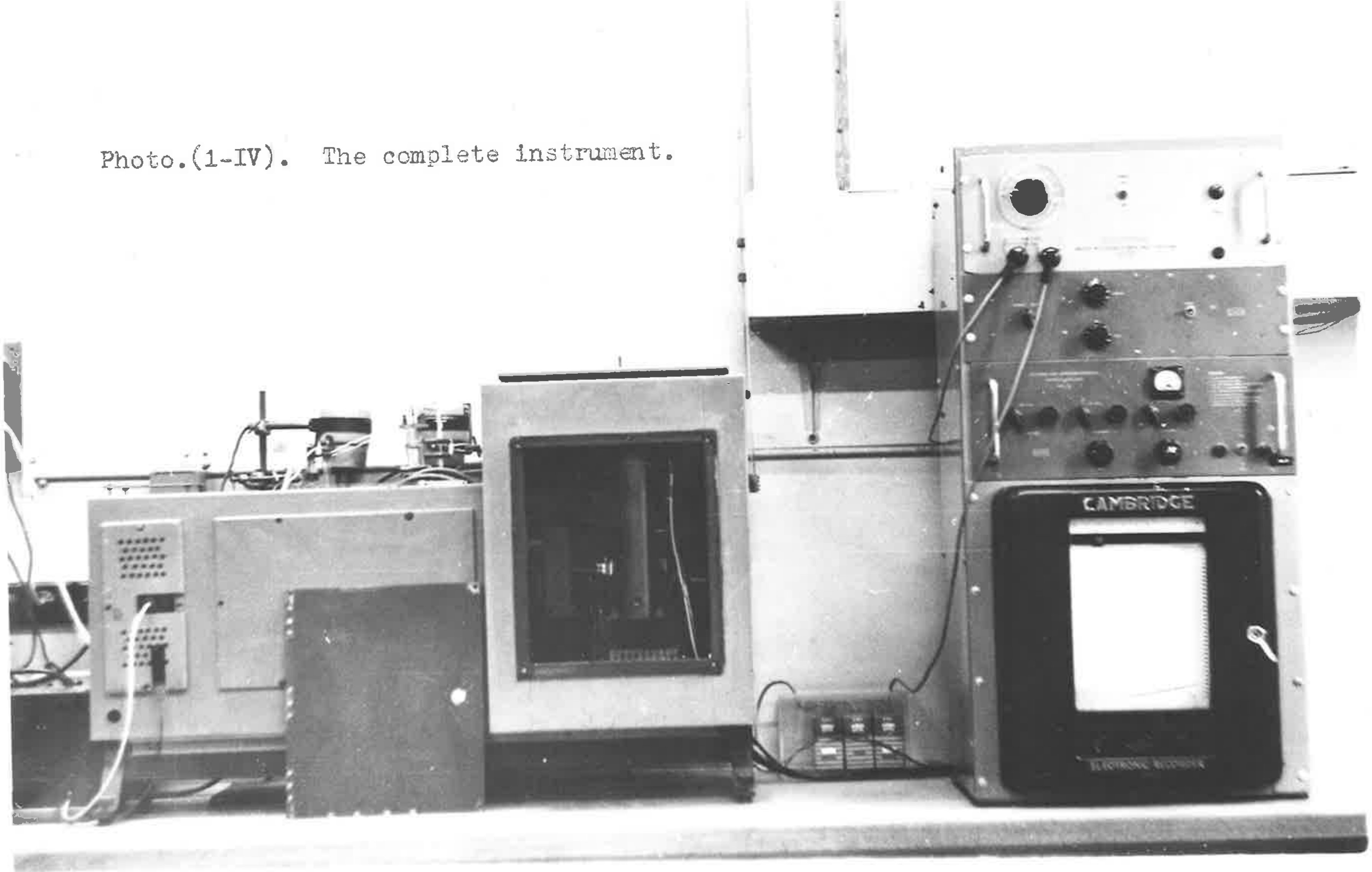


Fig.(3-IV). The injection pipette.

Note.* Non-solvent on diagram.

Photo.(1-IV). The complete instrument.



3. The Principle of Operation and Calibration.

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

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

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

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

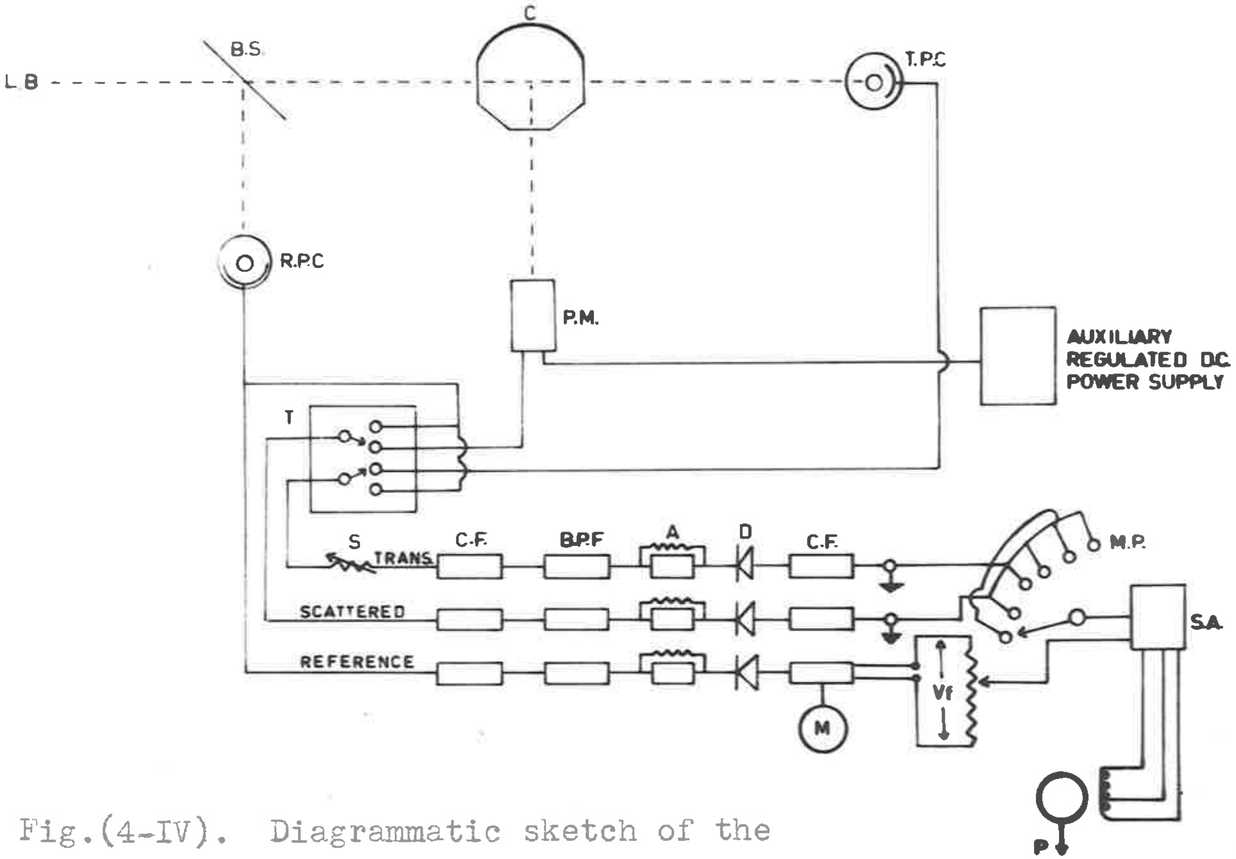


Fig.(4-IV). Diagrammatic sketch of the amplifier and recording system.

the reference channel, whence a fixed ratio of the two should be obtained on the recorder.

The transmitted and scattered component amplifier and detector chains are identical with the reference channel, so that as far as is possible, amplifier characteristics are eliminated from the measurements. The amplifier equipment incorporates regulated power supplies, and sufficient negative feed-back has been included to achieve acceptable linearity. The general arrangement of the complete system is shown in Fig.(4-IV).

4. The Constant Volume Cell and Dilution Correction.

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

$$\gamma = \frac{V}{V_o + V} \qquad (1\text{-IV})$$

where V is the volume of non-solvent added in the mixture and V_o is the original volume of solution. In the constant volume cell, γ does not change according to equation (1-IV) since the same volume increment of solution is ejected as is added. The correct relationship has been established by Bischoff and Desreux[16] as follows. If the system has the composition γ and a volume of non-solvent dV is added to the constant volume cell V_o, then a volume increment γdV is ejected from the cell and the actual increase in volume of non-solvent, dVp, is given by

$$dVp = dV - \gamma dV \qquad (2\text{-IV})$$
$$= dV(1 - \gamma)$$

The change in γ is

$$d\gamma = \frac{dVp}{V_o} = dV\left(\frac{1 - \gamma}{V_o}\right) \qquad (3\text{-IV})$$

on integration

$$V = - V_o \ln (1 - \gamma) \qquad (4\text{-IV})$$

$$\text{or} \quad \frac{V}{V_o} = - \ln (1 - \gamma) \qquad (5\text{-IV})$$

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

$$C = C_o (1 - \gamma) \qquad (6\text{-IV})$$

If the Beer-Lambert law holds, then τ (turbidity) is proportional to C (concentration) and equations (5-IV) and (6-IV) may be combined so that,

$$\frac{V}{V_o} = - 2.3 \log \frac{\tau}{\tau_o} \qquad (7\text{-IV})$$

The turbidity and the volume of addition of non-solvent can be measured directly from the instrument. Thus a plot of V/V_0 vs. $- \log \tau/\tau_0$ should give a straight line of slope 2.3. Equation (7-IV) has been verified experimentally by diluting a solution of $4.0 \times 10^{-4}\%$ fluorescein and also an approximate 0.5% solution of colloidal silica. The results are shown in Fig.(5-IV). Good agreement over a considerable range of γ was obtained. The effect of the rate of addition of non-solvent on equations (5-IV) and (6-IV) was checked and it was found that there was no observable difference over the range of addition rates employed.

5. The Measurement of the Turbidity.

Oth and Desreux[11] have shown that it is necessary to take into account the intensities of both the scattered and transmitted light, since during a titration the light incident to the scattering volume decreases as the solution becomes more turbid. However, if the scattering volume is at the centre of the cell and the light path in the 90° direction is equal to one half the length of the cell, then

$$i^*_{90}/I^*_o = (i_{90}/I_t) \text{ measured} \qquad (8\text{-IV})$$

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

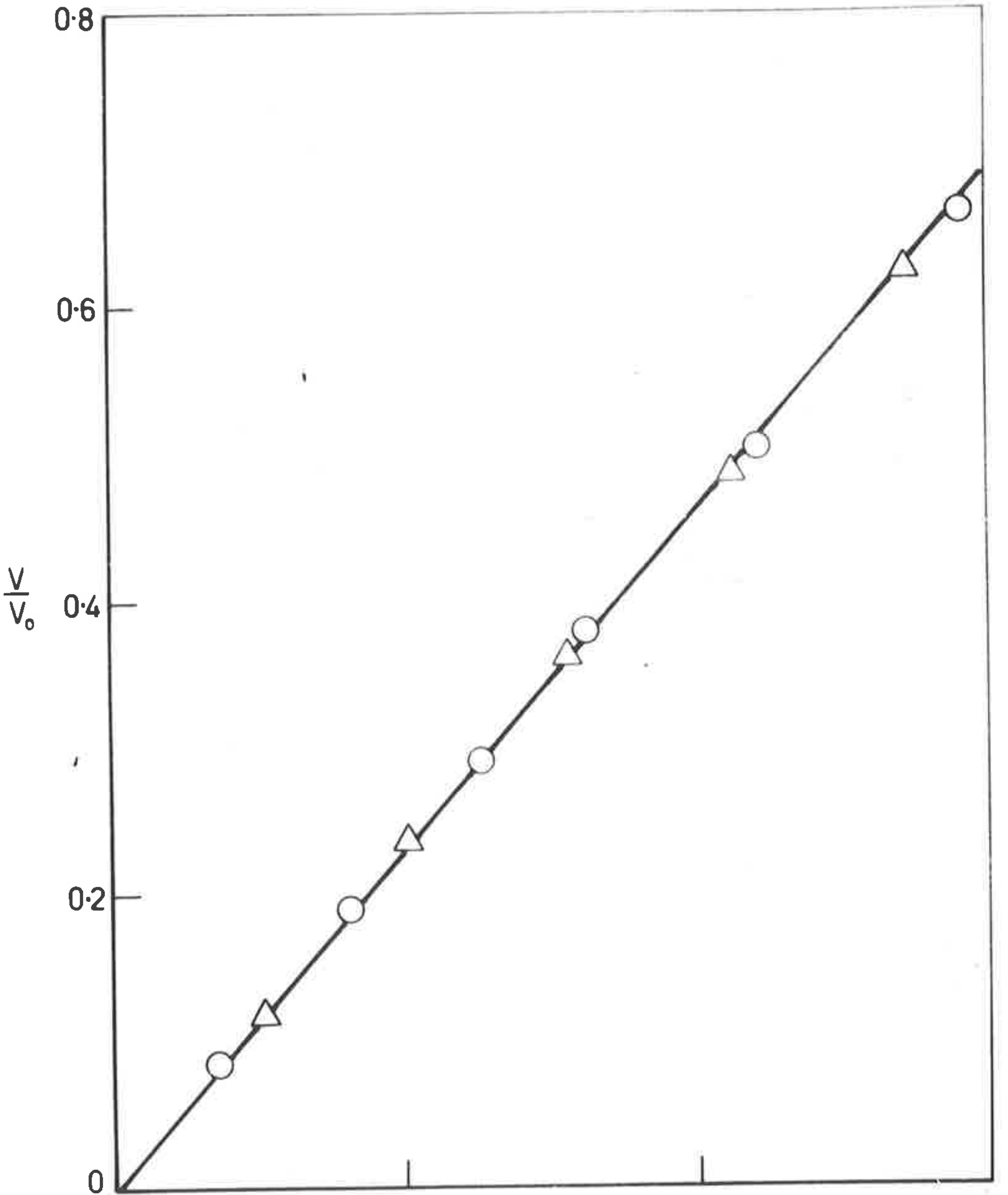


Fig.(5-IV). Plot of V/V_0 vs. - log τ/τ_0.

The solid line is the theoretical slope 2.3, (▲) fluorescein, (○) colloidal silica.

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

$$I = I_o e^{-\tau L} \qquad (9\text{-IV})$$

for solutions of colloidal silica at various concentrations and at several wavelengths. The values were compared with those obtained using a Unicam photo-electric absorptiometer (S.P.500), and the agreement was found to be very good.

The colloidal silica was firstly diluted to approximately 3% with water, centrifuged at 13,000 r.p.m. for 2 hours to remove dust and large aggregates and then diluted to required values of turbidity. The results measured on the turbidimeter are shown in Fig.(6-IV). The absolute concentrations were not determined, but have been expressed on a relative scale in which the stock solution has been called unit concentration. At levels of high turbidity the Beer-Lambert law is not obeyed, however with the limits of turbidity normally encountered ($\tau \text{cm}^{-1} < 0.1$) there is a linear relationship.

Colloidal silica was used to calibrate the scattered light, since it has been shown to exhibit no selective absorption and negligible dissymmetry and depolarization.[19] The calibration constant is defined by the expressions,

$$\tau = C.S_{90} = 2.303\ D/L \qquad (10\text{-IV})$$

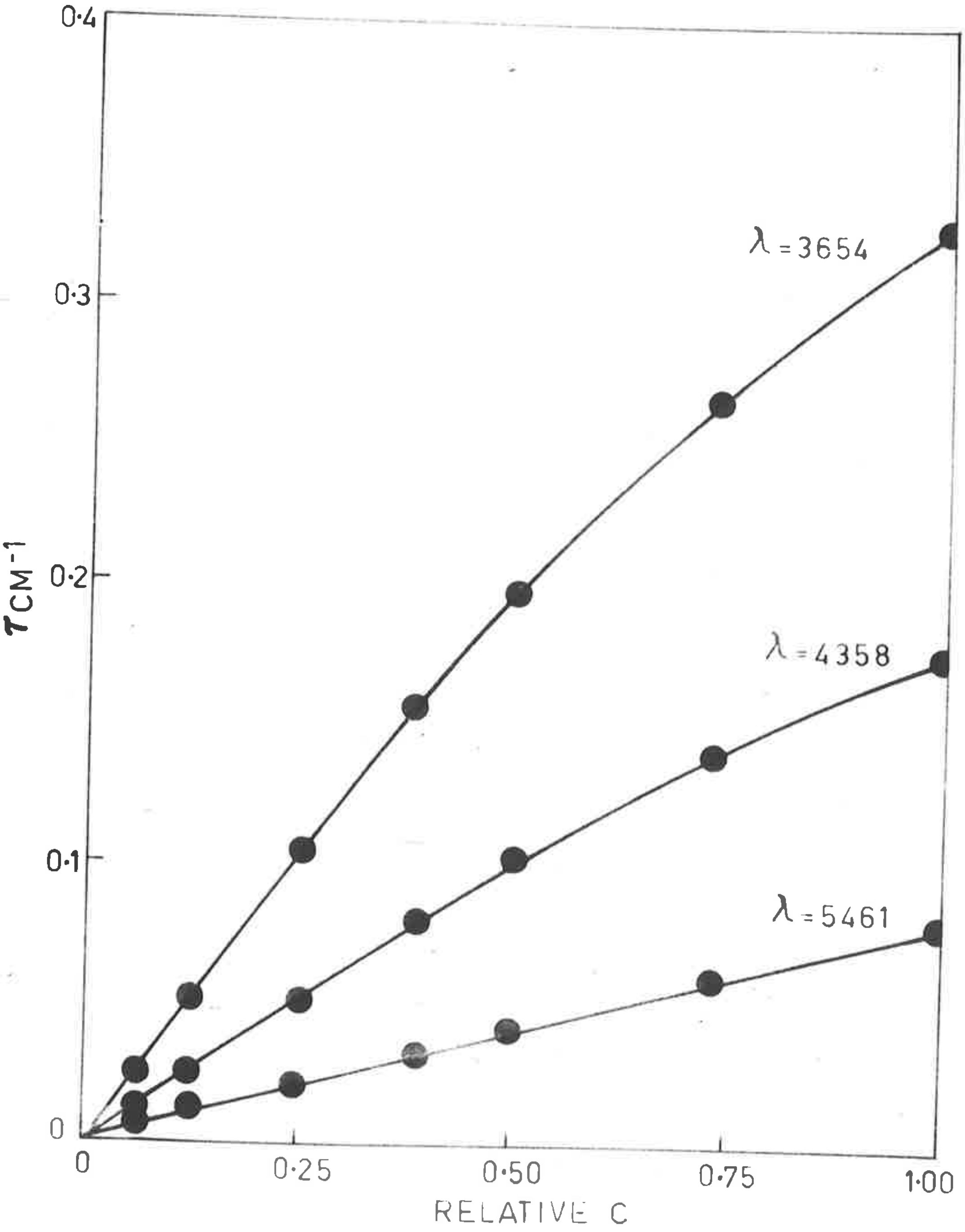


Fig.(6-IV). Turbidity (τ cm^{-1}) vs. relative concentration for colloidal silica. Turbidities have been measured on the turbidimeter at 3654, 4358 and 5461 A.

where C is the calibration constant, S_{90} is the reading at 90° recorded on the chart, D is the optical density of the solution obtained from transmission measurements and L is the length of the cell in cm. Before calibration could be effected, however, corrections had to be made to the measurement of the intensity of the scattered light at 45, 90 and 135°. These corrections had to be applied to ensure that the three mirror systems which reflect the scattered light to the photo-multiplier were each equivalent.

The light scattering cell was filled with dilute colloidal silica and the photomultiplier assemby rotated to bring the 45° light path into the 90° position. The process was repeated for the 135° position. The ratio of the 45 and 135° readings to that at 90° was then applied as a correction. It was found that the correction factor at 45° was 1.43 and that at 135°, 1.56. To test the validity of these corrections several solutions of colloidal silica of differing turbidity were placed into the light-scattering cell. The intensities of the scattered light were recorded and corrected for volume and polarization effects. The results of a typical experiment are shown in Table (1-IV).

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

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

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

The turbidity measured by transmission should be related to the ratio of the intensity of the scattered light at 90° and the intensity of the transmitted light, for a symmetrical scattering medium, such as colloidal silica. The relationship between (i_{90}/I_t) measured and turbidity has been checked and a linear relationship does exist at low turbidity values as shown in Fig. (7-IV). In checking this relationship it was found necessary to correct the measured values for differences in the spectral response of the photomultiplier and the photocell. It was also necessary to take into account the voltage dependence of the photomultiplier channel and to calibrate the recorder scale setting

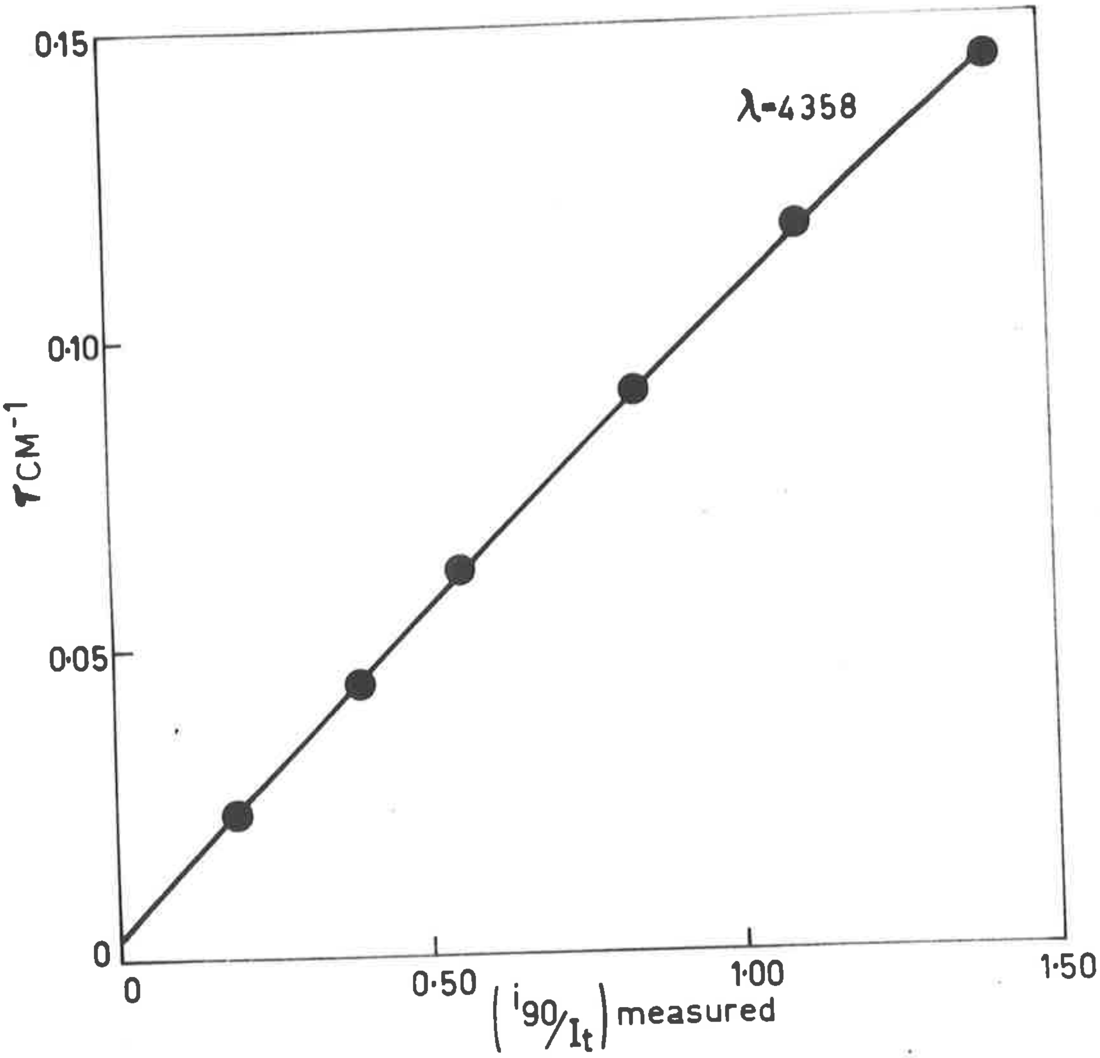


Fig.(7-IV). (i_{90}/I_t) measured plotted against the turbidity (τ) for colloidal silica at λ = 4358 Å.

Photo.(2-IV). The perspex block used as a calibration constant in the turbidimeter.

accordingly (see Chapter VII). Since the photocell and the photomultiplier both had maximum spectral response at $\lambda = 4358$ Å, this wavelength was chosen for all subsequent measurements. Having calibrated the instrument, the recorder scale can then be checked using a standard scattering medium such as the perspex block, shown in Photo (2-IV). This perspex block has been machined and polished to the exact dimensions of the semi-octagonal cell in Fig.(2-IV). Slight variations in light intensity and voltage can thus be compensated for before an experiment is begun.

6. Discussion.

The turbidimetric titration apparatus, which was designed specifically for the study of dilute polymer solutions, was carefully calibrated before use. The results of this calibration showed that the optics and cell designed were satisfactory and that the operation of the titration system obeyed the usual dilution laws. The application of the method to dilute polymer solutions is described in Chapter V.

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CHAPTER V.

A Turbidimetric Titration Study on Polystyrene and the Block Copolymers of Styrene and Methyl Methacrylate.

1. Introduction.

Turbidimetric titration has been used widely in recent years for both the qualitative[1-5] and quantitative[6-13] examination of polymer solutions. As a means of determining molecular weight distribution, the method has many advantages over fractionation techniques. The quantity of material necessary to carry out an analysis is small and reproducibility can readily be obtained. The reproducibility of the results, however, is determined by the standardisation of the experimental conditions, such as the temperature, rate of stirring, rate of addition of non-solvent and a proper choice of the starting concentration. It is also necessary to correct for optical effects, dilution and changes in the scattering pattern of the polymer suspension.

In the past, assumptions as regards shape and dispersity of the precipitated species have been made when interpreting the results. Only recently[16-18] have attempts been made to elucidate the behaviour of polymer particles precipitated from solution by the addition of non-solvent. The choice of the solvent-precipitant system will, however, affect the results. The system must be sufficiently selective in its ability to cause a good separation of the polymeric species and it must not produce coagulation. The latter factor is extremely important, particularly near the end of the titration, and is often contributory to unsatisfactory results.

It is desirable that the solvent and the precipitant have the same or very nearly the same refractive index. It has been the practice in turbidimetric titrations to relate the intensity of the scattered light from the suspended precipitate to the actual amount of polymer present. However, the scattering power of a polymer precipitate is a function of the refractive index difference between it and the medium in which it is suspended. Thus, relating the measured turbidity directly to the mass of the suspended polymer is only valid when the solvent and the precipitant have the same or very nearly the same refractive index. It was for this reason that the following studies were carried out using butanone as the solvent and isopropanol as the precipitant. The refractive indices for butanone ($n = 1.3740$) and isopropanol ($n = 1.3736$) have been measured[19] at a wavelength of 5460 Å. To reduce the effects of multiple scattering and coagulation to a minimum, very dilute solutions (0.0004 - 0.002 g/100 ml) were used in all titrations. The rate of addition of non-solvent was also reduced to a minimum (0.01 - 0.02 ml/min) to allow effective equilibrium to be established.

The turbidimetric titration studies were carried out in order to determine whether the method could be applied quantitatively to the measurement of molecular weight and molecular weight distribution. These studies were carried out on polystyrene samples prepared by an anionic technique described[20] elsewhere. Evidence will be presented to show that the molecular weight distribution of these polystyrene samples is not as good as that obtained using the modified purging technique employed in the preparation of the block copolymers (see Chapter III). The method was developed so as to provide a rapid check on the heterogeneity of the block copolymers and the parent polystyrenes.

2. Size and Shape of the Precipitated Particles.

The scattering pattern of the precipitated particles was examined independently in the early stages of the titration and after complete precipitation, in order to show changes in size and shape of the precipitated species. It has been suggested[22,23] that the size of the particles formed during a precipitation is a function of the degree of saturation of the solution, and not necessarily the molecular weight. It was therefore decided to keep the starting concentration as low as possible.

For particles which are small compared to the wavelength of the light in the suspending medium, the angular variation of the scattered intensity for unpolarized light is given by the Rayleigh relationship,

$$i_\theta = K I_o (1+\cos^2\theta) \qquad (1\text{-}V)$$

where $$K = \frac{8\pi^4\alpha^2}{r^2\lambda^4}$$

i_θ is the intensity of the scattered light measured at an angle θ to the incident beam I_o, and at a distance r from isotropically small particles of polarizability α ; λ is the wavelength of light in the medium.

For large particles the scattered intensity is no longer symmetrical about $\theta = 90^\circ$, but decreases as a function of the angle of observation θ . To correct for this loss of scattered intensity, the function $P(\theta)$ is introduced into equation (1-V), so that

$$i_\theta = K\, I_o(1+\cos^2\theta)\,.\, P(\theta) \qquad (2\text{-V})$$

$P(\theta)$ is known as the particle scattering factor, and Debye[24] has shown that for spheres up to one wavelength in diameter and whose refractive index is very nearly equal to that of the surrounding medium,

$$P(\theta) = \left[\frac{3}{x^3}\;(\sin x - x\cos x)\right]^2 \qquad (3\text{-V})$$

where $$x = 2\pi D/\lambda' \sin\ \theta/2 \qquad (4\text{-V})$$

and λ' is the wavelength of light in the medium. The scattering at any angle for a sphere of any given D/λ' can thus be calculated using equation (3-V). For large spherical particles the asymmetry of scattering is usually expressed by the dissymmetry function Z, where

$$Z = \frac{i_\theta}{i(\pi - \theta)} \qquad (5\text{-V})$$

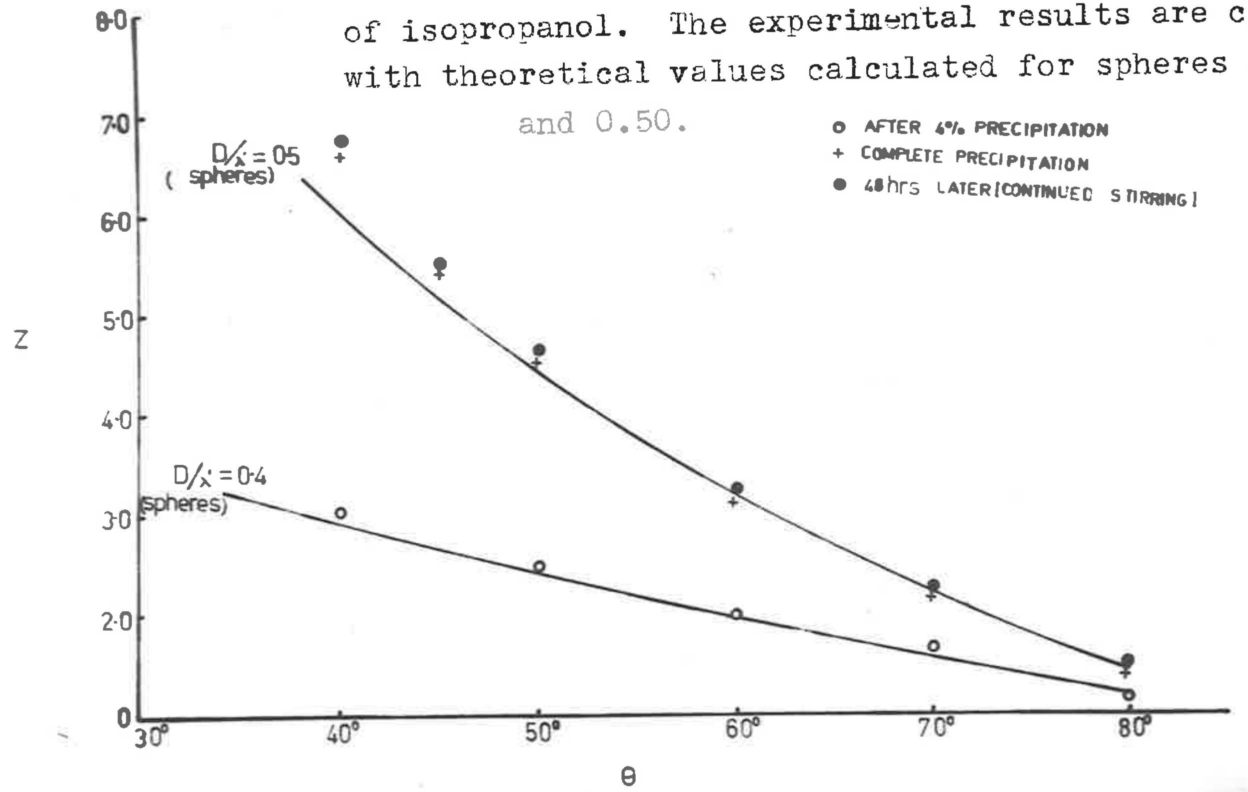
Tables of the dissymmetry $Z = i_{45^o}/i_{135^o}$, and the corresponding correction factor $P(\theta)$ as a function of the characteristic D/λ' value have been evaluated[25,26] for spherical particles, rods, monodisperse coils and polydisperse coils. Recent calculations by Heller[35] have shown that using the above equations and employing the particle scattering factor

P(θ), can lead to large errors in the final result, particularly when the dissymmetry is large. It is evident that for very large particles the Rayleigh-Gans-Debye treatment has certain limitations and the more complicated Mie[36] theory should be employed.

A sample of polystyrene ($\overline{Mw}$ = 77,000), whose initial concentration (C_o) in butanone was 0.0012 g/100 ml, was titrated with isopropanol at a rate of 0.02 ml/min at a temperature of 25 ± .02°C. Samples were carefully removed from the titration cell at 4% and at complete precipitation. The samples were removed using dust-free pipettes and carefully added to the light-scattering cell of the Peaker P.C.L. Light-scattering apparatus described in Chapter VII. The light-scattering cell was so designed that it could be effectively thermostated to 25 ± .02°C. The angular distribution of the intensity of the scattered light was then measured over the range of angles from 40 to 140° at 10° intervals. The dissymmetry values calculated for the precipitated polymer particles and corrected for solvent scattering have been plotted against the angle of observation θ as shown in Fig.(1-V).

The sample taken during the early stages of the precipitation has been examined and the experimental points fall very close to the theoretical curve calculated for a spherical particle of size D/λ' = 0.40. At complete precipitation

Fig.(1-V). The variation of the dissymmetry (Z) of scattered light with angle (θ) for polystyrene ($\overline{Mv}$ = 77,000) precipitated from butanone by addition of isopropanol. The experimental results are compared with theoretical values calculated for spheres of D/λ' = 0.40 and 0.50.



there is some deviation in the forward or low angle scattering region, where an increase in the dissymmetry was observed. The dissymmetry values at complete precipitation lie very close to the theoretical values calculated for a spherical particle of size $D/\lambda' = 0.50$. Although this treatment is only approximate, it appears than an increase in particle size has taken place during the titration. However, the shape of the suspended polymer particles has remained essentially spherical. These results differ from those obtained by Hastings and Peaker,[17] who conducted similar studies on polystyrene, using the system benzene-methanol. These authors[17] found a departure from the spherical model. The observed dissymmetries were much lower than the calculated values. However, Hastings and Peaker[17] recognized that if the particle size exceeded one wavelength in diameter, then the angular distribution would change from a smooth function to one showing maxima and minima. If aggregation were to take place, then the increase in particle size would tend to shift the maxima into the very low forward angle region, causing a decrease in the forward angle scattering and hence a decrease in the measured dissymmetry. The results of Sloan[27] seem to verify these observations. However, there appears to be no observable aggregation of the polymer suspension in the butanone-isopropanol system. This may be the result of using dilute solutions and the very slow addition of the precipitant in well standardized conditions. The stability of the polystyrene-butanone-isopropanol system has been demonstrated by the fact that after 48 hours there was negligible change in the scattering pattern as shown in Fig.(1-V). During this period the polymer suspension was continually stirred and thermostated at 25 ± .02°C.

During the examination of the light-scattering pattern of the polymer suspension, the most difficult operation was transferring the sample from the titration cell without allowing it to be contaminated by dust. Although every precaution was taken, the possibility that some contamination occurred cannot be entirely overlooked.

3. The Measurement of the Turbidity of the Polymer Suspension.

It has been the practice in turbidimetric titration to relate the intensity of the scattered light to the amount of polymer in suspension at any given instant. However, this is only valid if the polymer is precipitated as uniform spherical particles, which have a diameter small ($\lambda'/10$) compared to the wavelength of the light (λ') in the medium under investigation. It is also essential that the refractive index of the solvent and the precipitant be very nearly identical. It was shown in the previous section (see 2) that the suspended polymer particles are essentially spherical in shape, although there is a definite change in their size as the titration proceeds. Obviously, it is essential to correct for change in size of the polymer suspension before the measured turbidity can be related to the quantity of material precipitated at any instant.

It is possible (see Chapter IV) to relate the intensity of the scattered light at 90° (i_{90}) and the intensity of the transmitted light (I_t) to the turbidity of a solution, which exhibits symmetrical scattering. A linear relationship between (i_{90}/I_t) meas. and the concentration has been shown [13,28] to be valid for dilute solutions of colloidal silica. However, with increased particle size the internal interference must be taken into account.

If the dissymmetry Z (i_{45}/i_{135}) is determined at each stage of the titration, it is then possible to calculate the value of x in equation (4-V), where

$$x = 2\pi D/\lambda' \sin \theta/2$$

and hence determine the particle scattering factor $P(\theta)$ at $\theta = 90$ of equation (3-V), where

$$P(\theta) = \left[\frac{3}{x^3} (\sin x - x\cos x)\right]^2$$

The observed intensity of scatter at 90° multiplied by the reciprocal of P(90) gives the value of the intensity that would have been observed had internal interference been absent. It is possible then to correct the ratio (i_{90}/I_t) meas. at each stage of the titration for the effect of particle size on the intensity of the scattered light. Fig. (2-V) is a plot of the function 1/P(90) denoted by f(z) against the dissymmetry (Z meas.).

However, the observed dissymmetry should be corrected [26,29] for the reflection of light at the glass/air and liquid/glass interface. For symmetrical scattering the Fresnel correction is negligible; however, it becomes appreciable when the dissymmetry becomes large, because the scattering at angles greater than 90° is augmented by the forward scattering of this reflected light. Taking both interfaces into account, the coefficient R for the glass/air interface is,

$$R = \left(\frac{n - 1}{n + 1}\right)^2 \qquad (6\text{-V})$$

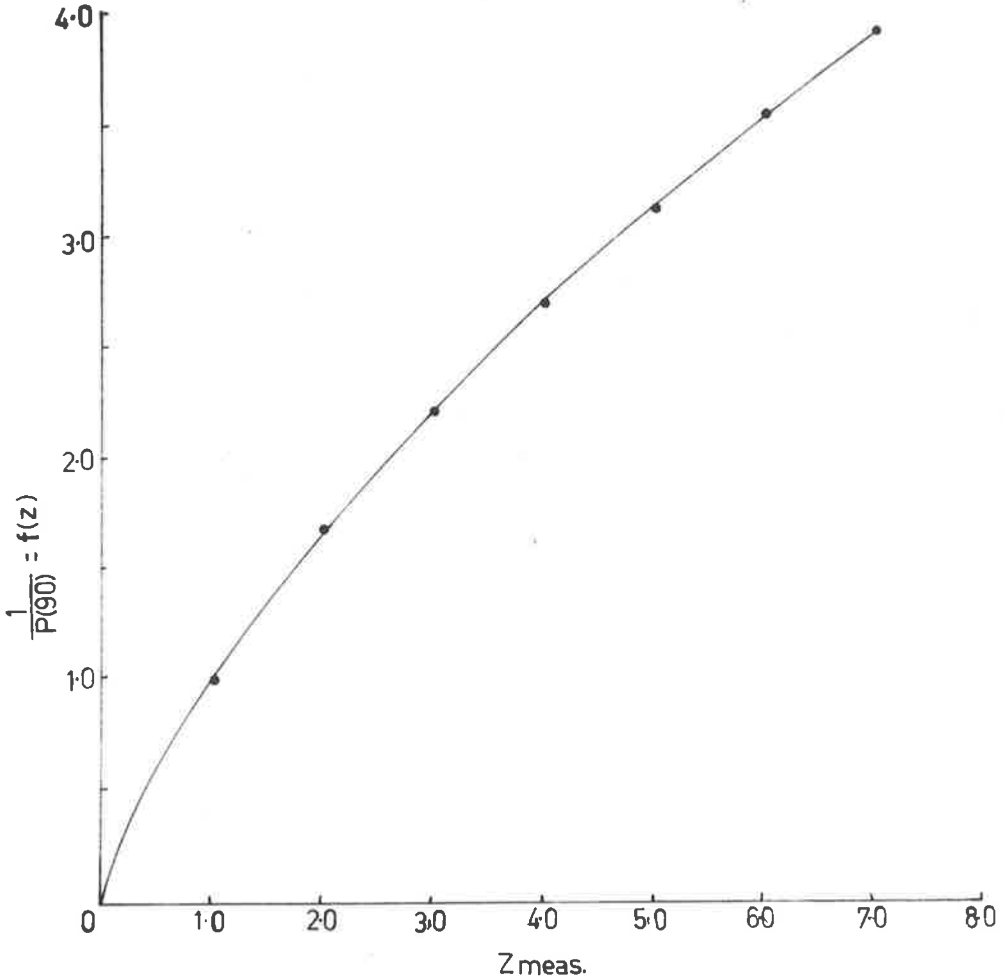


Fig.(2-V). The function 1/P(90) = f(z) plotted against the dissymmetry Z meas. for spherical particles.

where n = refractive index for the glass.

For the liquid/glass interface the coefficient r is given by,

$$r = \left(\frac{n/n_o - 1}{n/n_o + 1}\right)^2 \qquad (7\text{-}V)$$

where n_o is the refractive index for the liquid.

The corrected value of the dissymmetry, Z, then becomes

$$Z = \frac{Z\text{obs.} - (1 - r)^2 R + r}{1 - \left[(1 - r)^2 R + r\right] Z\text{obs.}} \qquad (8\text{-}V)$$

Taking the value of n for quartz glass at $\lambda = 4358\ \mathring{A}$ as 1.467 and the value for n_o as 1.38 for the butanone-isopropanol mixture, Z becomes

$$Z = \frac{Z\text{obs.} - 0.037}{1 - 0.037\text{obs.}} \qquad (9\text{-}V)$$

Each value of Z observed was corrected in this manner. The true value of Z, corrected for Fresnel reflections and optical effects due to the method of measurement (see Chapter IV), has been designated Zmeas. This value was used in Fig. (2-V) and all subsequent measurements. It was not necessary to correct the observed dissymmetries measured on the P.C.L. light-scattering instrument, as the cell was designed to eliminate Fresnel corrections (see Chapter VII).

To test whether the corrected value of (i_{90}/I_t)meas. was in fact proportional to the amount of polymer suspension present at any one stage, as has been proposed, a sample of polystyrene (Mw = 77,000) and having an initial concentration in butanone of 0.0013 g/100 mls was titrated to complete precipitation, and treated as follows. A mixture of butanone and isopropanol of exactly the same composition as that determined from the point of precipitation, was added as a diluent to the titration cell. Care was taken in preparing the solvent-precipitant mixture free from dust and thermostating it to the same temperature as the polymer suspension in the titration cell. The value of the intensity of the scattered light at $\theta = 90^{\circ}$ for the solvent-precipitant mixture was subtracted from that of the polymer suspension. The value for (i_{90}/I_t)meas. corrected for particle size has been plotted against the polymer concentration as shown in Fig.(3-V). It can be seen that over a considerable concentration range the corrected (i_{90}/I_t)meas. value is proportional to the concentration of the polymer precipitate.

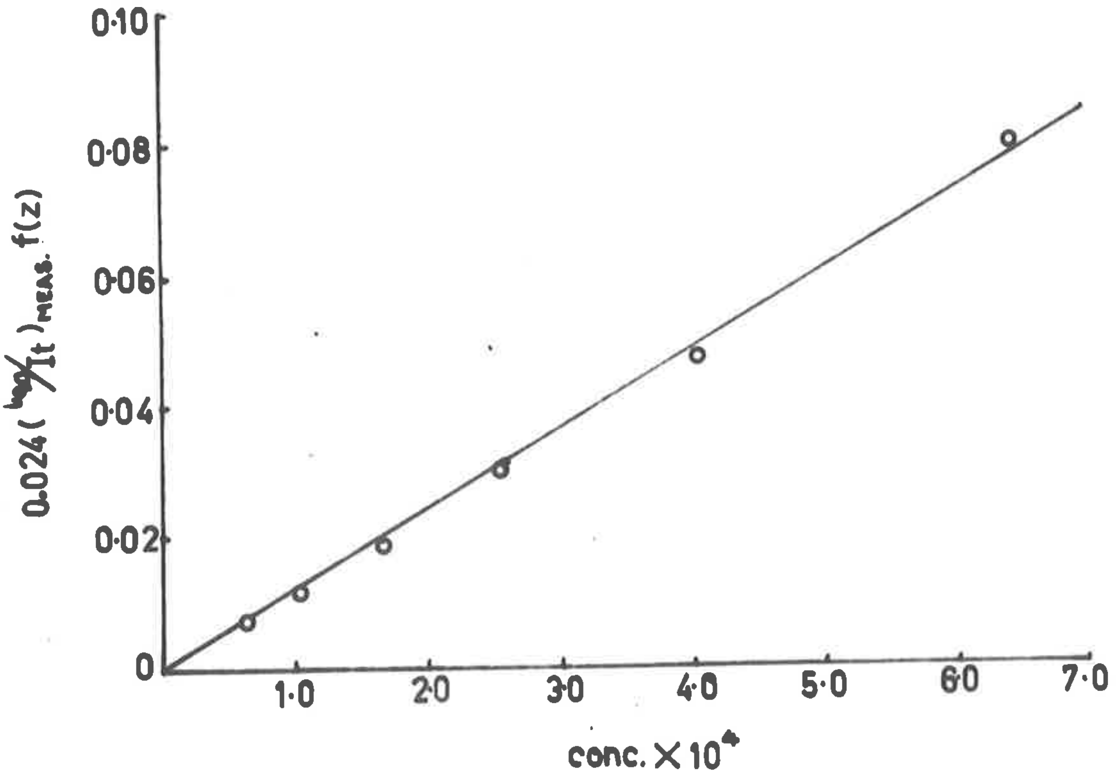


Fig.(3-V). $(i_{90}/I_t)_{meas.}$ corrected for particle size from Fig.(2-V) and plotted against concentration of the polymer suspension. Polystyrene sample $\overline{Mv}$ = 77,000.

4. Solubility as a Function of Concentration and Molecular Weight.

In a turbidimetric titration, precipitation is brought about by the slow and continuous addition of non-solvent to a dilute solution of the polymer. It is usual to designate the composition of the solution at any point of precipitation by a function,

$$\gamma = \frac{V}{V_o + V} \qquad (10\text{-}V)$$

where V is the volume of non-solvent added and V_o is the original volume of solution in the cell. When a cell of the constant volume type is used, however, we have the relation:-

$$\frac{V}{V_o} = -\ln\,(1 - \gamma) \qquad (11\text{-}V)$$

In determining the point of precipitation for a polymer of known molecular weight, the precipitation point is often taken as that point at which turbidity is first detected. However, even when turbidimetric titrations are carried out on monodisperse polymer, the material is always precipitated over a small range of γ. If the onset of turbidity is taken as the point of precipitation, then this point will be weighted toward the higher molecular weight region. An alternative procedure is to take the point corresponding to 50% precipitation as read from the titration curve. This method also has its limitations as has been pointed out in section 6 of this Chapter. However, in this study the point of precipitation was taken as that point corresponding to the point of 50% precipitation and has been designated γp.

In order to obtain quantitative data concerning molecular weight and molecular weight distribution is is essential to establish an empirical relationship between molecular weight, concentration and the point of precipitation. This has been done using polymer samples of known molecular weight and narrow distribution.

It was assumed for the purpose of this study that the molecular weight precipitating at any point depends only upon the stage of the titration (γ) and the concentration at some fixed value of γ, say at $\gamma = \gamma_o$; where γ_o corresponds to a point before non-solvent has been added to the solution. Let the concentration at this point be C_{γ_o}. It was therefore simply necessary to determine the concentration of each polymer species before the addition of precipitant. It is common practice in turbidimetric titrations to add a known volume of precipitant to the polymer solution before beginning the actual titration. The volume of precipitant added is so chosen as not to be too close to the point of precipitation, in fact far enough removed to allow effective titration to be carried out. The actual value of γ can then be calculated from the relationship,[13]

$$(1 - \gamma)\text{actual} = (1 - \gamma)\text{initial}(1 - \gamma)\text{apparent} \qquad (12\text{-V})$$

where the initial value of γ is the value after the initial addition of non-solvent before titration, and the apparent, the value as determined from the amount of non-solvent added at any point of the titration. The concentration C can then be calculated from the actual value of γ, if C_o is known, from the relation

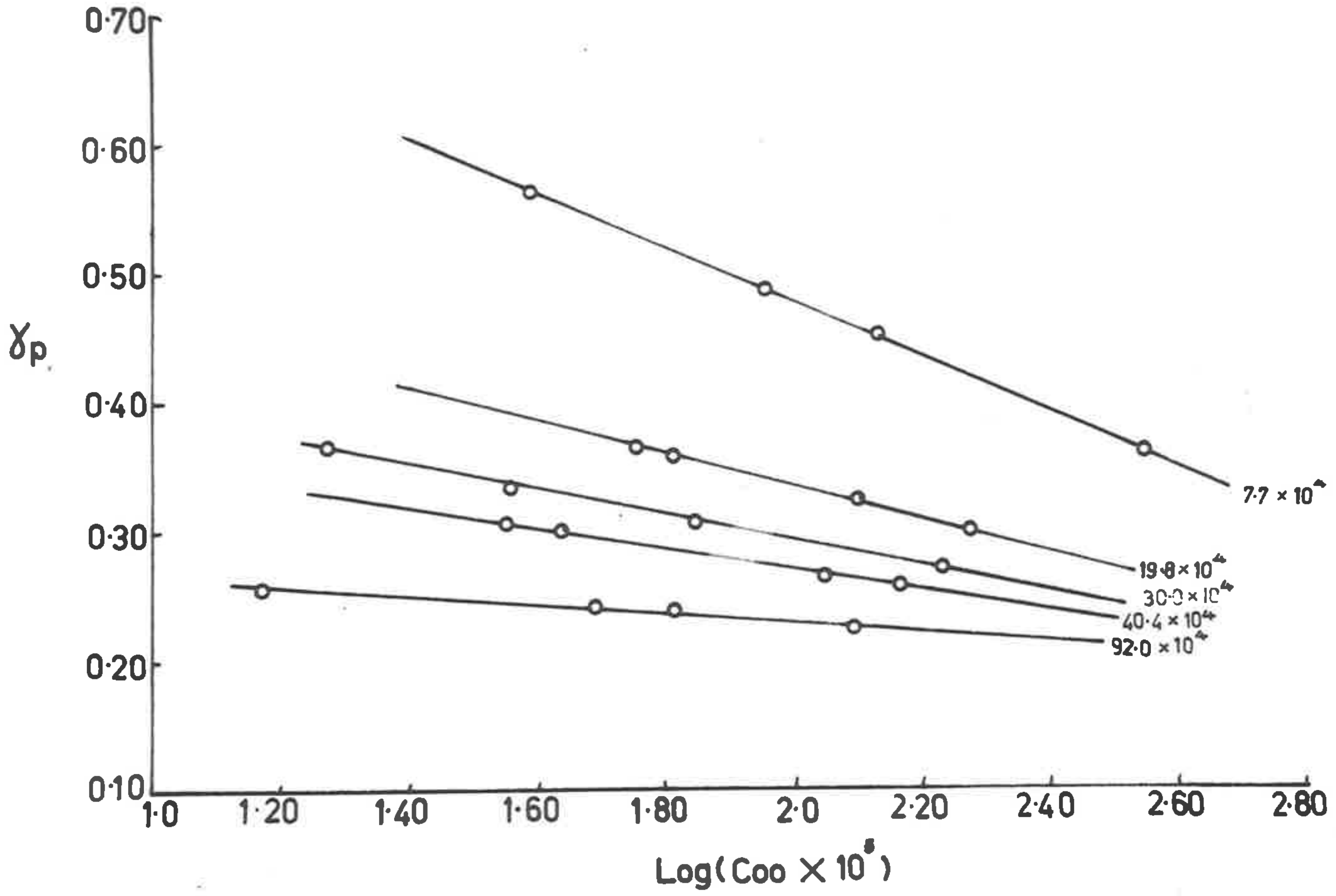
$$C = C_o(1 - \gamma) \qquad (13\text{-V})$$

The values of the concentration $(C\gamma_o)$ at the fixed value of $\gamma = \gamma_o$ can thus be calculated. These concentrations have been designated C_{oo}.

Several polystyrene samples in which the molecular weights were determined from viscosity measurements in toluene,[31] were titrated in the apparatus previously described[28] (see Chapter IV) and the values of γ_p and C_{oo} determined as outlined above. The molecular weight range covered was from 77,000 to 920,000.

The values of γ_p were plotted against log C_{oo} and the results shown in Fig.(4-V). Extrapolation suggests that there is a critical value of C_{oo} for which all molecular weights are precipitated on reaching some critical value of γ_p. Thus for the most efficient separation of molecular weights it is essential that only low concentrations be used. From the data shown in Fig.(4-V) the relationship between γ_p

Fig.(4-V). The point of precipitation γ_p plotted against the log of the concentration Coo for five polystyrene samples in the butanone-isopropanol system.



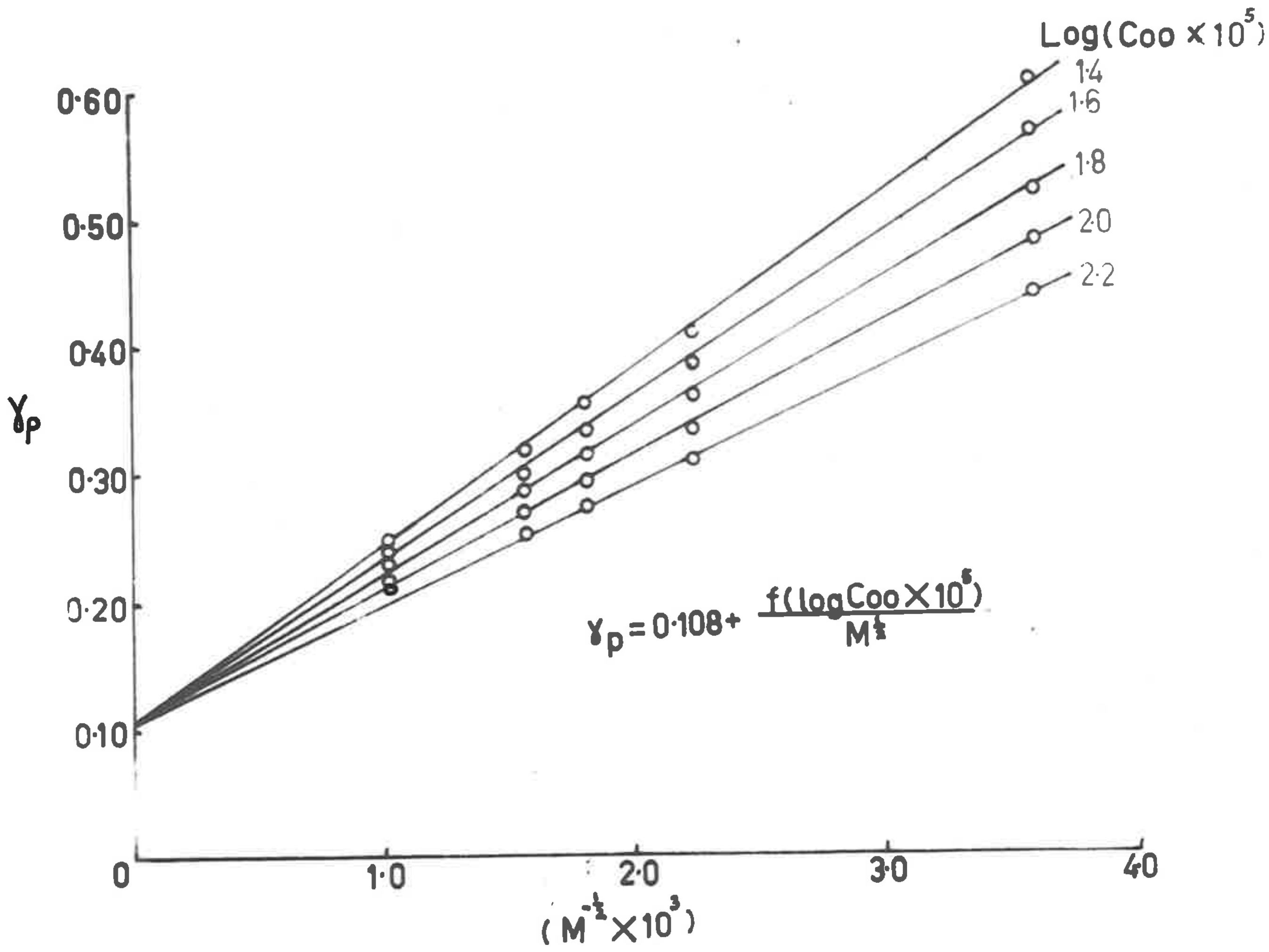
and C_{oo} is found to be of the form,

$$\log C_{oo} = a - b\gamma_p \qquad (14\text{-V})$$

where a and b are constants for a particular polymer and solvent-precipitant system. The results show that a solubility relationship does hold, which is similar to those reported previously.[30] The concentration C_{oo} of equation (14-V) is not, however, the polymer saturation concentration.

From the data in Fig.(4-V) it was possible to determine a relationship between the point of precipitation γ_p, the initial polymer concentration C_{oo} and the molecular weight, M. This was achieved by plotting γ_p against $M^{-\frac{1}{2}}$ for a series of initial polymer concentrations C_{oo}. The results of this plot are shown in Fig.(5-V). The relationship between γ_p and $M^{-\frac{1}{2}}$ appears to be linear with log C_{oo} as parameter. However, if emphasis is placed on the high molecular weight region of the curve, it appears to be slightly curved in the region of M = 920,000. This arises because of the difficulty in obtaining the exact location of the point of precipitation for high molecular weight samples. The higher the molecular weight the less precise is the point of precipitation.

From the data in Fig.(5-V) it can be shown that the relationship between γ_p, molecular weight M and the concentration C_{oo} is given by, Fig.(5-V). The plot of γ_p against $M^{-\frac{1}{2}}$ for five initial polymer concentrations. Polystyrene in the butanone-isopropanol system.



$$\gamma_p = X + Y M^{-\frac{1}{2}} \tag{15-V}$$

where X = 0.108. Y is a function of the concentration, C_{oo}, and may be evaluated from the slopes of the various C_{oo} lines of Fig.(5-V). These slopes were plotted against C_{oo} as shown in Fig.(6-V). The slope of this line is Y. An equation fitting procedure was also used to evaluate Y. From Fig.(6-V) it was found that,

$$Y = 218.13 - 57.85 \log (C_{oo} \times 10^5) \tag{16-V}$$

Thus the relationship between the point of precipitation γ_p, the concentration C_{oo} and the molecular weight M, turns out to be

$$\gamma_p = 0.108 + \frac{(218.13 - 57.85 \log (C_{oo} \times 10^5))}{M^{\frac{1}{2}}} \tag{17-V}$$

Thus, knowing the point of precipitation and the initial concentration, it is possible to determine the molecular weight at any stage during a titration. Having shown that the intensity of the scattered light at 90° and the transmission can be related to the weight of material present in the titration cell at any instant, it is possible to investigate quantitatively the determination of molecular weight and molecular weight distribution. However, there are certain corrections and limitations which must be observed before quantitative emphasis can be placed on the results.

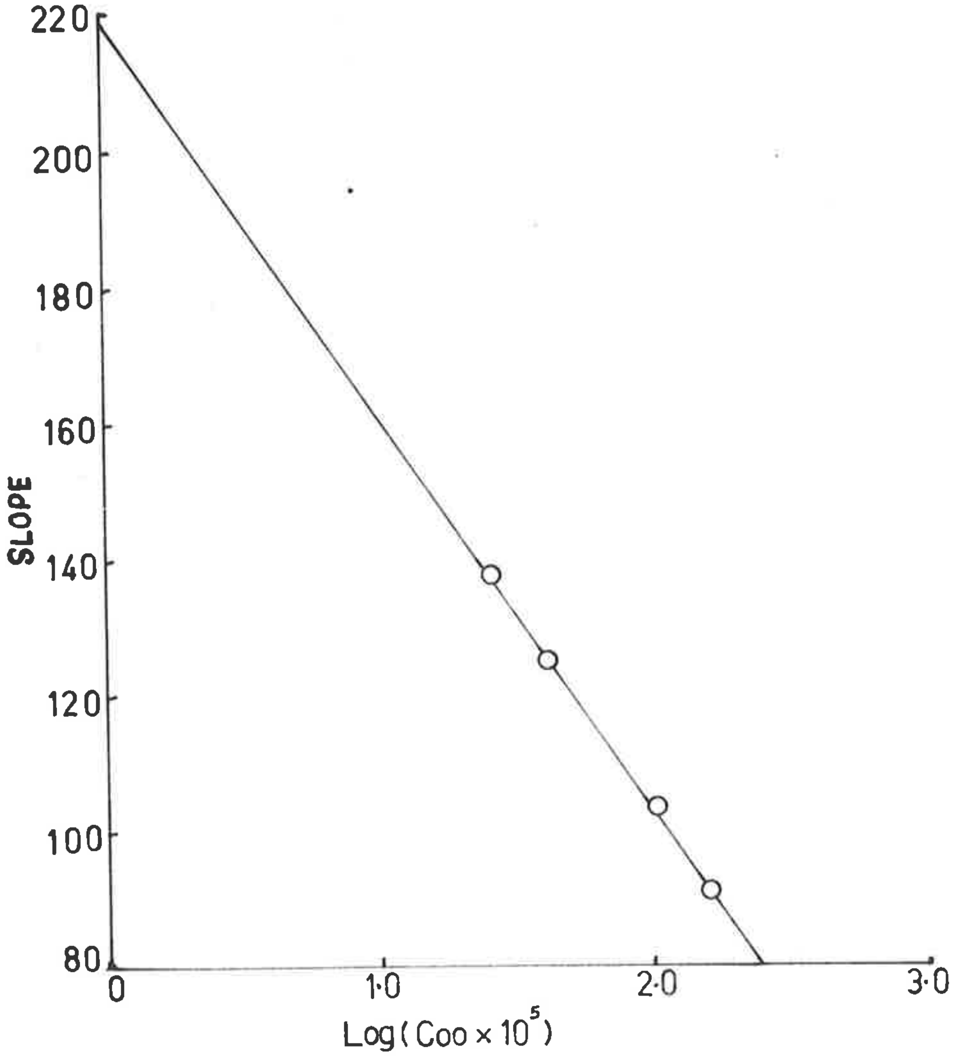


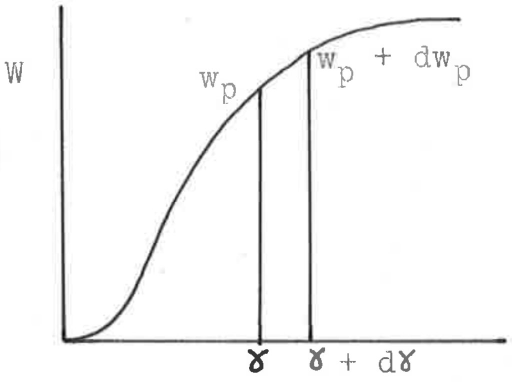
Fig. (6-V). The slopes determined from the various Coo lines of Fig. (5-V) plotted against log (Coo x 10^5)

Perhaps the most important precautions to be observed are the correction for loss of polymer precipitate in the constant volume cell and the exact location of the precipitation point.

5. Correction for Loss of Polymer Suspension.

The constant volume cell has several advantages over the open type of cell used by some workers in the turbidimetric titration studies. The relatively small volume, ease of thermostating and the rapidity of titration are the main advantages. However, the disadvantage is that some of the polymer suspension is lost by overflow as the titration proceeds. This means that the weight of material observed at any instant is not an accumulative weight which is required for quantitative interpretation of molecular weight distribution. It was therefore necessary to correct for loss of polymer precipitate, and the following procedure was adopted. Consider a titration curve of the type shown in Fig.(7-V), where weight of precipitate in the cell is shown plotted against the stage of the titration, γ .

Fig.(7-V)



In the interval between γ and $\gamma + d\gamma$ an amount of precipitate w_p will be reduced by $(w_p + dw_p)d\gamma$. Hence the actual loss of precipitate in this interval lies between these two extremes. Denoting this loss by $d(w_p)$LOST, we have

$$w_p d\gamma < d(w_p)\mathrm{LOST} < (w_p + dw_p)d\gamma \qquad (18\text{-V})$$

Thus in the limit $d\gamma \rightarrow o$

$$d(w_p)\mathrm{LOST} = w_p d\gamma \qquad (19\text{-V})$$

Therefore the total loss up to any stage γ_i is given by,

$$(W_p)\mathrm{LOST} = \int_o^{\gamma_i} w_p d\gamma \qquad (20\text{-V})$$

Hence the total weight of precipitate produced up to γ_i (denoted by $(W_p)_i$) is given by,

$$(W_p)_i = (w_p)_i + \int_o^{\gamma_i} w_p d\gamma \qquad (21\text{-V})$$

where $(w_p)_i$ is the amount of polymer left up to γ_i.

The sequence denoted by (21-V) may not converge rapidly, however the limit of the sequence can be determined using Aitkens $-d^2$ process.[32] If the last three values of the sequence are denoted by n, n-1 and n-2, then the limit denoted by $(W_p)\infty$ is

$$(W_p)\infty = \lim_{i \rightarrow \infty} (W_p)_i = (W_p)_n - \frac{\left[(W_p)_n - (W_p)_{n-1}\right]^2}{\left[(W_p)_n - 2(W_p)_{n-1} + (W_p)_{n-2}\right]}$$

(22-V)

The expression (22-V) becomes most accurate when the deviations $(W_p)_\infty - (W_p)_i$ form a geometric progression.

To determine the integral of equation (21-V) the range of γ over which the titration was carried out was divided into equal intervals, $\Delta\gamma$, giving then

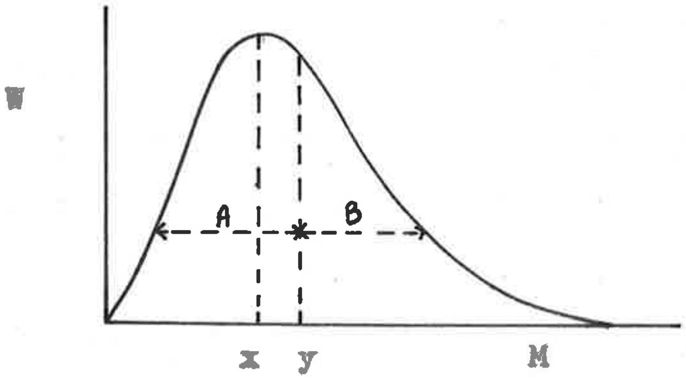
$$(W_p)_{LOST} \doteqdot \Delta\gamma \sum_{n=o}^{i-1} (W_p)_n \qquad (23\text{-}V)$$

The actual titration curve was corrected for the loss of polymer precipitate in this manner and all calculations were carried out on the corrected values.

6. Location of the Point of Precipitation and its Relation to Molecular Weight.

Consider a molecular weight distribution curve of the type shown in Fig.(8-V).

Fig.(8-V).



For a distribution of this type there are three characteristics, which are related to its shape; a) the weight modal molecular weight, which corresponds to the point x on the distribution curve. This point corresponds to the greatest weight of material having a molecular weight x; b) the weight median molecular weight denoted by y, where the area under the curve in A is equal to the area under the curve in B, and c) the weight mean molecular weight, which cannot be located by visual inspection. For a continuous distribution of molecular weights the weight mean molecular weight $(\overline{M_w})$, may be defined by,

$$\overline{M_w} = \int_0^\infty WMdM \qquad (24\text{-}V)$$

Since W was measured in arbitrary units in the data to be described, it is no longer true to assume that the area under the molecular weight distribution curve is unity, i.e.,

$$\int_0^\infty W dM \neq 1 \qquad (25\text{-V})$$

therefore it is necessary to introduce $\int_0^\infty W dM$ as a scale factor, giving

$$\overline{M_w} = \frac{\int_0^\infty WM dM}{\int_0^\infty W dM} \qquad (26\text{-V})$$

If the molecular weight distribution were symmetrical, then the weight modal, weight median and weight mean molecular weights would be identical. Thus the assumption that the point of precipitation at half weight of material precipitated corresponds to the molecular weight, as determined from viscosity measurements, could be in error. The point thus located would correspond to the weight median molecular weight for skewed distribution curves.

For curves of moderate skewness it is possible to relate the weight modal, weight median and weight mean molecular weights, by an assumption of the form,

$$\text{mean} - \text{mode} = 3(\text{mean} - \text{median}) \qquad (27\text{-V})$$

Thus if the distribution curve is moderately skewed, then the weight modal and weight median molecular weights may be determined, and using the assumption of equation (27-V) the weight mean molecular weight may be estimated.

7. Determination of Molecular Weight and Molecular Weight Distribution from the Experimental Data.

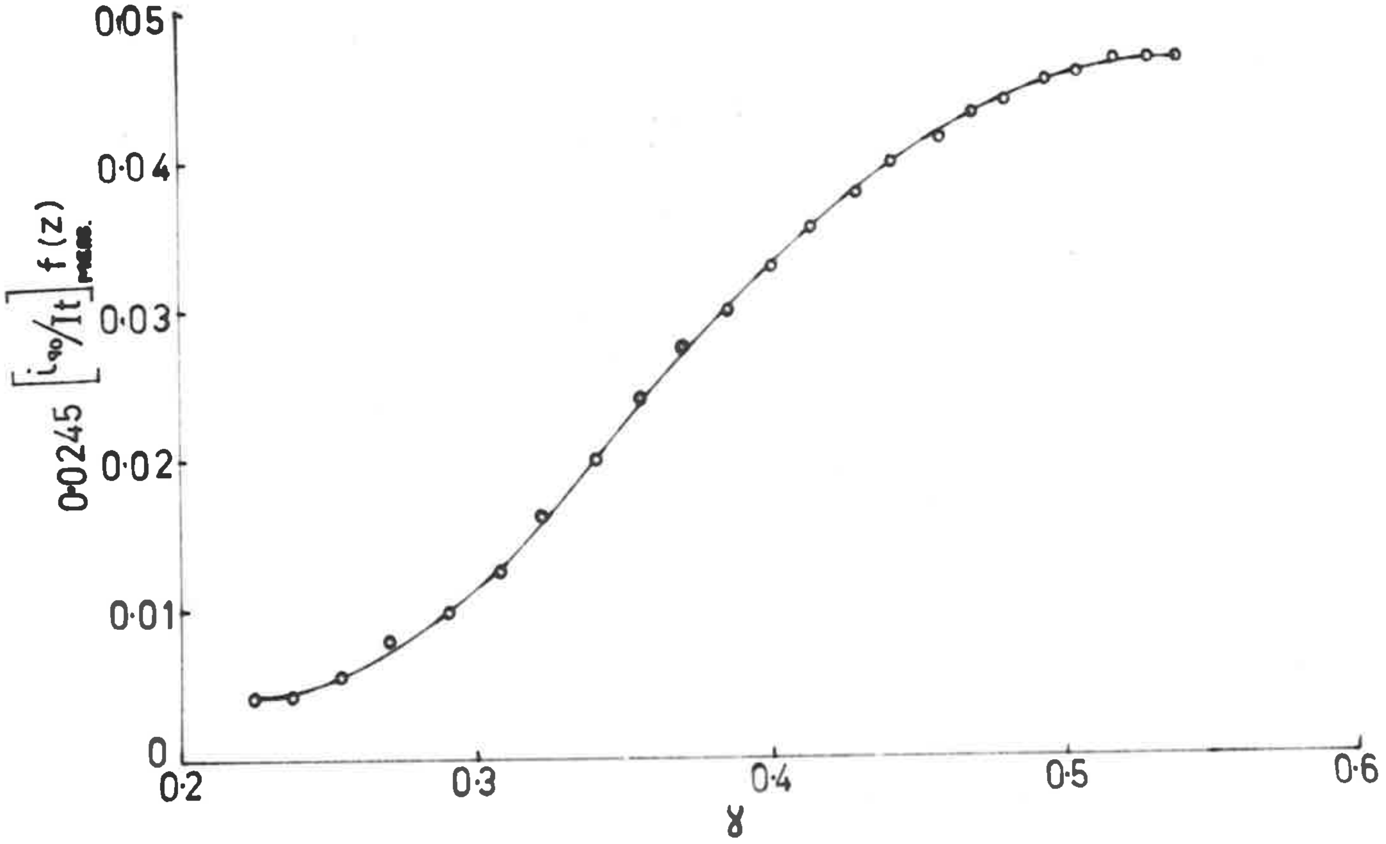
Two samples of polystyrene, sample P1 ($\overline{Mv} = 1.98 \times 10^5$) and sample P2 ($\overline{Mv} = 4.04 \times 10^5$), were chosen for analysis. The titration curve of sample P1 is shown in Fig.(9-V). This curve was corrected for loss of polymer precipitate using the method outlined in section 5 of this Chapter. Having determined the initial concentration ($C_{oo} = 56.8 \times 10^{-5}$) the molecular weights at constant intervals of γ were determined from equation (17-V). From the arbitrary weight values and the corresponding molecular weights the integral molecular weight distribution curve (Fig.10-V) was constructed. The differential molecular weight distribution was obtained from the integral curve by graphical differentiation (Fig.10-V).

To determine the weight mean molecular weight from this data it was necessary to construct the curve of the product of weight by molecular weight (WM) and plot this against molecular weight M. According to the definition of weight mean molecular weight, equation (26-V)

$$\overline{Mw} = \frac{\int_0^\infty WMdM}{\int_0^\infty WdM}$$

thus the area of the WM against M curve, divided by the area

Fig.(9-V). The titration curve for P1 (1.98×10^5). $0.0245 \left[i_{90}/I_t \right]_{meas.}$ f(z) plotted against the point of precipitation γ.



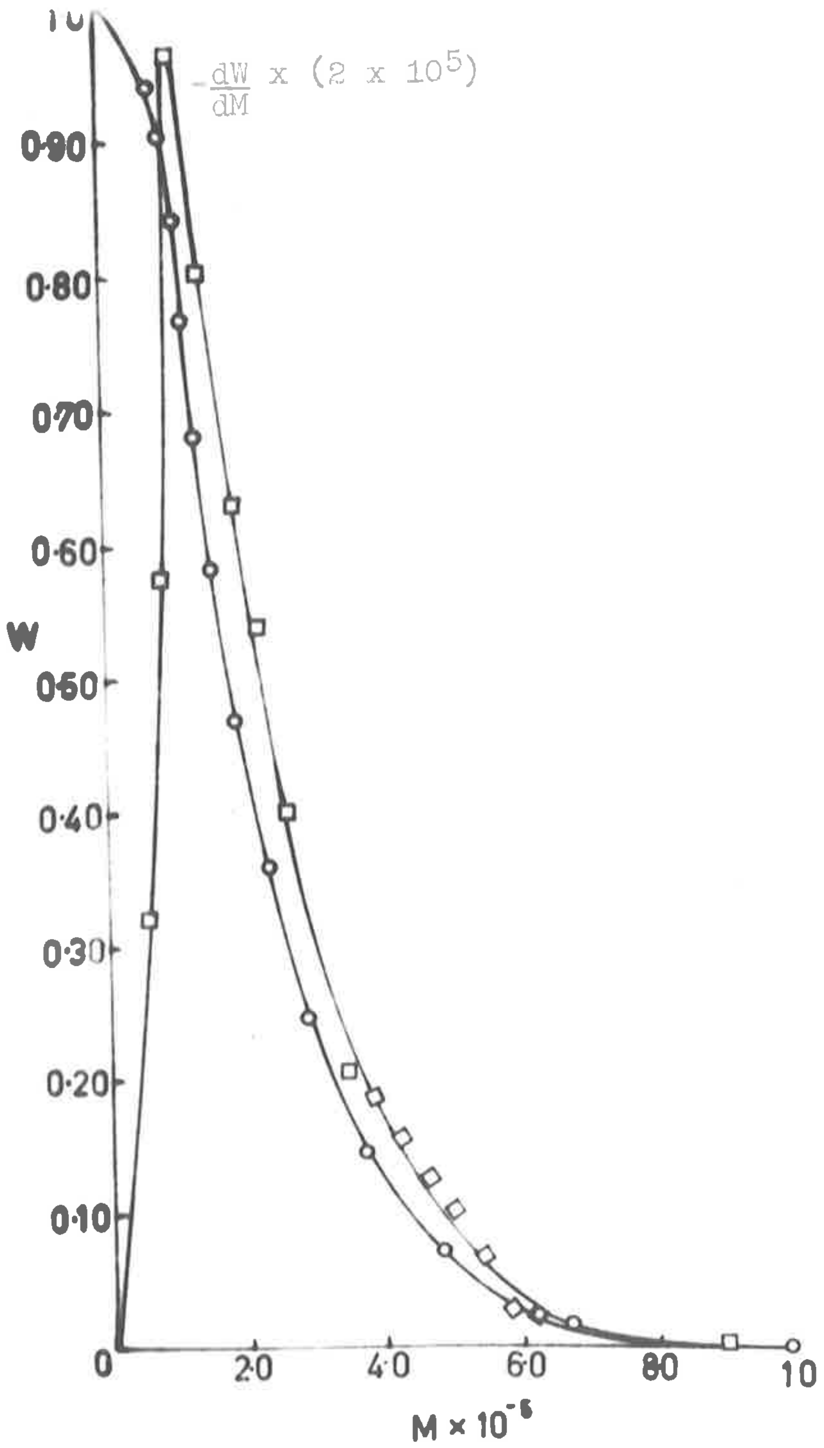


Fig.(10-V). The integral and differential molecular weight distribution curve for sample P1.

of the W against M curve gives the weight mean molecular weight. The areas were determined using a planimeter and the weight mean molecular weight found to be 2.10×10^5. This is within 6% of the actual value (1.98×10^5) found by viscosity.

Using the approximation of equation (29-V), where

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

the weight mean molecular weight for P1 was found to be 2.20×10^5. This value is 10% higher than that determined by viscosity measurements. Overestimation is probably due to the fact that the molecular weight distribution curve for P1 is more than moderately skewed.

The curve of the distribution of molecular weights by number of moles was also determined, by dividing each weight fraction by its molecular weight, and this curve is shown in Fig.(11-V). The number mean molecular weight was determined in a manner similar to that outlined above for determining the weight mean molecular weight. The number mean molecular weight, $\overline{MN}$, was found to be 1.42×10^5. Thus the ratio of the weight mean to the number mean molecular weight was found to be 1.48, indicating that sample P1 had a rather broad molecular weight distribution.

For polystyrene sample P2 ($\overline{Mv} = 4.04 \times 10^5$) the titration curve is shown in Fig.(12-V). This curve was

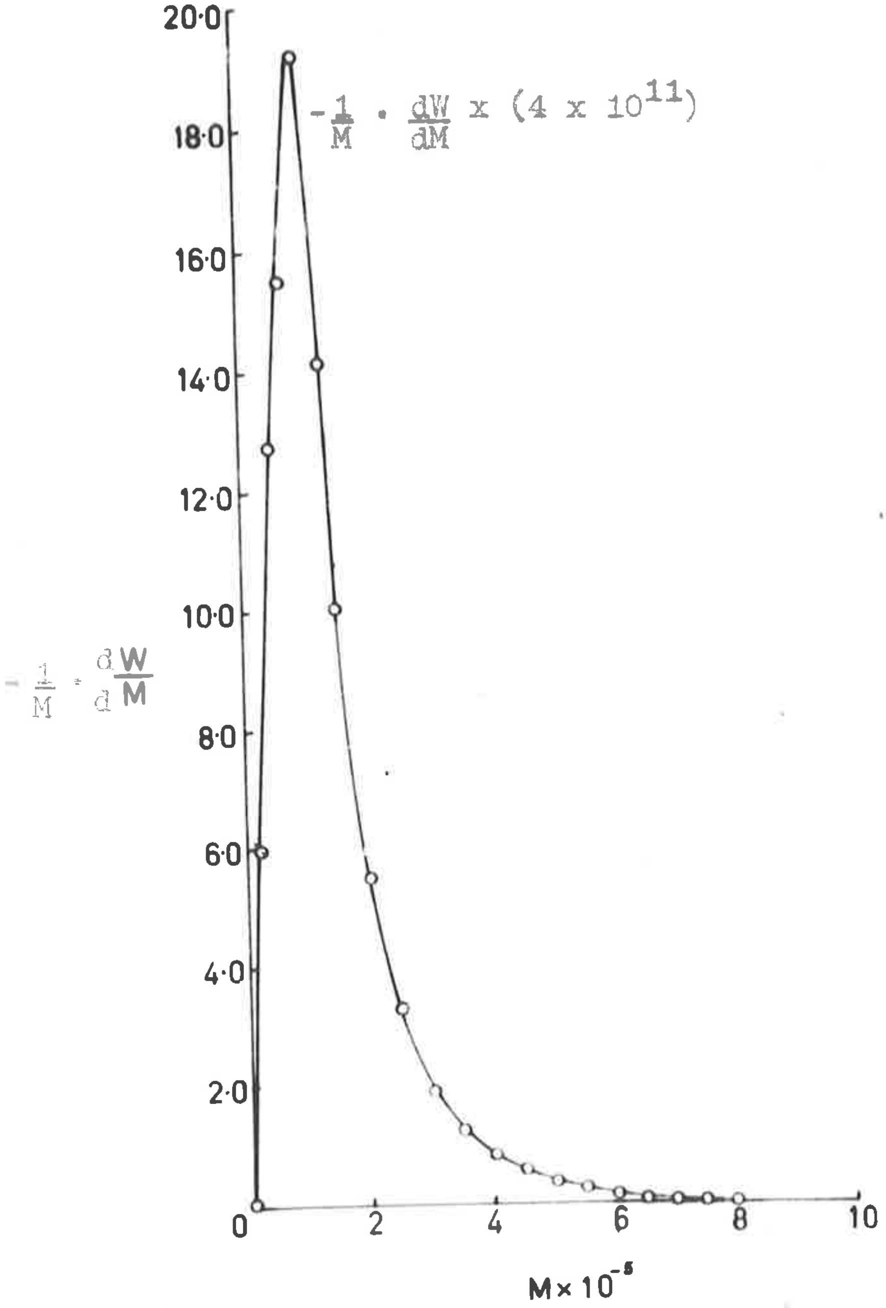


Fig.(11-V). The distribution of molecular weights by number of moles proportional to w/M where w = -(dW/dM) for sample P1.

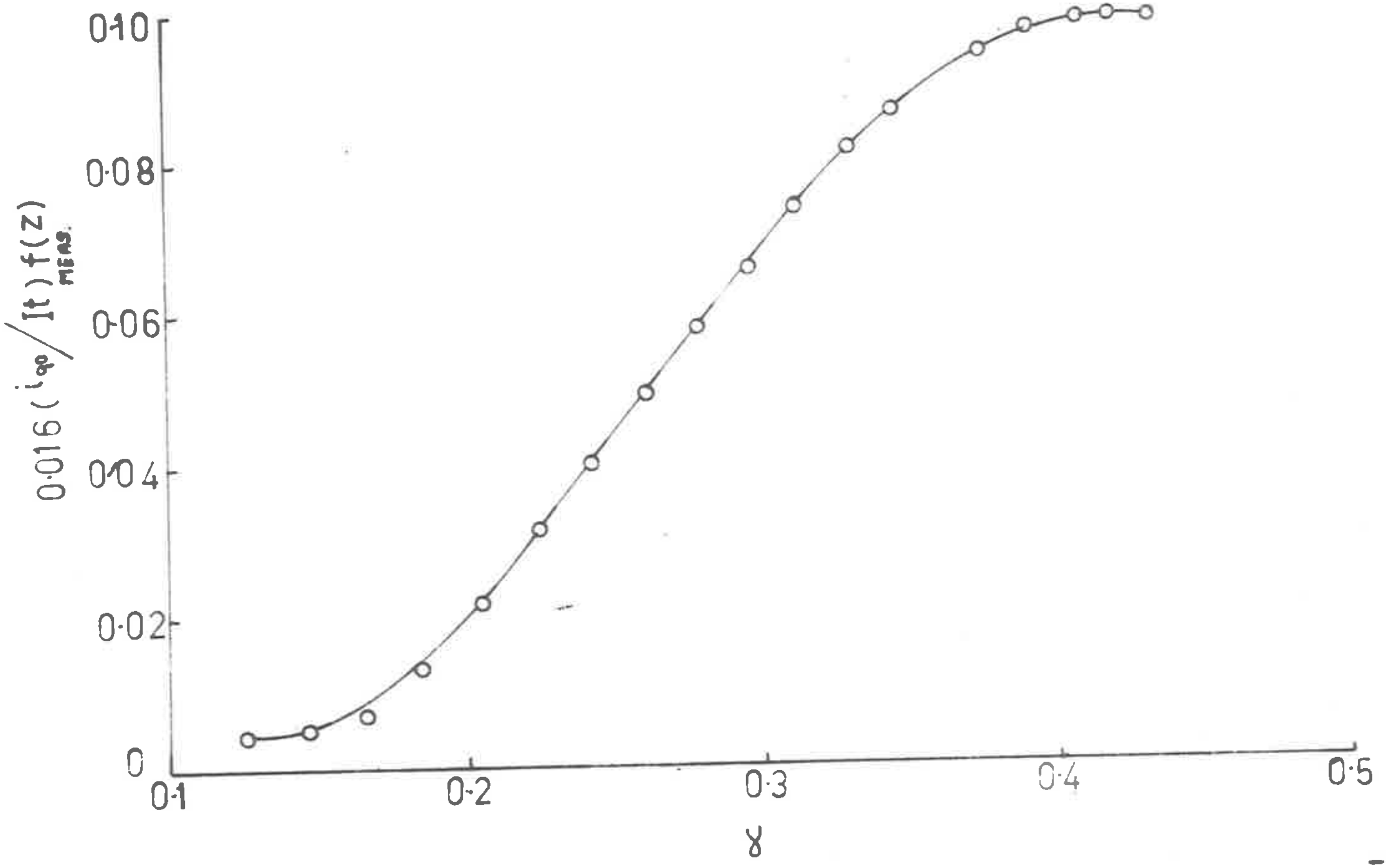


Fig.(12-V). The titration curve for sample P2. $C_{oo} = 11.3 \times 10^{-4}$ (g/100ml).

converted to an integral type curve and finally to the differential molecular weight distribution curve in a manner similar to that outlined above for sample P1. However, the range of molecular weights fell outside the limit of calibration, and the curves could only be constructed with any certainty up to the point shown in Fig.(13-V).

It was not possible to obtain the weight mean molecular weight by the area method outlined for polystyrene sample P1. However, using the approximation method of equation (27-V), the weight mean molecular weight was found to be 4.40×10^5, which is within 10% of the value determined by viscosity (4.04×10^5). Considering the assumptions made in the analysis, the results are reasonably good.

It is interesting at this stage to compare the results obtained from an ultracentrifuge analysis on two polystyrene samples prepared anionically, but using different techniques. The results of this qualitative analysis are shown in Photos.(1-V) and (2-V). Both samples (in toluene, Chapter VII) were spun in the same rotor at 50,740 r.p.m. and a wedge window was used to displace the images. The top image of Photo.(1-V) and Photo.(2-V) is that for a polystyrene sample prepared in a one step polymerization procedure using sodium naphthalene, at -78°C, as initiator. This sample had a molecular weight from viscosity measurements of 2.50×10^5. The bottom image in both photos. is that for a polystyrene

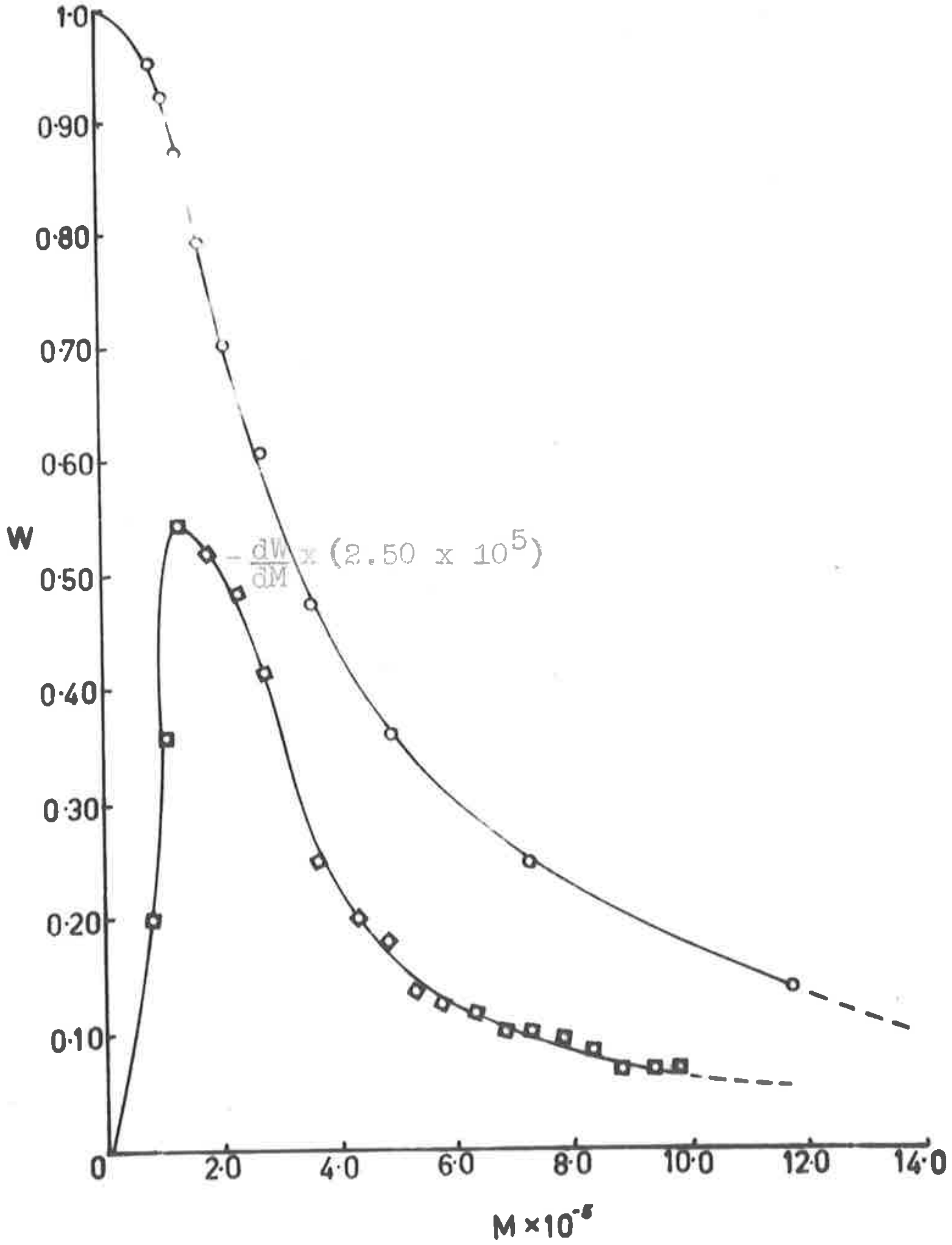


Fig.(13-V). The integral and differential molecular weight distribution curves for sample P2. The weight distribution curve is characterized by the scale factor $-(dW/dM) \times (2.50 \times 10^5)$.

Photo (1-V) taken after 15 minutes and Photo (2-V) after 1 hour for the centrifuge run of two polystyrene samples prepared anionically, but using different preparative techniques.

Photo (1-V)

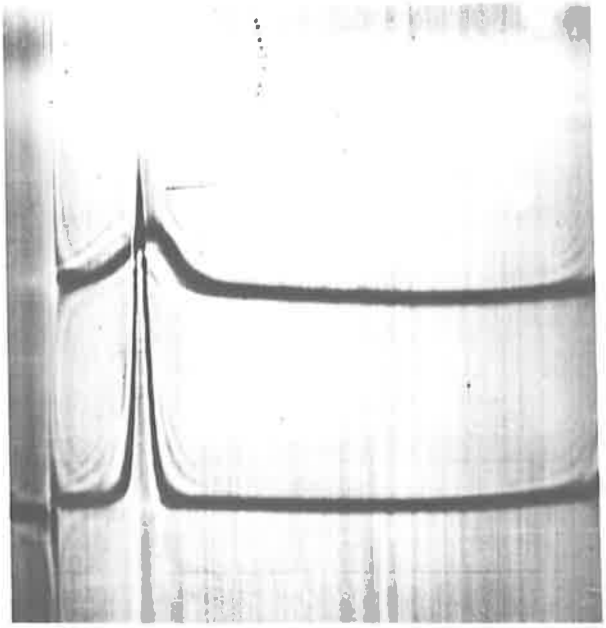
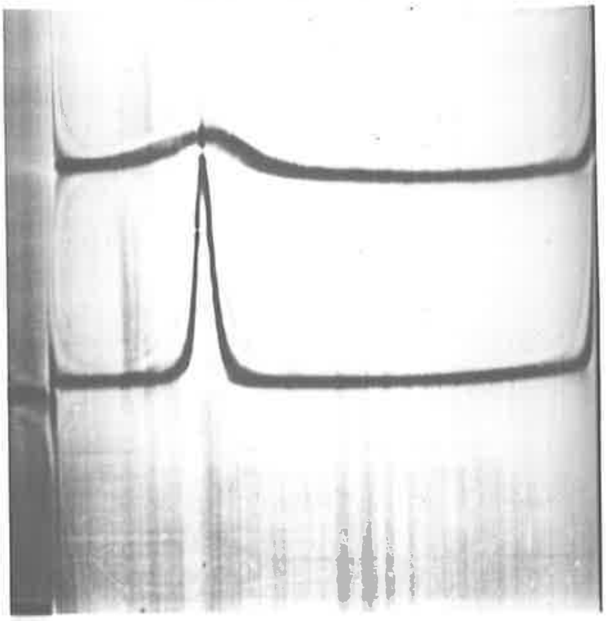


Photo (2-V)



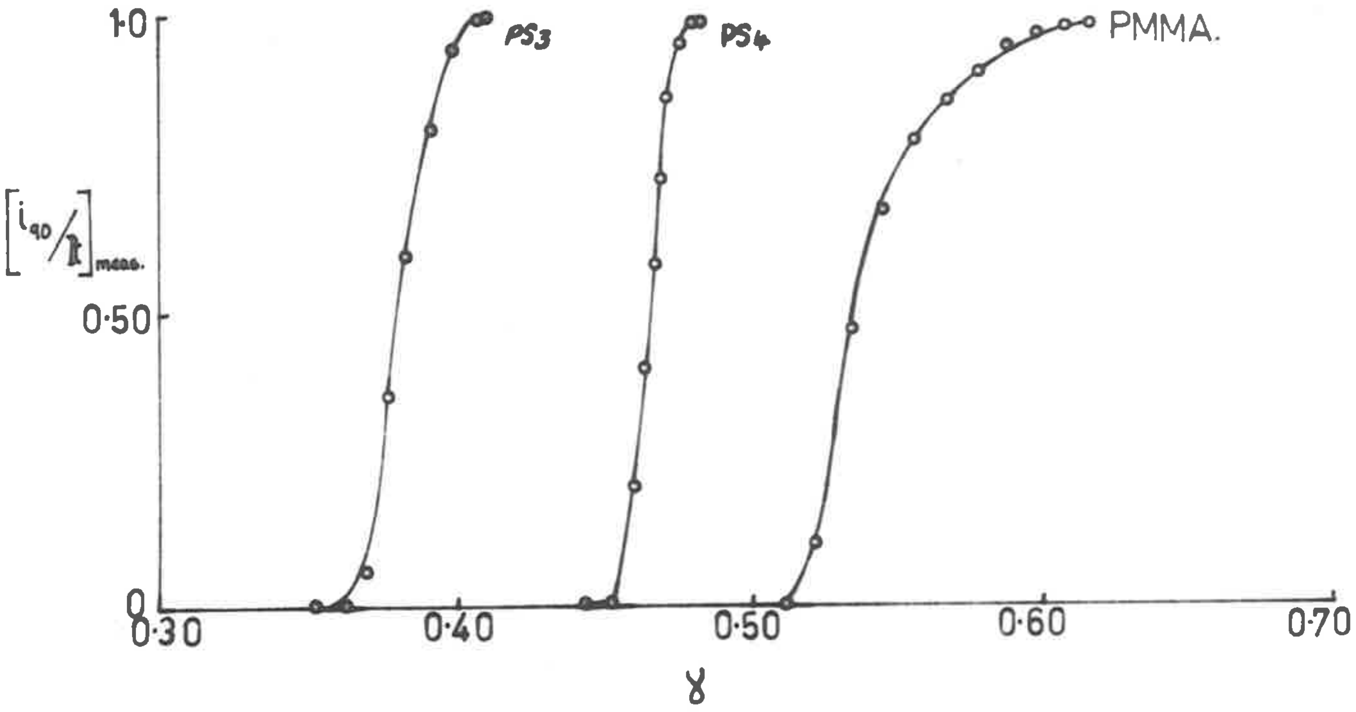
sample ($\overline{Mv} = 3.20 \times 10^5$) prepared by the purging technique (see Chapter III) using sodium biphenyl as initiator. It is evident that the purging technique produces the more monodisperse product. Photo.(2-V) was taken after 1 hour, and it shows very little change for the bottom sample, but the top sample is characterised by a low molecular weight tail.

8. Examination of the Block Copolymers of Styrene and Methyl Methacrylate.

In the preceding sections of this Chapter it has been shown that the fractionation of a homopolymer is critically dependent on its concentration and molecular weight. It has been suggested,[21] however, that a block copolymer will no longer fractionate as a function of overall molecular weight. To test this hypothesis requires a series of well characterized and homogeneous block copolymer samples and a knowledge of the solubility behaviour of both homopolymers.

Two polystyrene samples (PS3 and PS4) prepared in the first stage of the synthesis of block copolymers B3 and B4 were titrated in the apparatus described, using butanone as the solvent and isopropanol as the precipitant. The titration curves for PS3 and PS4 are shown in Fig.(14-V). The ratio of the scattered light at 90° and the transmitted light, that is (i_{90}/I_t)meas., has been normalized, complete precipitation being put equal to unit turbidity. Corrections normally applied to the measured turbidity have been ignored, as such constants were not determined for polymethyl methacrylate or the block copolymers. The molecular weights (PS3 = 162,000 and PS4 = 103,000) were determined by viscosity measurements in toluene, using the relation between viscosity and molecular weight derived by Green.[31] The starting concentration of PS3 was 0.00076 g/100 mls and

Fig.(14-V). The turbidimetric titration curves for polystyrene samples PS3 and PS4 and a polymethyl methacrylate sample PMMA.



PS4, 0.000622 g/100 mls. The precipitation points, corresponding to half the weight of material precipitated, were found to be 0.38 for PS3 and 0.465 for PS4.

A sample of polymethyl methacrylate, also prepared anionically[20] and which had a molecular weight of 800,000 determined by viscosity measurement in toluene, was also titrated. The polymethyl methacrylate was found to be more soluble in butanone than polystyrene, and the precipitatiom point was found to be 0.535. For a sample of polymethyl methacrylate having the same molecular weight as the polystyrene samples, the precipitation point, γ_p, would be greater than 0.535. In order to obtain the same intensity of scatter as that measured for polystyrene, it was necessary to use a larger starting concentration for the polymethyl methacrylate. The reason for this was that the refractive index increment for polymethyl methacrylate in butanone is much smaller than for polystyrene in butanone. The starting concentration for the polymethyl methacrylate sample was 0.0035 g/100 mls. From Fig.(14-V) it can be seen that the polystyrene samples are reasonably homogeneous and are precipitated over a small range of γ. The polymethyl methacrylate sample (PMMA) was also precipitated over a small range, but appeared less homogeneous than the polystyrene samples PS3 and PS4.

It is essential to distinguish between the block copolymers and mechanical mixtures of both homopolymers. This was done by titrating a mixture of polystyrene (0.00030 g/100 mls) block copolymer (0.00041 g/100 mls) and polymethyl methacrylate (0.00051 g/100 mls). The results of such a titration with polystyrene PS4, block copolymer B4 and the polymethyl methacrylate sample PMMA are shown in Fig.(15-V). The polystyrene, being the least soluble of the three polymers, was precipitated first and is shown as precipitating in the range A to B on the titration curve. Between B and C the block copolymer B4 precipitated and between C andD the polymethyl methacrylate PMMA came out of solution. By comparing the points of precipitation for polystyrene and polymethyl methacrylate from Fig.(14-V) and taking the concentration into consideration, it is thus possible to designate points of precipitation for the polystyrene and polymethyl methacrylate samples. The block copolymer sample B4 is seen to have a solubility between that of the pure homopolymers,and its precipitation range is shown to be between the inflection points B and C on the titration curve.

The block copolymer samples were then titrated individually and the titration curves for each sample B1, B2, B3 and B4 are shown in Fig.(16-V). The block copolymers precipitated as a single species and were uncontaminated by homopolymer. The precipitation point γ_p was determined for

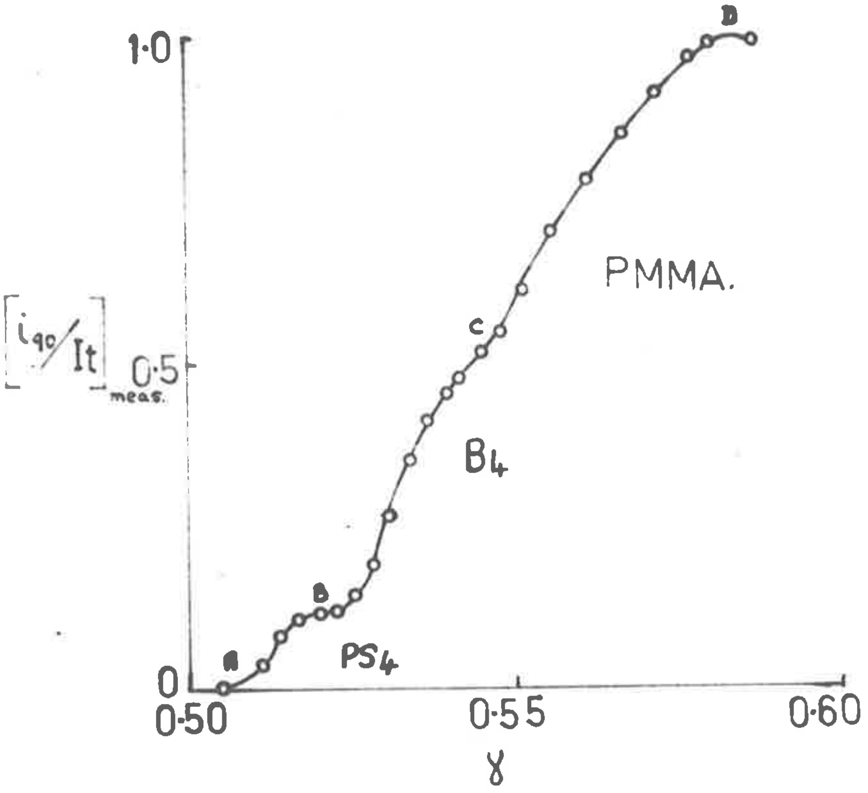


Fig.(15-V). The turbidimetric titration curve for a mixture of polymers, PS4, B4 and PMMA.

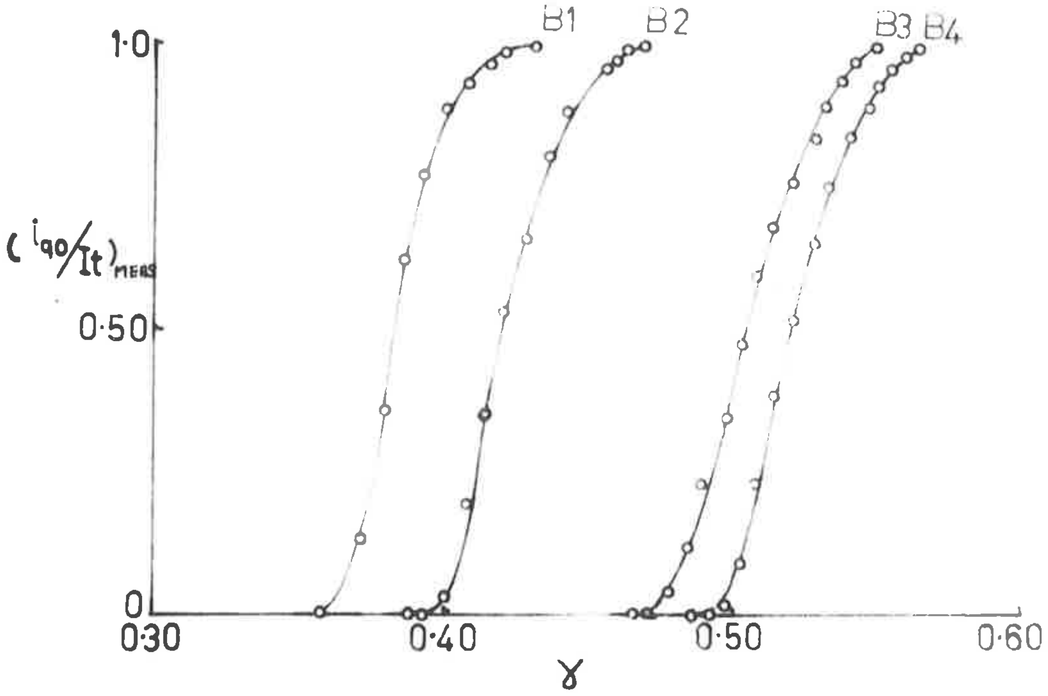


Fig.(16-V). Turbidimetric titration curves for block copolymer samples.

the block copolymers in a manner analogous to that for the polystyrene samples. The point of precipitation γ_p, together with block copolymer composition, molecular weight and the Huggins constant k_H, determined from the viscosity measurements in Chapter VI, are listed in Table (1-V).

Table (1-V). The point of precipitation γ_p, molecular weight, composition and Huggins constant k_H for block copolymer samples B1, B2, B3 and B4 in methyl ethyl ketone at 25°C.

Sample	Mol.wt.x 10^5	% styrene	γ_p	k_H
B4	2.30	48	.520	.34
B3	2.86	62	.505	.37
B2	3.70	70	.421	.38
B1	4.70	85	.384	.47

As can be seen from Table (1-V), as the molecular weight increases, the point of precipitation γ_p decreases, and the Huggins constant increases. Obviously the Huggins constant may be used as a measure of solubility. From Table (1-V) it can be seen that the greater the value of k_H the less soluble the block copolymer and the smaller k_H, the more soluble is the block copolymer in methyl ethyl ketone. For block copolymer samples B1, B2, B3 and B4 the solubility increases as the molecular weight decreases, which is in accord with the normal solubility laws of polymer solutions. It appears that the prediction of Kilb and Bueche[21] that the fractionation of block copolymers no longer depends simply on the number of segments in the polymer, is not obeyed for these block copolymer samples. It must be realized, however, that accompanying the decrease in molecular weight is an increase in polymethyl methacrylate content. The effect of lowering the molecular weight is therefore enhanced by the presence of the more soluble polymethyl methacrylate segments, especially in methyl ethyl ketone.

Schlick and Levy[34] found that with block copolymers of styrene and isoprene in toluene, the solubility was enhanced by decreasing the block size, the overall molecular weight remaining constant. This also contrasts with Kilb and Bueche's[21] predictions. It is obvious, however, that the type of monomers used in the synthesis of block copolymers and the solvents used in the investigation of their dilute solution behaviour, will markedly affect the results obtained.

Discussion.

The results indicate that the turbidimetric titration method is extremely useful as a guide to an average molecular weight and molecular weight distribution. The quantitative aspect of the results is, however, open to criticism. It has been assumed that the scattering power of the polymer suspension is independent of molecular weight and dependent only on the solvent-precipitant composition. The exact relationship between molecular weight and the scattering power of a polymer suspension is not known, although observations by Boyer[33] suggest that it is not a large factor.

Analysis of the polystyrene samples used in the original calibration suggests that their molecular weight distribution is not as narrow as that found by other workers.[20] However, qualitative analysis of two samples, PS3 and PS4, prepared by the modified purging technique (Chapter III), showed them to be more homogeneous than the samples used to calibrate the instrument.

The method has the advantage that molecular weight distribution curves can be readily constructed, and the value obtained for the weight mean molecular weight for sample P1 only deviated from the viscosity value by about 6%. Although it was not possible to compare the molecular weight distribution curve obtained by the turbidimetric method, with a gravimetric fractionation analysis on the same polymer, the method nevertheless offers the advantage of speed.

Examination of the block copolymers using the turbidimetric titration technique showed the distinction between the behaviour of mechanical mixtures and block copolymers. The titration curves indicated that the samples were reasonably homogeneous and their solubility was some function of overall molecular weight

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CHAPTER VI.

Viscosity, Osmometry and Light-Scattering Studies on the Block Copolymers of Polystyrene and Polymethyl methacrylate.

1. Viscosity.
   - a) Introduction.
   - b) Viscosity study on the block copolymer samples and the evaluation of the Huggins constant.

2. Osmometry.
   - a) Osmotic pressure measurements on the polystyrene and block copolymer samples.
   - b) Determination of thermodynamic parameters from osmotic pressure measurements.

3. Light-scattering.
   - a) Determination of the second virial coefficient and the root mean square end-to-end distance for the block copolymer samples.
   - b) Calculation of the expansion factor α, and the functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\overline{r}_0{}^2/M)^{\frac{1}{2}}$ for the block copolymer samples.

Discussion.

References.

CHAPTER VI.

1. Viscosity.

a) Introduction.

Four block copolymer samples (B1, B2, B3 and B4) were prepared and isolated, together with the parent polystyrene (PS1, PS2, PS3 and PS4) used in each synthesis. The viscosities of the polystyrene samples were determined in toluene and the limiting viscosity numbers converted to molecular weight, using the relationship between viscosity and molecular weight derived by Green[1]. The viscosities of the block copolymers were carried out in four solvents; toluene, methyl ethyl ketone, carbon tetrachloride and nitroethane. These solvents were chosen because they differ in their behaviour towards the parent homopolymers. Toluene is a better solvent for polystyrene than for polymethyl methacrylate; methyl ethyl ketone is a fair solvent for polymethyl methacrylate but a poorer solvent for polystyrene; carbon tetrachloride is a good solvent for polystyrene but rather poor for polymethyl methacrylate; and nitroethane is a good solvent for polymethyl methacrylate but a non-solvent for polystyrene. The results of these measurements are shown in Figs.(1-VI) and (2-VI).

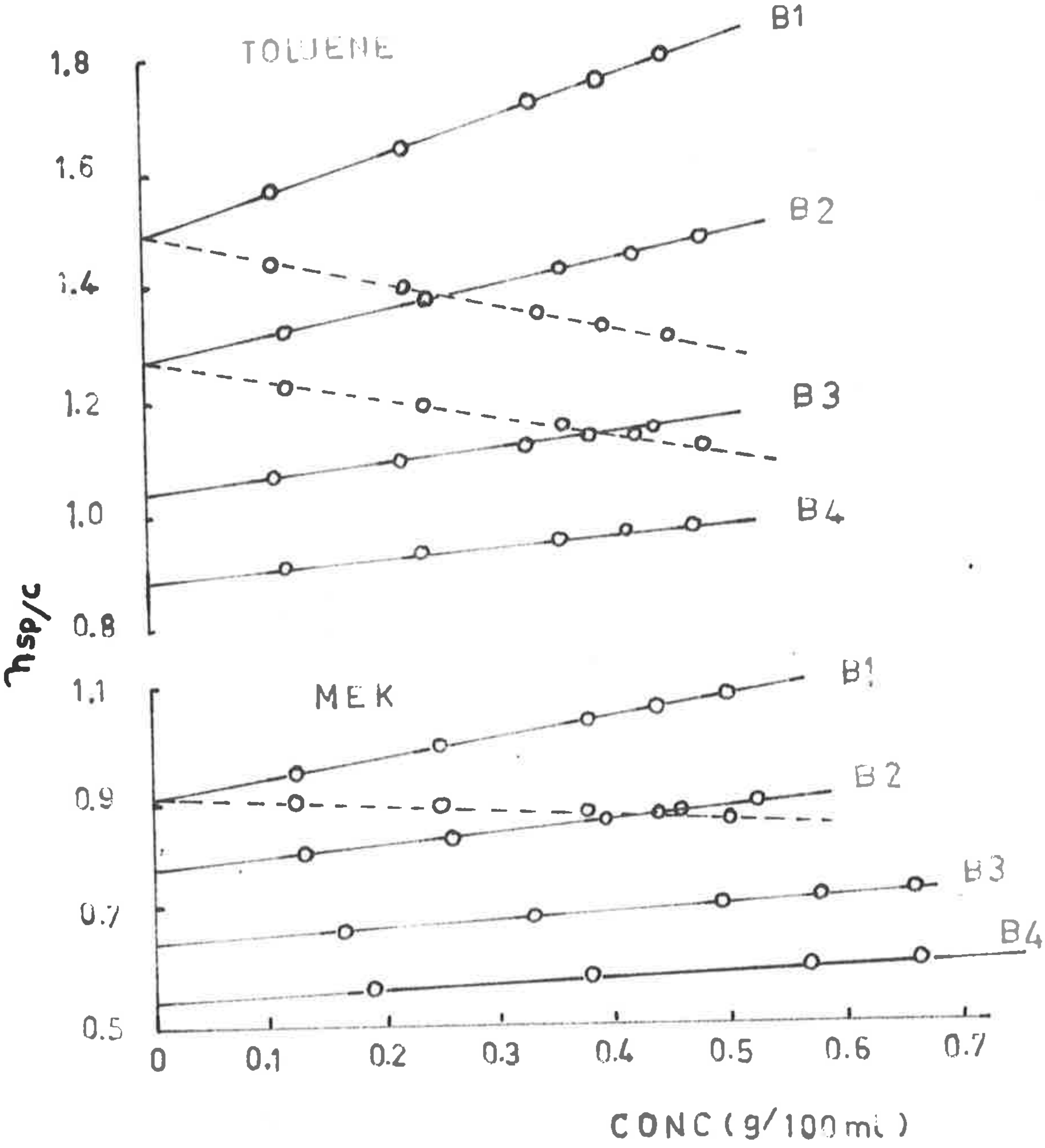

Fig.(1-VI). Viscosity plots for the block copolymer samples in toluene and methyl ethyl ketone (MEK)

The osmotic pressure measurements on the polystyrene samples were determined in toluene, as were the osmotic pressure and light-scattering studies on the block copolymers. The results showed that the polystyrene samples had a fairly narrow molecular weight distribution. The ratios of the viscosity average molecular weight to the number average molecular weight were higher than values reported previously by other authors[2,3] using the same preparative technique. The viscosity average and number average molecular weights together with their ratios are listed below in Table (1-VI).

Table (1-VI). The molecular weights of the polystyrene samples and the ratio $\overline{M_v}/\overline{M_N}$.

Sample	$[\eta]$ dl/g.	$\overline{M_v} \times 10^{-5}$	$\overline{M_N} \times 10^{-5}$	$\overline{M_v}/\overline{M_N}$
PS1	1.274	3.83	3.42	1.12
PS2	0.867	2.40	2.12	1.13
PS3	0.654	1.62	1.40	1.16
PS4	0.472	1.03	0.90	1.14

The osmotic pressure and light-scattering studies on the block copolymers indicated that their molecular weight distribution was not as narrow as that of the parent polystyrene samples. It must be pointed out, however, that the molecular weight for block copolymers determined from light-scattering could be high by a factor of approximately 1.1. The results of Bushuk and Benoit[4] indicate that the light-scattering molecular weight in the case of block copolymers depends largely on the solvent and the value of the refractive index increment. The larger the refractive index increment, the closer are the true and apparent molecular weights for block copolymers. The weight average and number average molecular weights for the block copolymers are listed in Table (2-VI).

Table (2-VI). The molecular weights of the block copolymers and the ratio $\overline{M_W}/\overline{M_N}$.

Sample	% PS.	$\overline{M_W} \times 10^{-5}$(L/S)	$\overline{M_N} \times 10^{-5}$	$\overline{MW}/\overline{M_N}$
B1	85	4.70	3.90	1.21
B2	70	3.70	3.02	1.23
B3	62	2.86	2.25	1.27
B4	48	2.30	1.88	1.22

b) Viscosity study on the block copolymer samples and the evaluation of the Huggins constant.

The viscosity study on the four block copolymer samples carried out in toluene, methyl ethyl ketone, carbon tetrachloride and nitroethane could be satisfactorily represented by the Huggins equations[5],

$$(\eta\,sp/c) = [\eta] + k_H[\eta]^2c \qquad (1\text{-VI})$$

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

where $k_H + k' = 0.50$

In studying the Huggins constant for each block copolymer in the four solvents used, comparison was made with the Huggins constant for each homopolymer and the measured value for the block copolymer. Cragg and Bigelow[6] have shown that the Huggins constant can be calculated for a mixture of polymers according to the relationship,

$$(k_H)m = \frac{(k_H)_A[\eta]^2_A\,W_A^2 + (k_H)_B[\eta]^2_B\,W_B^2 + 2(k_H)_A(k_H)_B[\eta]_A[\eta]_B W_A W_B}{([\eta]_A W_A + [\eta]_B W_B)^2} \qquad (3\text{-VI})$$

where $(k_H)_A$ and $(k_H)_B$ are the Huggins constants for each homopolymer and W_A and W_B the weight fraction of each polymer present in the mixture. The limiting viscosity numbers of each homopolymer are denoted by $[\eta]_A$ and $[\eta]_B$. This equation was derived[6] assuming the existence of hydrodynamic forces only; the existence of thermodynamic interaction in solution being ignored. The technique of preparation allowed for the isolation of the parent polystyrene in the first stage of the synthesis. The molecular weight of the polymethyl methacrylate, attached to each end of the polystyrene chain, was calculated assuming the difference between the molecular weight of the block copolymer, determined from light-scattering and the molecular weight of the polystyrene from viscosity measurements. The limiting viscosity numbers for polymethyl methacrylate in toluene and methyl ethyl ketone were determined using the data of Chinai and co-workers[7]. For polystyrene in toluene and methyl ethyl ketone the equations of Green[1] were used. Thus it was possible to determine the $(k_H)m$ value for the block copolymer, assuming it to be a mechanical mixture of homopolymers and that thermodynamic interactions were non-existent. These values, together with actual measured values for the block copolymers and the parent homopolymers in toluene, are listed in Table (3-VI). The limiting viscosity numbers have been measured in decilitres/gram and the Huggins constant for polymethyl methacrylate was taken from the data of Alfrey, Goldberg and Price[8].

Table (3-VI). The limiting viscosity number and the Huggins constant for the block copolymer and parent homopolymers in toluene at 25°C.

Sample	% PS	$[\eta]$ dl/g	(k_H) meas.	(k_H)m from (3-VI)
PMMA	0	-	0.38	-
B4	48	0.887	0.22	0.24
B3	62	1.038	0.24	0.27
B2	70	1.274	0.27	0.29
B1	85	1.496	0.30	0.33
PS1	100	1.274	0.35	-

The results of Table (3-VI) are represented graphically in Fig.(3-VI), where (k_H) measured and (k_H)m calculated from equation (3-VI), have been plotted against percentage weight composition of polystyrene present in the block copolymer. The values of (k_H)m calculated, have been represented by the solid line of best fit, the actual points have not been shown. The experimental values of k_H are shown and a dashed line of best fit has been drawn through these points. No points were available between 0 and 48% PS content, so that the shape of both curves remains uncertain in this region. The values of the Huggins constant for the block copolymers measured experimentally are all lower than those of either homopolymer, or the values calculated from equation (3-VI).

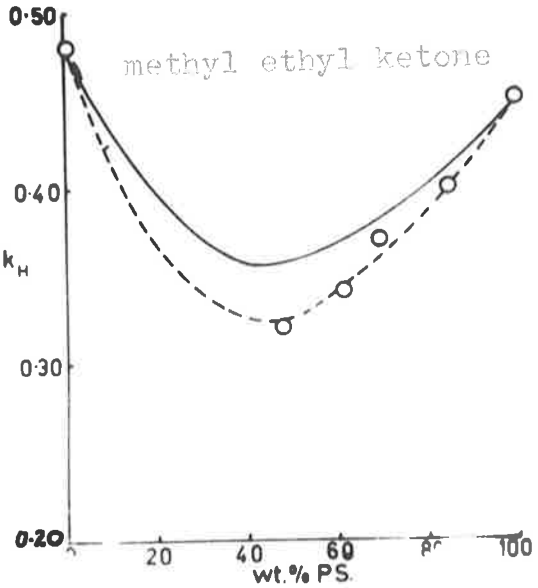

Fig.(4-VI)

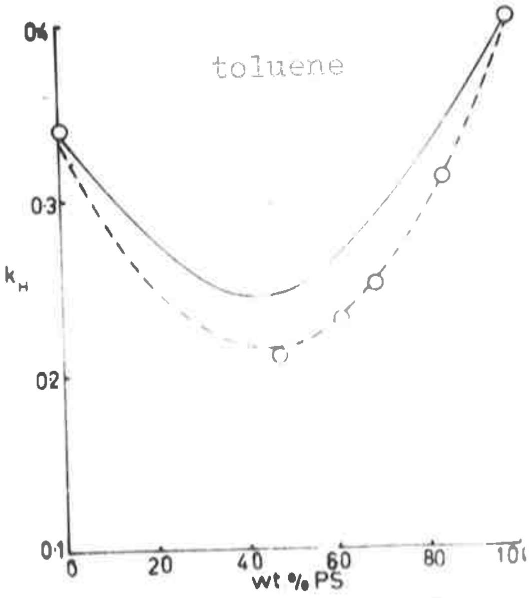

Fig.(3-VI)

Figs.(3-VI) and (4-VI). The variation of the Huggins constant, measured (-----) and calculated (———), with block copolymer composition in toluene and methyl ethyl ketone respectively.

The deviations from the Cragg and Bigelow[6] function are negative and they appear to pass through a minimum value at about 50% PS content for the block copolymer. The results indicate the existence of thermodynamic interactions, which suggests a greater repulsion between block copolymer molecules than between pairs of polystyrene or pairs of polymethyl methacrylate molecules. The results also seem to indicate a smaller positive interaction between block copolymer molecules than between polystyrene and polymethyl methacrylate molecules. The same effect was observed in methyl ethyl ketone as was observed in toluene. The data for the homopolymers and the block copolymers is listed in Table (4-VI). The data has been represented graphically in Fig.(4-VI).

Table.(4-VI). The limiting viscosity number and the Huggins constant for the block copolymers and parent homopolymers in methyl ethyl ketone at 25°C.

Sample	% PS	$[\eta]$ dl/g	(k_H) meas.	(k_H)m.calc.
PMMA	0	-	0.44	-
B4	48	0.545	0.31	0.34
B3	62	0.641	0.33	0.37
B2	70	0.773	0.35	0.38
B1	85	0.904	0.41	0.47
PS1	100	0.665	0.50	-

In carbon tetrachloride the variation of the Huggins constant with composition is more marked, because of the large difference in solubility of the two homopolymers in this particular solvent. The results have been tabulated in Table (4-VI) and graphed in Fig.(5-VI). The Huggins constant values from equation (3-VI) were not determined for the block copolymer samples in carbon tetrachloride.

Table (4-VI). Limiting viscosity number and Huggins constant for the block copolymer and parent homopolymers in carbon tetrachloride at 25°C. The values of k_H for PMMA and PS are taken from the data of Alfrey, Goldberg and Price[8].

Sample	% PS	$[\eta]$ dl/g	(k_H) meas.
PMMA	0	-	0.80
B4	48	0.732	0.41
B3	62	0.860	0.40
B2	70	1.059	0.38
B1	85	1.170	0.36
PS	100	-	0.39

From Fig.(5-VI) it can be seen that the k_H values fall sharply to about 50% polystyrene content, then remain fairly constant up to 100% polystyrene content for the block copolymer. A qualitative explanation being

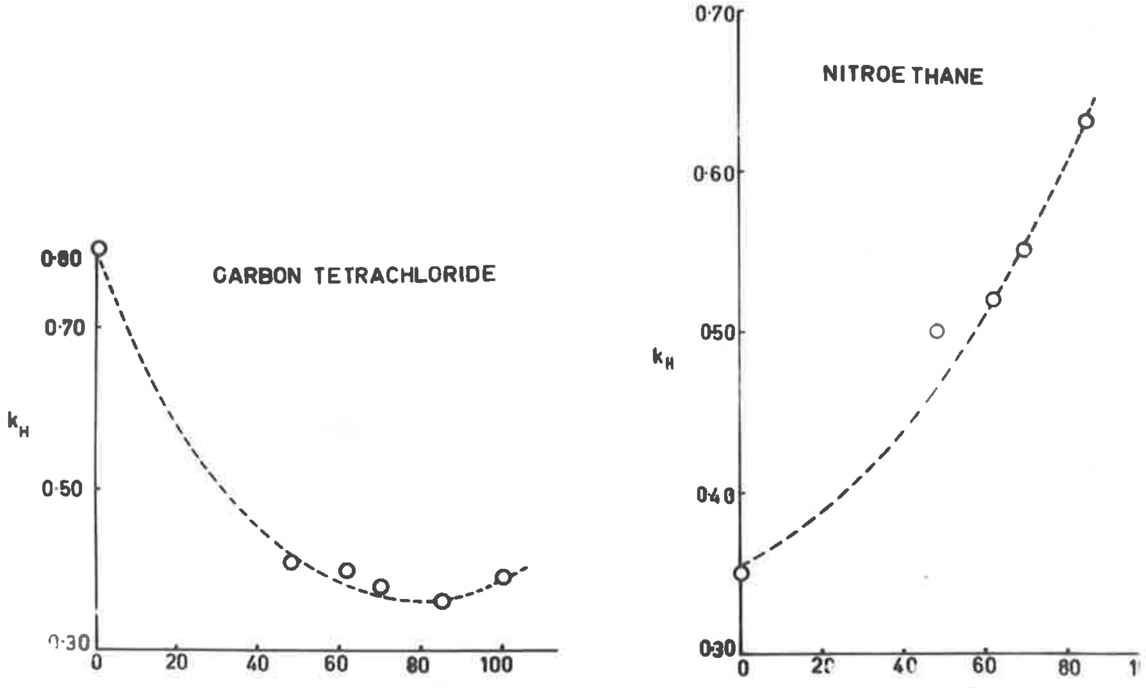

Fig.(5-VI)

Fig.(6-VI)

Figs.(5-VI) and (6-VI). The variation of the measured Huggins constant (-----) with block copolymer composition in carbon tetrachloride and nitroethane respectively.

that in carbon tetrachloride, polymethyl methacrylate will tend to occupy a minimum hydrodynamic volume, polymer-polymer contacts being favoured more than polymer-solvent contacts. As the percentage polystyrene content of the block copolymer is increased, so will the tendency for polymer-solvent contacts be increased. It appears that at about 50% polystyrene content the polymer-polymer and polymer-solvent contacts are about equal and increasing the polystyrene content only has a very small effect on the value of the Huggins constant.

In nitroethane the effect of the composition of the Huggins constant is more marked still. The results have been tabulated in Table (5-VI) and the experimental values are shown graphically in Fig.(6-VI).

Table (5-VI). The limiting viscosity number and Huggins constant for the block copolymers and polymethyl methacrylate (reference 8) measured in nitroethane at 25°C.

Sample	% PS	$[\eta]$ dl/g	(k_H) measured.
PMMA	0	-	0.35
B4	48	0.531	0.50
B3	62	0.462	0.52
B2	70	0.345	0.55
B1	85	0.198	0.63
PS	100	Insoluble	

In nitroethane it was found that as the limiting viscosity number decreased, the Huggins constant increased, indicating increased aggregation of the block copolymer with increasing polystyrene content. The results in Fig. (6-VI) show that with increasing polystyrene content the k_H values tend to rise very sharply and perhaps approach some limiting composition value, beyond which the block copolymer will be insoluble in nitroethane.

It must be realised, however, that not an inconsiderable error may be involved in the calculation of the Huggins constant (see Chapter VII). For example, for a k_H value of 0.40 the error in determining k_H may be as high as ± 0.02. It is essential that particular care be taken, especially with small limiting viscosity numbers. This is the case with nitroethane and may explain the scatter of points in Fig.(6-VI). Though small errors may be involved, the negative deviations for the k_H values in Figs.(3-VI) and (4-VI) are too consistent to be discounted. Although the Huggins constants calculated from equation (3-VI) were to act only as a guide, evidence for strong thermodynamic interaction is shown. The actual shape of all four curves should be interpreted with reservation, because of the few points used in their determination.

2. Osmometry.

a) Osmotic pressure measurements on the polystyrene and block copolymer samples.

Osmotic pressure measurements for the polystyrene and block copolymer samples were performed in toluene. The plot of (π/cRT) against c for the four polystyrene samples (PS1, PS2, PS3 and PS4) are shown in Fig.(7-VI). The plots are best represented by curved lines, in accord with the theoretical relationship[9],

$$\pi/cRT = \frac{1}{\overline{M_N}} \left[1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots. \right] \quad (4\text{-VI})$$

If higher terms in equation (4-VI) are ignored, and taking $\Gamma_3 = g\Gamma_2$, where g is the proportionality factor, having the value $\frac{1}{4}$ in good solvents,[10] then equation (4-VI) can be rewritten so that,

$$(\pi/cRT)^{\frac{1}{2}} = \overline{M_N}^{-\frac{1}{2}} \left[1 + \tfrac{1}{2} \Gamma_2 c \right] \quad (5\text{-VI})$$

In Fig.(8-VI) the data for the polystyrene samples has been plotted in the form $(\pi/cRT)^{\frac{1}{2}}$ versus c. Straight lines were obtained, as has been observed before.[11,14] The osmotic pressure data obtained for the polystyrene samples is shown in Table (6-VI).

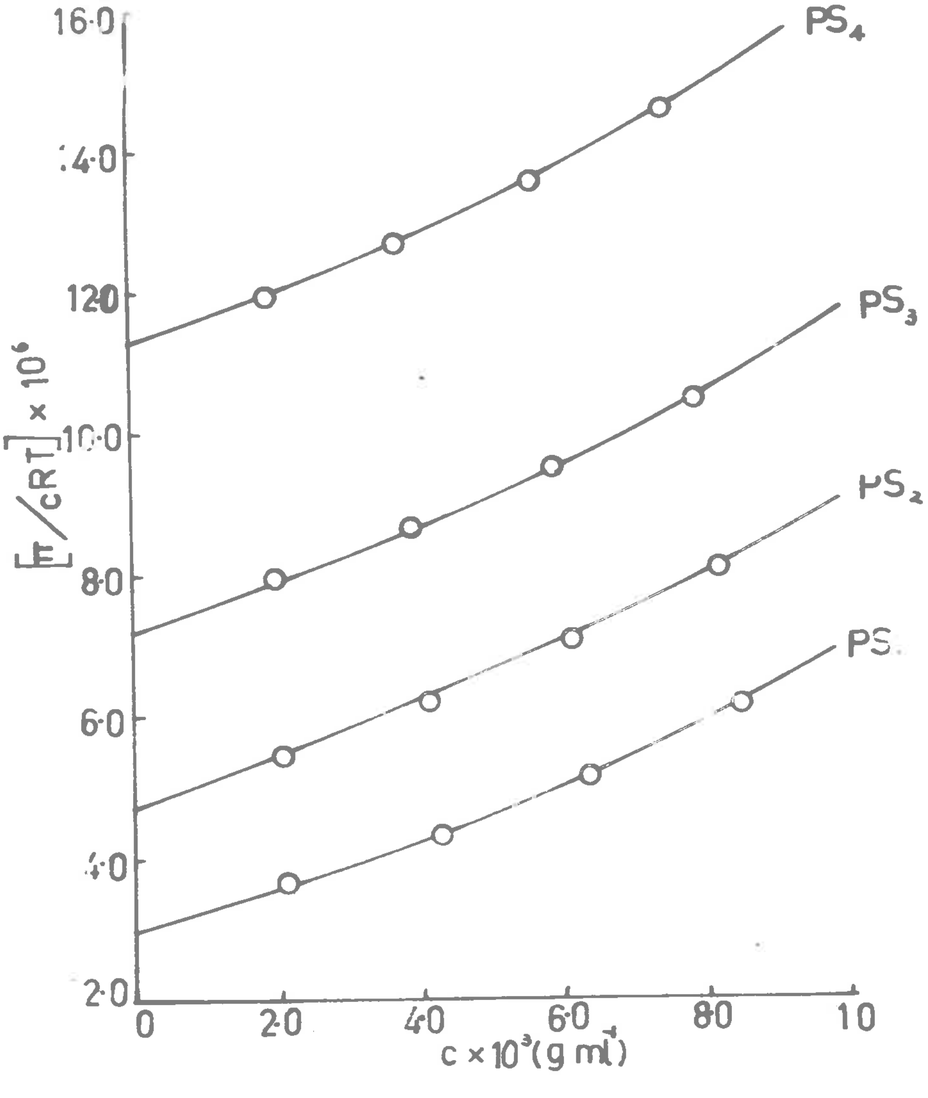

Fig.(7-VI). The plot of π/cRT against concentration c for the polystyrene samples in toluene at 25°C.

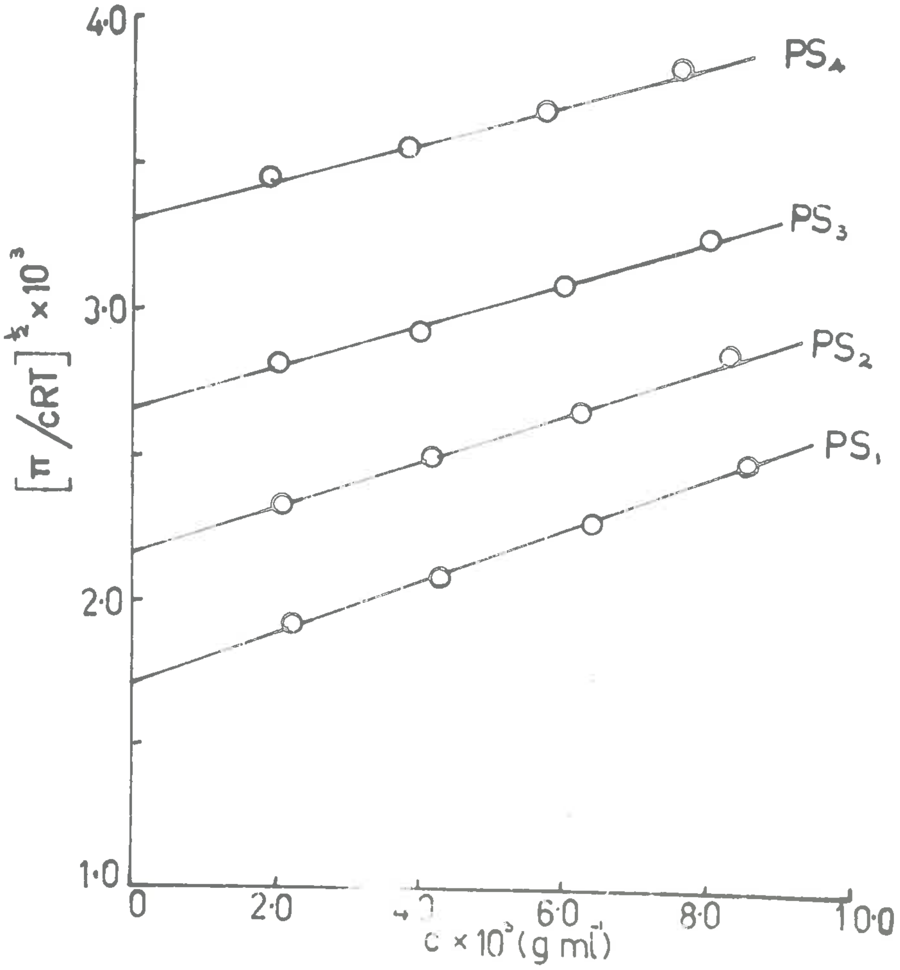

Fig.(8-VI). The plot of $(\pi/cRT)^{\frac{1}{2}}$ against the concentration c for the polystyrene samples in toluene at 25°C.

Table (6-VI). The osmotic pressure coefficients and the number average molecular weights for the polystyrene samples in toluene at 25°C.

Sample	$\overline{M_N} \times 10^{-5}$	$\Gamma_2 (cm^3 g^{-1})$	$A_2 \times 10^3 (cm^2 g^{-2})$
PS1	3.42	105.3	0.307
PS2	2.12	71.3	0.336
PS3	1.40	52.4	0.374
PS4	0.90	37.8	0.420

The block copolymers were examined in the same manner as the polystyrene samples above. The plot of (π/cRT) versus c for the block copolymer samples (B1, B2, B3 and B4) yielded curved lines, as was observed in the case of the polystyrene samples. This is shown in Fig.(9-VI). Plotting $(\pi/cRT)^{\frac{1}{2}}$ against c gave almost straight lines as shown in Fig.(10-VI). This is in contrast to the recent results of Burnett and co-workers,[14] who found that for block copolymers of styrene and methyl methacrylate the plot of $(\pi/cRT)^{\frac{1}{2}}$ against c produced curves that were convex towards the concentration axis. The results of the data plotted in Fig.(10-VI) indicate that the proportionality constant g, is very close to $\frac{1}{4}$ for the block copolymers as is observed with most homopolymers in a good solvent.

The osmotic pressure coefficients are set out in Table (7-VI).

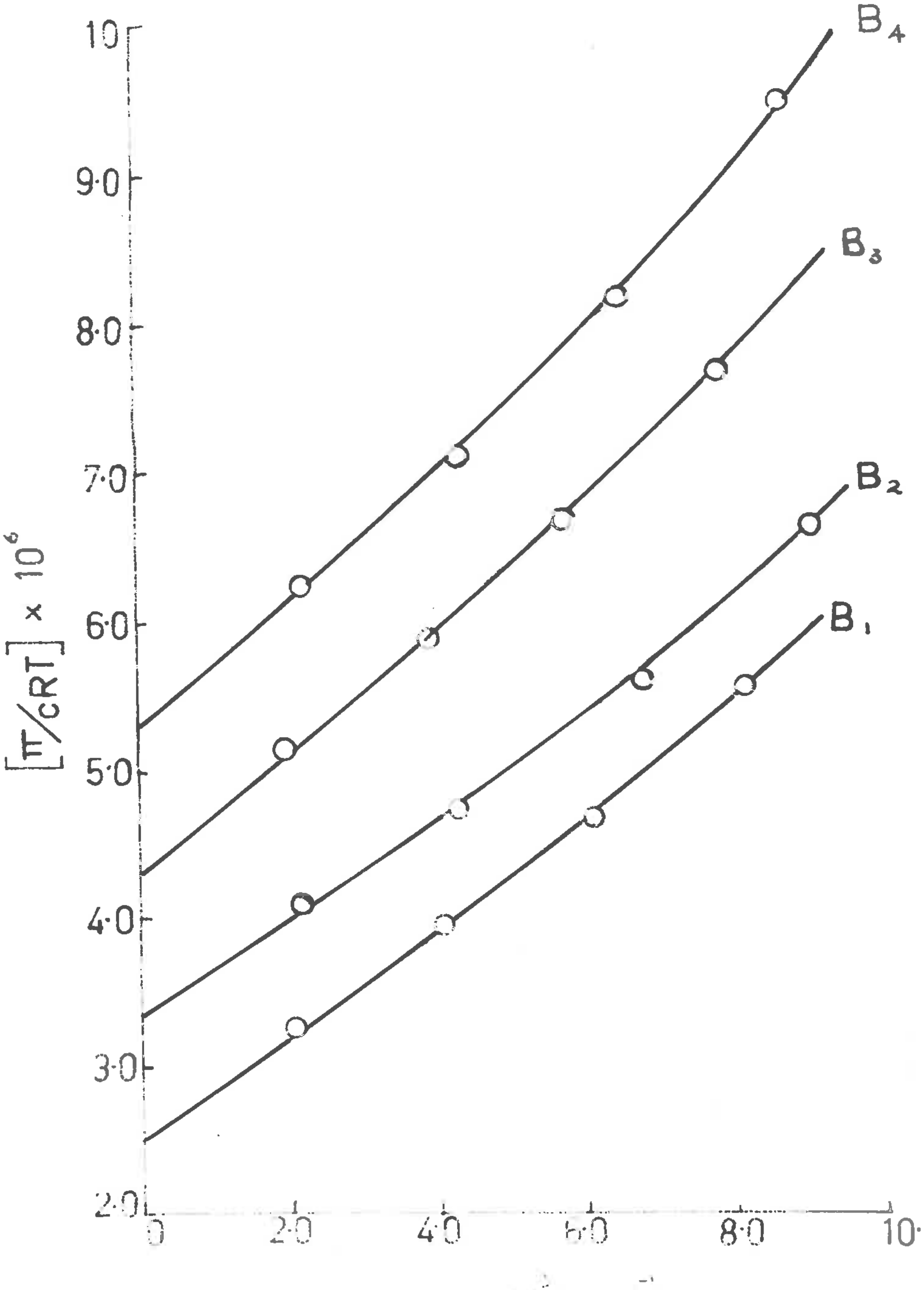

Fig.(9-VI). The plot of (π/cRT) against concentration c for the block copolymer samples in toluene at 25°C.

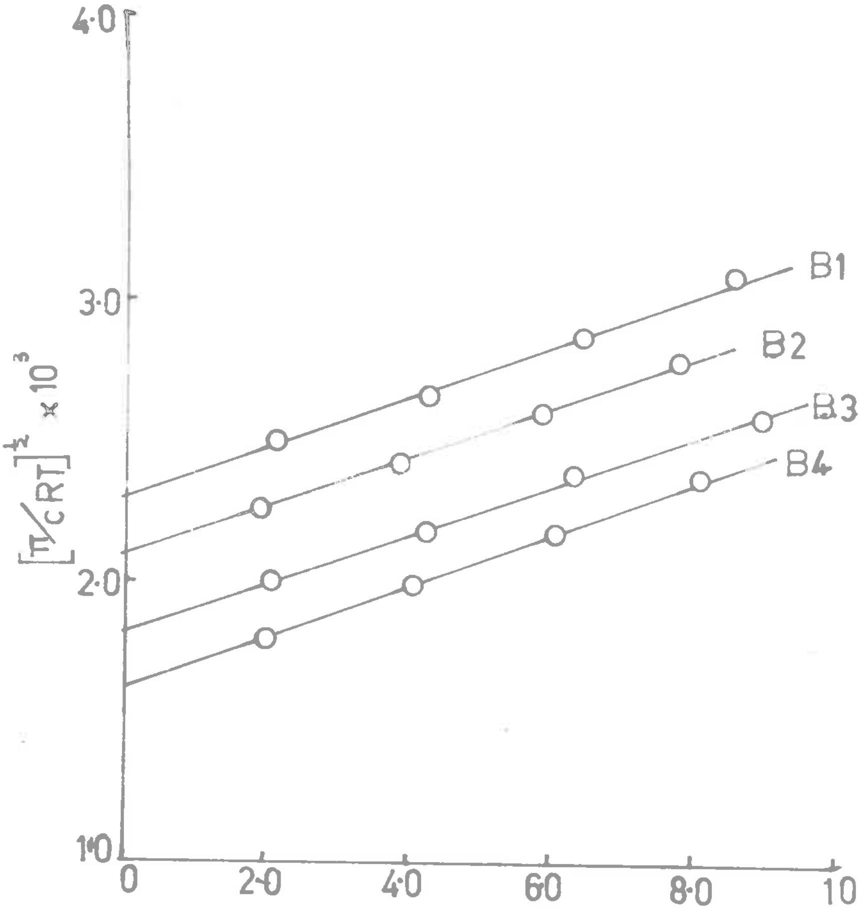

Fig.(10-VI). The plot of $(\pi/cRT)^{\frac{1}{2}}$ against concentration c for the block copolymer samples in toluene at 25°C.

Table (7-VI). Osmotic pressure coefficients for the block copolymers in toluene at 25°C.

Sample	% PS	$\overline{M_N} \times 10^{-5}$	$\Gamma_2(cm^3g^{-1})$	$A_2 x10^3(cm^2g^{-2})$
B1	85	3.90	115.0	0.295
B2	70	3.02	97.3	0.324
B3	62	2.25	81.4	0.362
B4	48	1.87	73.9	0.394

The results in Table (7-VI) show a decrease in the second virial coefficient A_2, with increasing molecular weight of the block copolymers. This behaviour is similar to that observed for homopolymers. The variation of the second virial coefficient A_2 with molecular weight for the polystyrene samples is shown in Table (6-VI).

The values of A_2 were obtained from the experimental data by graphical analysis. The possible variation of the second virial coefficient with the composition of the block copolymers is perhaps masked by the variation with molecular weight. The data in Table (7-VI) shows that as the polystyrene content of the block copolymer decreases, the second virial coefficient A_2 increases. However, in order to test the validity of any variation of A_2 with composition, it would be necessary to keep the molecular weight constant and vary the composition. By contrast, Burnett and co-workers[14] obtained a near constant second virial coefficient A_2, independent of block copolymer composition. In the work of Burnett and co-workers[14] the molecular weights of the block copolymers were almost constant and the composition range covered was from 50-74% polystyrene content by weight. The fact that the second virial coefficients A_2 for polystyrene and polymethyl methacrylate are almost the same in toluene, might explain why A_2 varies little with block copolymers of constant molecular weight, but varying composition. However, since A_2 is nearly the same for each homopolymer, changes in molecular weight of the block copolymer might then be expected to produce changes in the corresponding second virial coefficient, as shown in Table (7-VI).

b) Determination of thermodynamic parameters from osmotic pressure measurements.

Flory[9] has shown that the temperature dependence of the second virial coefficient A_2 can be expressed by an equation of the form,

$$A_2 = (\bar{v}^2/V_1)\psi_1(1 - \theta/T)\,F(x) \qquad (8\text{-VI})$$

where $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of the solvent, ψ_1 is the entropy of dilution parameter, θ is the Flory temperature and $F(x)$ a function of the excluded volume[15] of the coiled polymer molecules. $F(x)$ is related to the degree of expansion of the coiled polymer molecules, such that $x = 2(\alpha^2-1)$, where α is the ratio of the root mean square end-to-end distance to the unperturbed dimensions of the polymer coil. At temperatures approaching the θ or Flory temperature, the function $F(x)$ becomes very small and is close to unity when $T \mathrel{\hat{=}} \theta$.

The osmotic pressure measurements for one block copolymer sample (B4 - 48% PS content) were determined at three temperatures, 15, 25 and 50°C. The osmotic pressure coefficients for this block copolymer are shown in Table (8-VI) and the plots of $(\Pi/cRT)^{\frac{1}{2}}$ against c at 15 and 50°C are shown in Fig.(11-VI).

Table (8-VI). Osmotic virial coefficients for block copolymer sample B4 in toluene at 15, 25 and 50°C.

Temp.(°C)	$\Gamma_2(cm^3g^{-1})$	$A_2 \times 10^3(cm^2g^{-2})$
15	64.0	0.342
25	73.9	0.394
50	95.1	0.509

The values of A_2 plotted against the reciprocal absolute temperature are shown in Fig.(12-VI). The extrapolation of these values to $A_2 = 0$ yields the θ or Flory temperature. The entropy of dilution parameter ψ_1, was determined from the slope of the line in Fig.

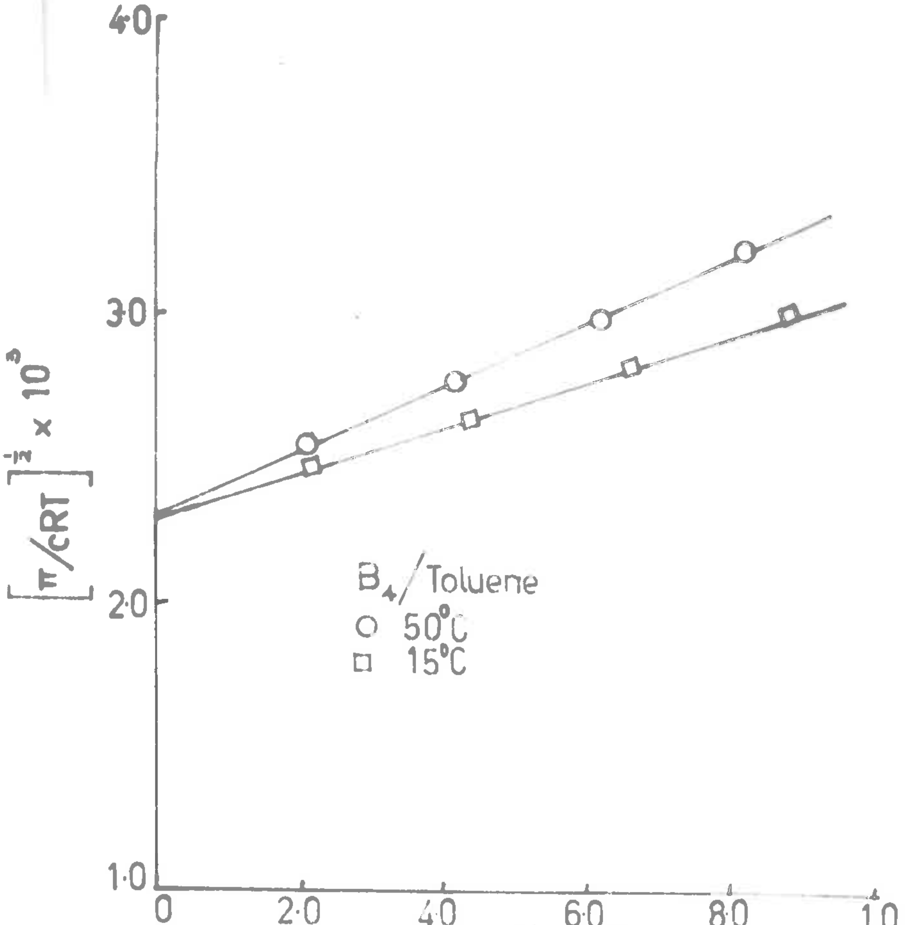

Fig.(11-VI). The osmotic pressures for block copolymer sample B4 in toluene at 50 and 15°C.

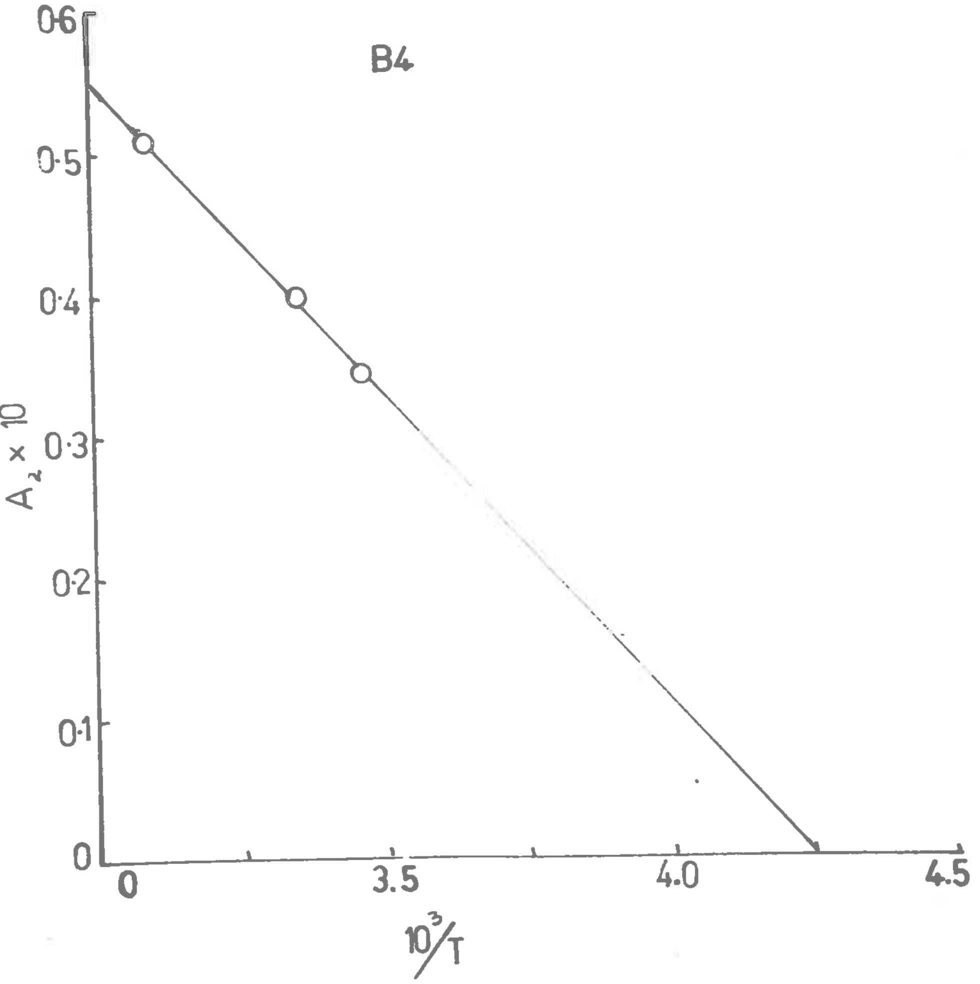

Fig.(12-VI). The osmotic second virial coefficient as a function of reciprocal temperature for block copolymer B4 in toluene.

(12-VI), because at T = θ the slope equals $\psi_1\theta(\bar{v}^2/V_1)$. The values of $\bar{v}$ for polystyrene and polymethyl methacrylate were determined using the relationship derived by Fox and Loshaek.[16] The value of $\bar{v}$ for the block copolymer was determined from the homopolymer values, assuming volume additivity to apply. Having determined θ and ψ_1, it is then possible to determine the heat of dilution parameter κ_1 at any desired temperature, because it has been shown[9] that,

$$\kappa_1 = \theta\psi_1/T \tag{9-VI}$$

the values of θ, ψ_1 and κ_1(25°C) for block copolymer sample B4 are listed in Table (9-VI). The θ, ψ_1 and κ_1(25°C) values for polystyrene in toluene have been published previously,[17,18] but there appears to be no published data for polymethyl methacrylate in toluene. Burnett and co-workers[14] have determined θ, ψ_1 and κ_1 (25°C) from the results of Schulz and Doll[19] and this data, together with that of polystyrene, is included in Table (9-VI).

Table (9-VI). The thermodynamic parameters θ, ψ_1 and κ_1 for polymethyl methacrylate, polystyrene and block copolymer (B4) in toluene.

Sample	% PS	°K	ψ_1	κ_1(25°C)
PMMA	0	95	0.08	0.02
B4	48	235	0.263	0.208
PS	100	160	0.11	0.06

Burnett and co-workers[14] determined the thermodynamic parameters for two of their block copolymer samples (C_1 and C_3), which had a percentage polystyrene content of 50 and 64% respectively. The findings of these authors[14] suggests that the thermodynamic parameters θ, ψ_1 and $\kappa_1(25^oC)$ all have a maxima about the middle of the composition scale. The values obtained for block copolymer sample B4 show a similar trend, although the values were lower than expected for a block copolymer of similar composition, determined from the data of Burnett and co-workers.[14]

Having determined ψ_1 and κ_1, it is then possible to determine the Flory-Huggins[20,21] interaction constant χ, which is related to ψ_1 and κ_1 by the relation,

$$\psi_1 - \kappa_1 = 0.50 - \chi \qquad (10\text{-VI})$$

For block copolymer B4, χ is 0.445. This compares favourably with previously reported values[14,22] determined for block copolymers of styrene and methyl methacrylate.

The data of Burnett and co-workers[14] indicates that θ and κ_1 pass through a maxima at about the middle of the composition scale. This has been interpreted[14] to mean that extra repulsive forces have been introduced into the polymer molecule as a result of joining two chemically different species together.

Qualitative evidence for the existence of extra intramolecular interactions in the block copolymers can be seen by a comparison of the limiting viscosity numbers of the block copolymers, with those of the parent homopolymers. In Fig.(13-VI) the log of the molecular weight of the block copolymers (light-scattering values) have been plotted against the log of the limiting viscosity number and compared with a similar plot, calculated for polystyrene using the equation of Green[1] and for polymethyl methacrylate, the equation of Chinai and co-workers.[7] A dashed line has been drawn through the points for the block copolymer samples. The results indicate that for any given molecular weight, the limiting viscosity number of a block copolymer will be greater than that of either homopolymer, indicating a more expanded configuration for the block copolymer. Even though the points lie close to a straight line, it should not be taken as indicative that viscosity of block copolymers obey an equation of the type $[\eta] = KM^{\alpha}$ The four block copolymers examined have a decreasing molecular weight, corresponding to a decrease in polystyrene content. The molecular weight range covered is also too narrow for a quantitative interpretation to be attempted. However, viscosity measurements by Stockmayer and co-workers[23] on a large number of random copolymers of styrene and methyl methacry-

Figs.(13-VI) and (14-VI). The log-log plot of molecular weight against limiting viscosity number for the block copolymers and parent homopolymers in toluene and methyl ethyl ketone at 25°C, respectively.

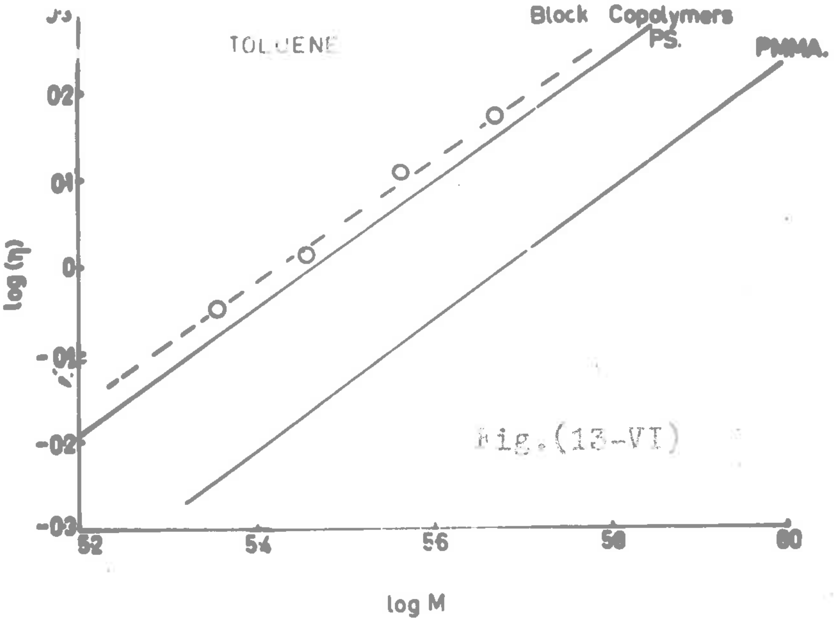

Fig.(13-VI)

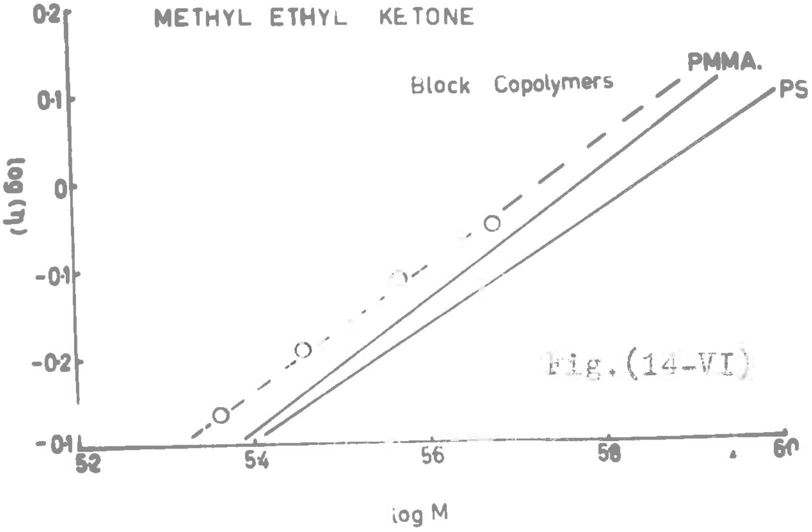

Fig.(14-VI)

late in methyl ethyl ketone, suggest that the data can be represented by an equation of the Mark-Houwink[24,25] type. These extra interactions were also observed in methyl ethyl ketone as shown in Fig.(14-VI).

The thermodynamic behaviour of dilute homopolymer solutions is dependent on three main factors: 1) the molecular weight, 2) the thermodynamic interaction parameters ψ_1, κ_1 and θ , which characterize the segment-solvent interaction, and 3) the shape and size of the molecules in solution. For block copolymers, it appears that the dispersity and composition of the polymer chains should also be considered.

Useful though the information obtained from osmotic pressure and viscosity measurements is, resort to an independent method to obtain information on shape and size of the polymer molecules in solution is desirable. For these determinations the light-scattering technique is usually employed. Light-scattering studies on the block copolymer samples are described in the next section.

3. Light-Scattering.

a) Determination of the second virial coefficient and the root mean square end-to-end distance.

Light-scattering studies on the four block copolymer samples were carried out in toluene. The method of calibration, purification of solvents and solutions, together with the determination of the refractive index increment for the block copolymer samples is described in Chapter VII.

The light-scattering data has been represented as a plot of $(Kc/R_\theta) \times 10^6$ against $\sin^2 \theta/2 + 20\,c$ according to the method proposed by Zimm[26]. The Zimm plots for the block copolymer samples are shown in Figs.(15-VI), (16-VI), (17-VI) and (18-VI). The molecular weights were determined according to the equation,

$$Kc/R_\theta = \frac{1}{\overline{M_W}} P(\theta) + 2A_2c + \ldots \qquad (11\text{-VI})$$

where $P(\theta)$ is the particle scattering factor and A_2 the second virial coefficient. The second virial coefficient A_2 was determined from the plot of $(Kc/R_\theta)_{\theta = 0}$ against c. These plots are presented as straight lines as shown in Fig.(19-VI). The molecular weights of the block copolymers together with the second virial coefficient are listed in Table (11-VI).

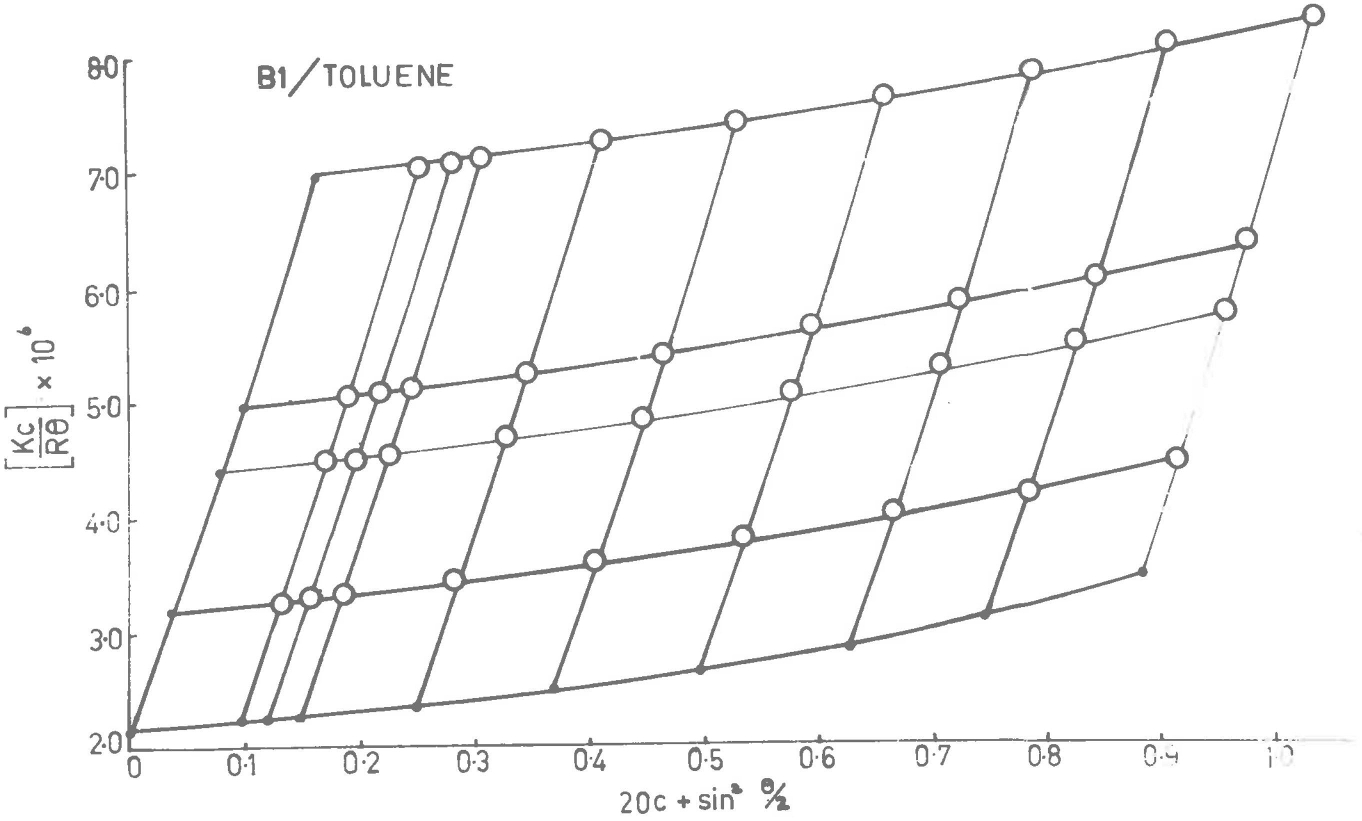

Fig.(15-VI). Zimm plot for block copolymer sample B1 in toluene at 25°C.

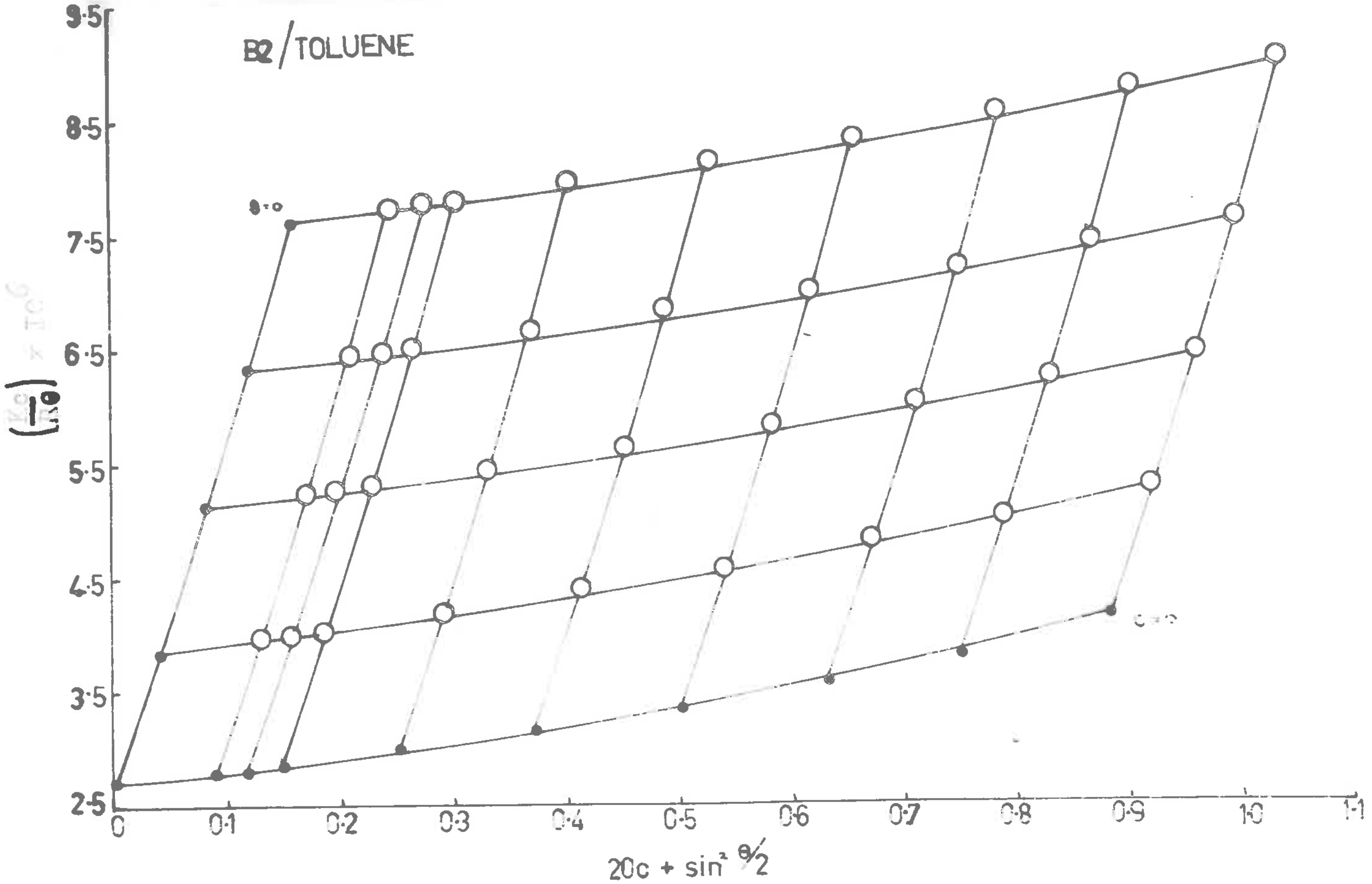

Fig.(16-VI). Zimm plot for block copolymer sample B2 in toluene at 25°C.

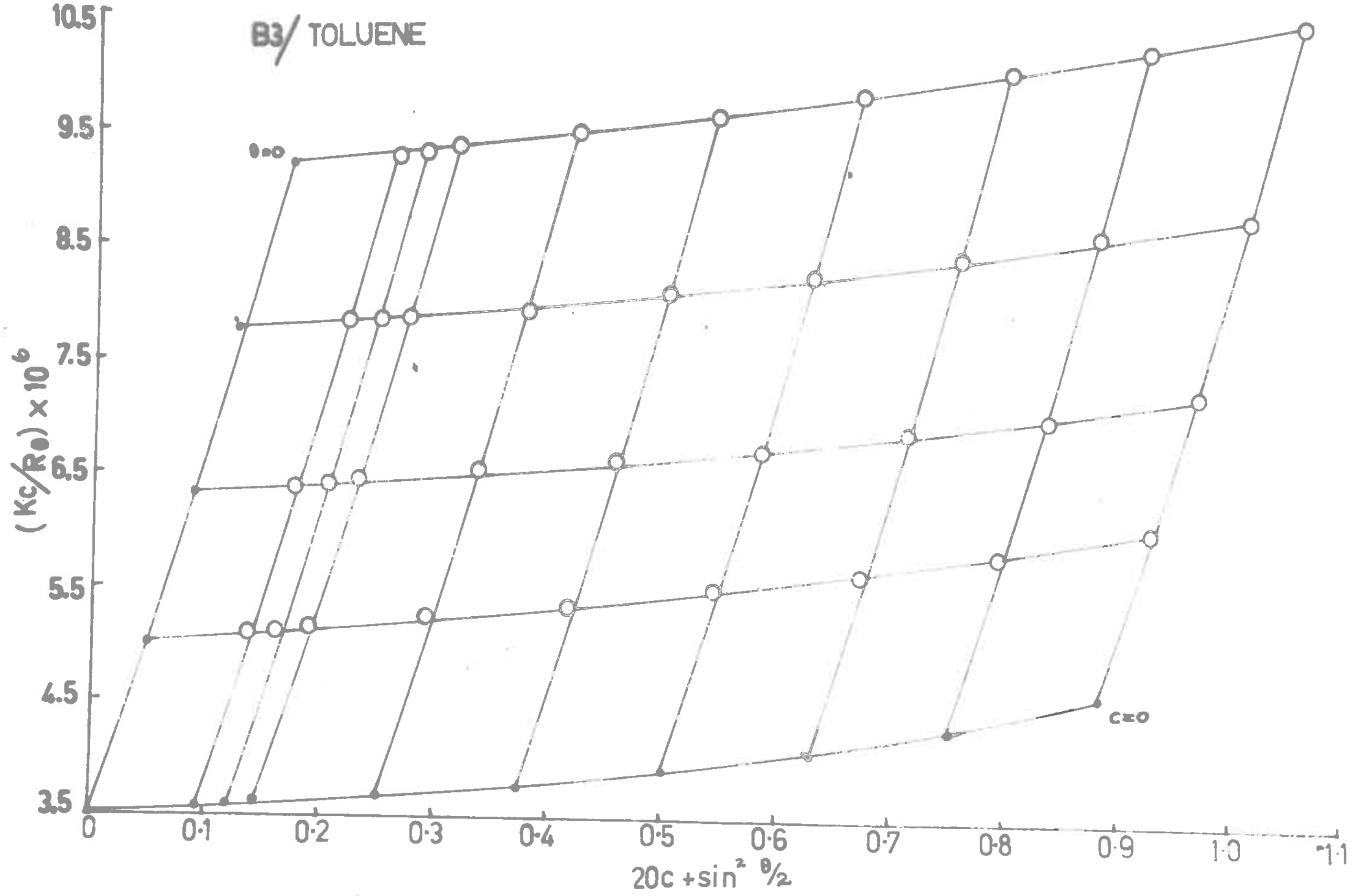

Fig.(17-VI). Zimm plot for block copolymer sample B3 in toluene at 25°C.

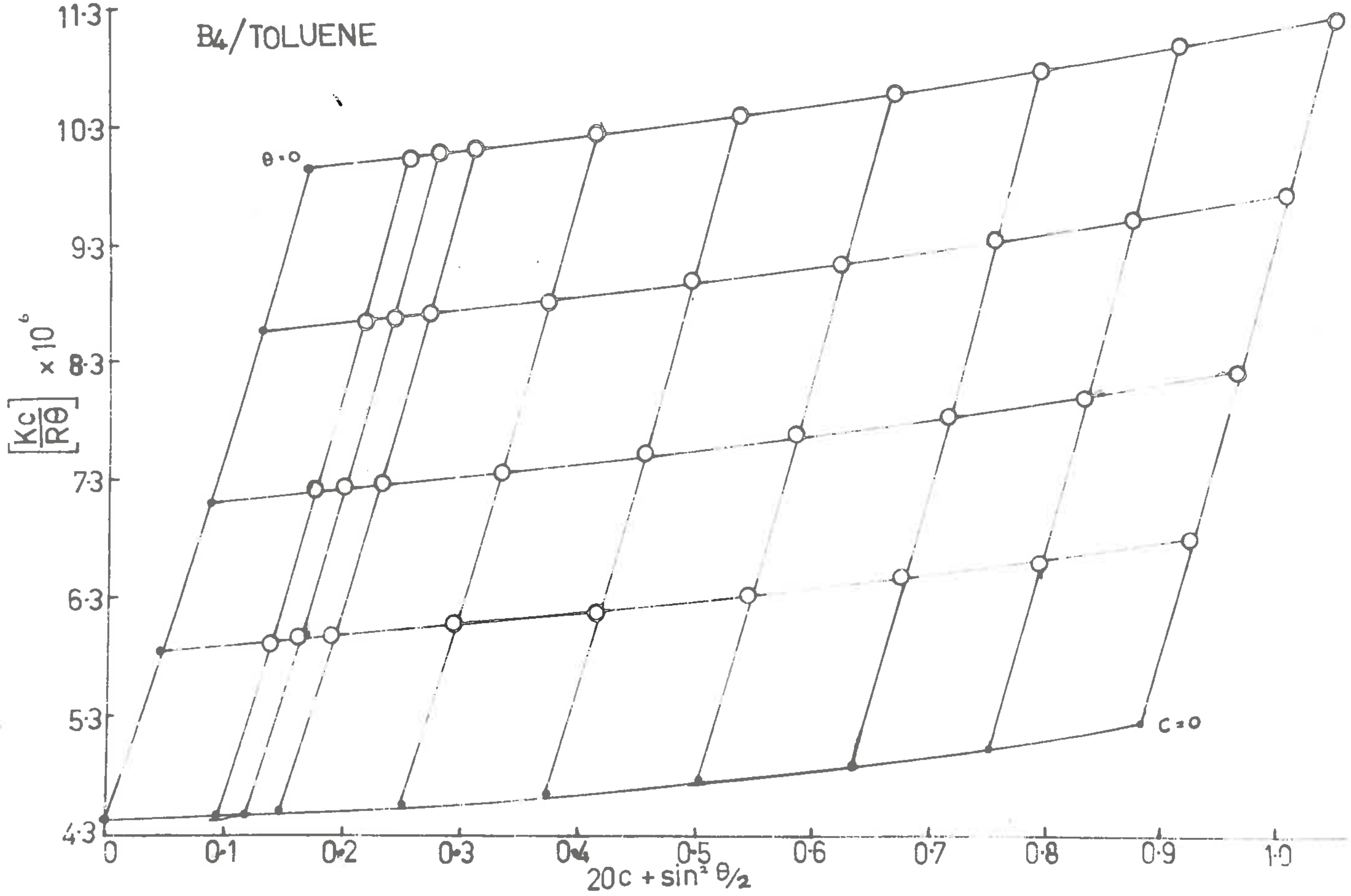

Fig. (18-VI). Zimm plot for block copolymer sample B4 in toluene at 25°C.

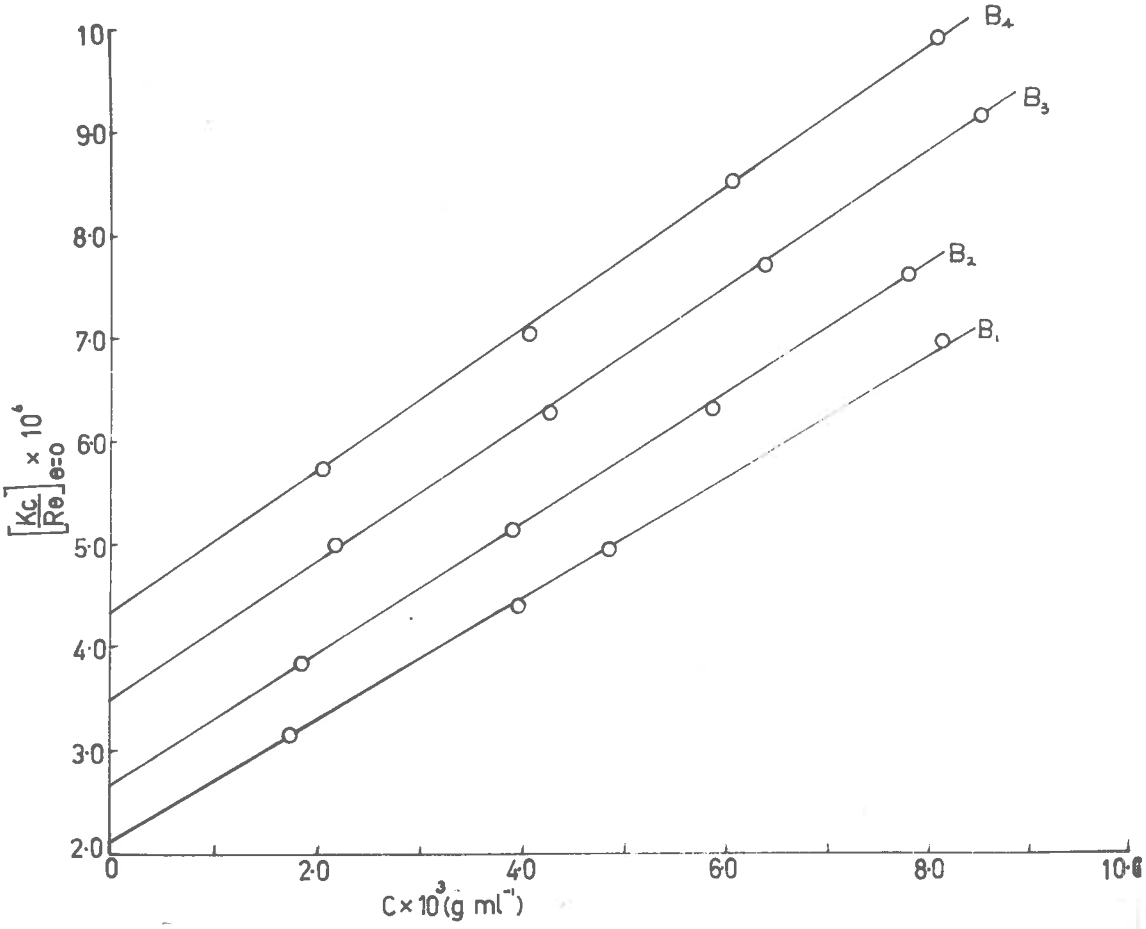

Fig.(19-VI). The variation of $(Kc/R)_{\theta=0}$ with concentration c for the block copolymer samples in toluene at 25°C.

Table (11-VI). The molecular weights and second virial coefficient for block copolymer samples (B1, B2, B3 and B4) measured in toluene at 25°C.

Sample	% PS	$\overline{M_W} \times 10^{-5}$	$A_2 \times 10^3 (cm^2 g^{-2})$
B1	85	4.70	0.301
B2	70	3.70	0.317
B3	62	2.86	0.324
B4	48	2.30	0.346

The second virial coefficient A_2 shows a slight increase with decreasing molecular weight as was observed with the A_2 values determined from osmotic pressure measurements. The values for A_2 determined from the light-scattering data are slightly lower than the values obtained from the osmotic pressure measurements listed in Table (7-VI).

The light-scattering technique also allows the z-average radius of gyration ($R_G z$) to be determined. This is obtained from the plot of $(Kc/R_\theta)c = o$ against $\sin^2\theta/2$, where the ratio of initial slope to the intercept is related to $(R_G z)^2$ by the equation,

$$\text{Initial slope/Intercept} = 16\pi^2 (R_G z)^2 / 3\lambda^2 \qquad \text{(12-VI)}$$

where λ is the wavelength of light in the medium under investigation.

Having determined $(R_G z)^2$ it is then possible to determine the z-average mean square end-to-end distance $(\bar{r}_z^{\,2})$, if a specific shape can be assumed for the polymer. For linear polymers in a good solvent the random coil structure is chosen and the relationship between $(R_G z)^2$ and $(\bar{r}_z^{\,2})$ for a coil is,

$$(R_G z)^2 = \frac{(\bar{r}_z^{\,2})}{6} \qquad (13\text{-VI})$$

Having determined $(\bar{r}_z^{\,2})$, it is then possible to combine this data with the molecular weight determined from light-scattering and the viscosity data (sect.1, this Chapter) to evaluate the Flory-Fox[9,27] universal parameter Φ. The universal parameter Φ is related to the molecular weight, viscosity and the end-to-end distance by the equation,[27]

$$[\eta] = \Phi\,(\bar{r}^{\,2})^{3/2}/M \qquad (14\text{-VI})$$

It must be realized, however, that the average dimensions of the coils are z-average values and not weight average values as required by equation (14-VI). The weight average mean square end-to-end distance is related to the z-value by the equation,

$$(\bar{r}_w^{\,2}) = (\bar{r}_z^{\,2})\,(Z + 1)/(Z + 2) \qquad (15\text{-VI})$$

where Z is the parameter in the distribution formula used by Zimm.[26] The choosing of different values of Z is a rather arbitrary procedure and they have been found,[23] for reasonably homogeneous polymers, to have less influence on $(\bar{r}_w^2)$ than is suggested by equation (15-VI). Thus the $(\bar{r}_z^2)$ values, determined from the Zimm plots in Figs.(15-VI), (16-VI), (17-VI) and (18-VI) were used for all subsequent calculations.

The dimensions of the block copolymer samples and those of polymethyl methacrylate and polystyrene of comparable molecular weight in toluene, together with the Flory-Fox universal parameter Φ, are listed in Table (12-VI).

The values for polystyrene were taken from the data of Outer, Carr and Zimm[28] and converted to dimensions in toluene, using the relationship

$$\frac{[\eta]_1}{[\eta]_2} = \frac{(\bar{r}_1^2)^{3/2}}{(\bar{r}_2^2)^{3/2}} \qquad \text{(16-VI)a}$$

where the subscripts 1 and 2 denote the values for the limiting viscosity number and end-to-end dimensions in separate solvents. The same procedure was used for determining the dimensions of polymethyl methacrylate, the data being taken from the work of Chinai and co-workers[7]. A small correction factor for the fact that the dimensions of polystyrene were originally measured[28] at 22°C has been ignored. The Flory-Fox parameter Φ also neglects a small correction factor for the effect of heterogeneity of the block copolymer samples.

Table (12-VI). The radius of gyration (R_Gz), the end-to-end distance $(\bar{r}_z^{2})^{\frac{1}{2}}$ and the universal parameter Φ, calculated for the block copolymer samples and the parent homopolymers in toluene at 25°C.

Sample	% PS	$\bar{M}_w \times 10^{-5}$	(R_Gz)Å	$(\bar{r}_z^{2})^{\frac{1}{2}}$Å	$\Phi \times 10^{-21}$
B1	85	4.70	287	703	2.02
B2	70	3.70	253	614	2.03
B3	62	2.86	216	530	2.00
B4	48	2.30	190	466	2.02
PS	100	5.42	272	666	-
PMMA	0	4.10	212	519	-

The universal parameter Φ, determined for the block copolymers, is approximately 2.0×10^{21}. This compares favourably with the values determined for homopolymers, the average value of which is 2.1×10^{21}.

It is essential that particular care be taken in determining the mean square end-to-end distance, as an error in determining $(\bar{r}_z^{2})$ will be magnified as it appears as a cubic function in equation (14-VI).

The radius of gyration and the mean square end-to-end distance for the block copolymer samples are all larger than the corresponding values determined for homopolymers of comparable molecular weight. This indicates a more expanded configuration for the block copolymers than for either homopolymer of comparable molecular weight in toluene.

b) Calculation of the expansion factor α, and the functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\overline{r_o}^2/M)^{\frac{1}{2}}$ for the block copolymer samples.

Flory and Fox[9,17] have described the effect of the solvent on configuration in terms of a molecular expansion factor α, so that

$$(\overline{r}^2)^{\frac{1}{2}} = \alpha(\overline{r_o}^2)^{\frac{1}{2}} \qquad \text{(16-VI)b}$$

where $(\overline{r}^2)$ is the mean square end-to-end distance for the polymer in a particular solvent at a particular temperature and $(\overline{r_o}^2)$ the unperturbed mean square end-to-end distance for the polymer at the θ or Flory temperature. The expansion factor α characterizes the intramolecular interactions between segments of the same molecule and these interactions are dependent on the thermodynamic parameters ψ_1 and κ_1; where ψ_1 is the entropy of dilution parameter and κ_1 the heat of dilution parameter. The intensity of the thermodynamic interactions, which characterize α can be expressed by the function $\psi_1(1-\theta/T)$ or its equivalent form $\psi_1 - \kappa_1$. The larger this thermodynamic function the greater is the value of α for a polymer of given molecular weight.

It was shown in equation (8-VI) that the temperature dependence of the second virial coefficient A_2, could be expressed by the equation,

$$A_2 = (\bar{v}^2/V_1)(\psi_1 - \theta/T)\, F(x)$$

or its equivalent form

$$A_2 = (\bar{v}^2/V_1)(\psi_1 - \kappa_1)\, F(x) \qquad (17\text{-VI})$$

where $F(x)$ is the excluded volume[15] function

and $$F(x) = 1 - x/2!2^{3/2} + x^2/3!3^{3/2} - \ldots. \qquad (18\text{-VI})$$

where x is related to the expansion factor α, by the equation,

$$x = 2(\alpha^2 - 1) \qquad (19\text{-VI})$$

From a knowledge of the function $(\psi_1 - \kappa_1)$ and the dimensions of the polymer molecule it is possible to determine x, because it may be shown[9,29] that

$$x = \frac{2\bar{v}^2 M^2}{V_1 N}(\psi_1 - \kappa_1)\left(\frac{3}{4\pi R_G^2}\right)^{3/2} \qquad (20\text{-VI})$$

where $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of the solvent, N is Avogadros number, M the molecular weight and (R_G) the radius of gyration. Having determined x, it is then possible to determine α, the expansion factor. It has been shown[14,22] that for the block copolymers of styrene and methyl methacrylate in toluene, the interaction constant χ remains constant over the entire composition range. This means that the function $\psi_1 - \kappa_1$ should be a constant, because

$$\psi_1 - \kappa_1 = 0.50 - \chi$$

The value of $\psi_1 - \kappa_1$ was determined for block copolymer sample B4 and found to be 0.055, which agrees with the values determined by Burnett and co-workers[14] for two block copolymer samples C1 and C3.

Using the value of 0.055 for $\psi_1 - \kappa_1$ and the radius of gyration for each block copolymer sample, the value of α was calculated from equations (20-VI) and (19-VI). Having determined α, it was thus possible to determine the function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$.

To determine $(\bar{r}_0{}^2/M)^{\frac{1}{2}}$ the function $\alpha = (\bar{r}^2/\bar{r}_0{}^2)^{\frac{1}{2}}$ was substituted into equation (14-VI) so that,

$$[\eta] = \Phi (\bar{r}_0{}^2/M)^{3/2} \alpha^3 M^{\frac{1}{2}} \qquad (21\text{-VI})$$

Thus a knowledge of α and Φ allows the calculation of $(\bar{r}_0{}^2/M)^{\frac{1}{2}}$.

The function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ should be independent of molecular weight M, for a given polymer-solvent system. Krigbaum and Flory[9,30] have shown, however, that the function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ has values which are lower at regions of high and low molecular weight. The values are essentially constant, however, in the molecular weight range normally encountered, that is, from 5×10^4 to 5×10^6. The function $(\bar{r}_o{}^2/M)^{\frac{1}{2}}$ is a constant, characteristic of the unperturbed dimensions of the particular polymer. It is however dependent on bond dimensions and angles and also on the hindrance to rotation.

The values of α, together with the functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\bar{r}_o{}^2/M)^{\frac{1}{2}}$ are listed in Table (13-VI). The values for polymethyl methacrylate were taken from the data of Chinai and co-workers[7] for a sample of molecular weight 4.10×10^5.

Table (13-VI). The molecular dimensions for the parent homopolymers and the block copolymer samples (B1, B2, B3 and B4) in toluene at 25°C.

Sample	α	α^3	$10^3(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$	$(\bar{r}_o{}^2/M)^{\frac{1}{2}} \times 10^{11}$
PMMA	1.154	1.540	0.83	680
B4	1.259	1.995	2.43	774
B3	1.280	2.097	2.50	782
B2	1.295	2.172	2.42	784
B1	1.334	2.354	2.64	773
PS3	1.291	2.151	3.56	711

From the data in Table (13-VI) it can be seen that the intramolecular expansion factor α^3 increases with molecular weight for the block copolymer samples on going from sample B4 ($M = 2.3 \times 10^5$) to sample B1 ($M = 4.70 \times 10^5$). The results indicate that the intramolecular interactions alter the molecular dimensions in a manner which increases with molecular weight, which is analogous to the theory[9] of homopolymers. The functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\overline{r}_o{}^2/M)^{\frac{1}{2}}$ do not vary markedly from block copolymer sample B4 (48% PS) to sample B1 (85% PS). The results differ from those of Burnett and co-workers[14], who found that the function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ increased quite suddenly from the value for pure polymethyl methacrylate to the value for pure polystyrene, over the composition range 50 - 70% styrene. These authors[14] also found that the unperturbed displacement length parameter $(\overline{r}_o{}^2/M)^{\frac{1}{2}}$ showed a sharp maximum at about 60% styrene content for the block copolymer. However, as has been pointed out,[14] care should be exercised when interpreting such data, because even though the parameters for intermolecular and intramolecular may be valid for homopolymers, the application to block copolymers may be doubtful.

The functions $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\overline{r}_o{}^2/M)^{\frac{1}{2}}$ have been plotted against chemical composition for the block copolymers as shown in Figs.(20-VI) and (21-VI) respectively. From Fig.(20-VI) it can be seen that although the value for $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ does increase from the value for pure polymethyl methacrylate to that for pure polystyrene, it

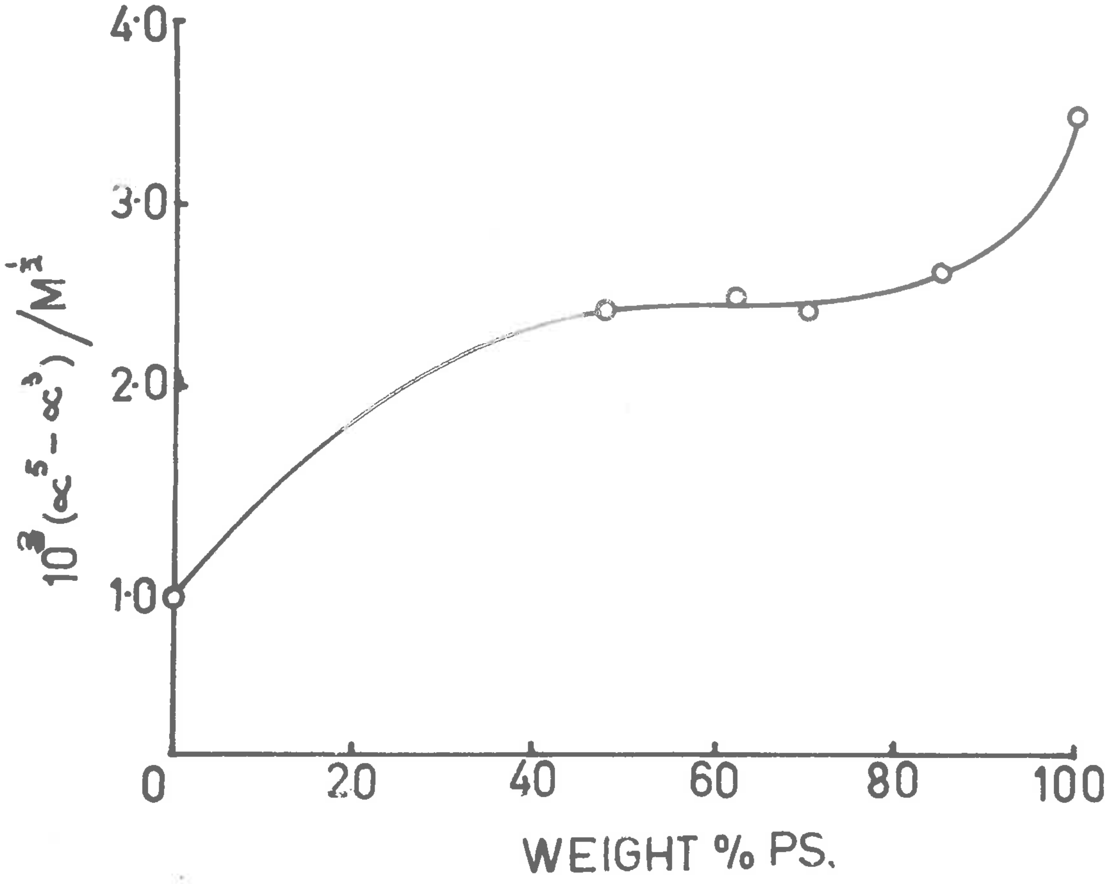

Fig.(20-VI). The configurational parameter $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ as a function of block copolymer composition in toluene.

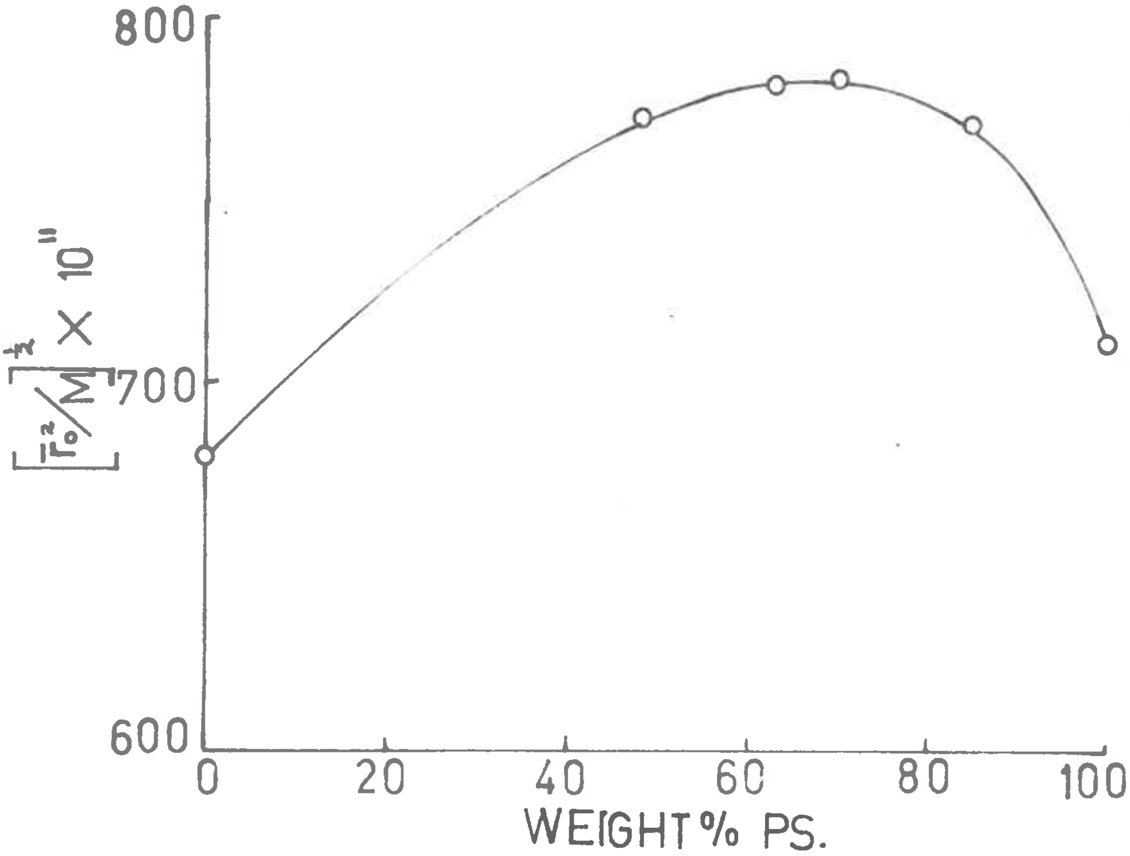

Fig.(21-VI). The configurational parameter $(\bar{r}_o^{2}/M)^{\frac{1}{2}}$ as a function of block copolymer composition in toluene.

remains essentially constant in the range 50 - 80% polystyrene content. In Fig.(21-VI) there does appear to be a slight maximum for $(\overline{r_o^2}/M)^{\frac{1}{2}}$, however, the values are essentially constant in the range 50 - 80% polystyrene content. Burnett and co-workers[14] have suggested an intramolecular phase separation for the block copolymers to explain the sharp variation in the configurational parameters observed for their block copolymers.

Dobry and Boyer-Kawenoki[31] have reported an intermolecular phase separation for polystyrene and polymethyl methacrylate homopolymers in benzene and an intramolecular analogy might be expected with the corresponding block copolymers in toluene. However, such a phenomenon was not observed in the data reported for the block copolymer samples studied.

Since Φ is a universal parameter and has been shown to be very close to 2.0×10^{21} for the four block copolymers examined, then it is possible to obtain the extension ratio α in a second solvent, provided the limiting viscosity numbers have been determined. Thus from equation (14-VI),

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\alpha_1^3}{\alpha_2^3} \qquad (22\text{-VI})$$

where $[\eta]_1$ and $[\eta]_2$ are the limiting viscosity numbers for the same polymer in two different solvents, denoted by the subscripts 1 and 2. The values for α , α^3 and $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ for the four block copolymer samples have been determined in methyl ethyl ketone using equation (21-VI) and the data is listed in Table (14-VI). The value of $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ for polymethyl methacrylate was taken from the data of Chinai and co-workers[7] for a sample of molecular weight approximately 3×10^5.

Table (14-VI). The molecular extension functions α , α^3 and $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ for the block copolymer and parent homopolymers in methyl ethyl ketone at 25°C.

Sample	α	α^3	$10^3(\alpha^5-\alpha^3)/M^{\frac{1}{2}}$
PMMA	-	-	0.3
B4	1.070	1.225	0.38
B3	1.090	1.296	0.46
B2	1.096	1.318	0.43
B1	1.124	1.422	0.54
PS3	1.106	1.352	0.75

From the data in Table (14-VI) it can be seen that the intramolecular expansion factor α^3 increases with molecular weight for the block copolymers as was observed in toluene. The plot of $10^3(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ against % polystyrene content of the block copolymer is shown in Fig.(22-VI). Although the points are rather scattered,

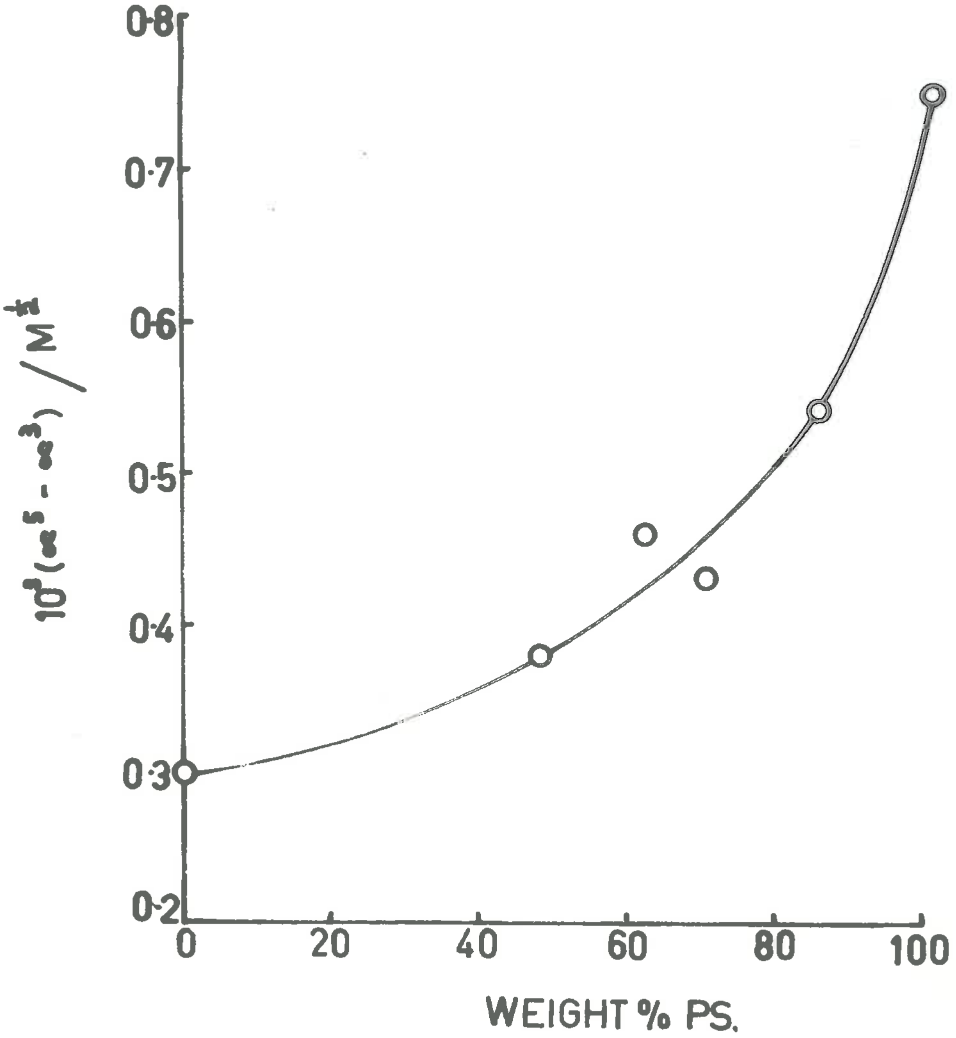

Fig.(22-VI). The configurational parameter $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ as a function of block copolymer composition in methyl ethyl ketone.

a smooth curve has been drawn. The function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ does increase from the value for pure polymethyl methacrylate to that for pure polystyrene. However, the change is gradual over the whole composition range and no sharp rise in the value of $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ at a specific composition for the block copolymers was observed.

The values for α, α^3 and $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ for the block copolymer samples in carbon tetrachloride was also calculated in a manner analogous to that used for the same polymers in methyl ethyl ketone. The results for the block copolymer samples only are listed in Table (15-VI).

Table (15-VI). The functions α, α^3 and $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ for the block copolymer samples in carbon tetrachloride at 25°C.

Sample	% PS	α	α^3	$10^3(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$
B4	48	1.180	1.646	1.36
B3	62	1.202	1.738	1.45
B2	70	1.217	1.805	1.44
B1	85	1.226	1.841	1.35

The function α^3 increases with increasing molecular weight, as was observed in toluene and methyl ethyl ketone. The function $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ seems to be essentially constant in the composition range studied and the values do not indicate a phase separation for the block copolymers in carbon tetrachloride.

Discussion.

The viscosity study on the four block copolymer samples indicated forces of a repulsive nature between block copolymer molecules. The fact that the measured Huggin constant k_H was smaller than that determined for either homopolymer, or for an equivalent mixture of homopolymers, indicated either a smaller positive interaction or a greater repulsion between the block copolymer molecules, than between polystyrene-polystyrene or polymethyl methacrylate-polymethyl methacrylate molecules, especially in toluene and methyl ethyl ketone. Qualitative evidence for the existence of intramolecular forces resulting in a more expanded configuration for the block copolymers, was shown by a comparison of the limiting viscosity number-molecular weight plot for the block copolymer, with a similar plot for both homopolymers.

The osmotic pressure measurements indicated a decrease in the second virial coefficient with increasing molecular weight, suggesting that A_2 for the block copolymers in toluene, behaves in a manner analogous to homopolymers. The second virial coefficient A_2 was determined at several temperatures for block copolymer sample B4, and the θ-temperature for the sample obtained by extrapolating these values to $A_2 = 0$. The thermodynamic functions ψ_1 and κ_1 were calculated for sample B4 and found to compare favourably with previously reported[14] values on block copolymers of similar composition. The Flory-Huggins interaction constant was also determined from the thermodynamic functions, and the value ($\chi = 0.445$) found to compare with previously reported values.[14,22]

The light-scattering data allowed the determination of the second virial coefficient A_2 by an independent method. Although the values for A_2 determined by the light-scattering technique were slightly lower than those determined by osmometry, the trend with molecular weight was in the same direction. The A_2 values for the block copolymer samples were slightly higher than those of the homopolymer of similar molecular weight, suggesting a more expanded configuration for the block copolymer.

The radius of gyration and the root mean square end-to-end distance were calculated and the values found to be larger than those found for homopolymers of similar molecular weight. The Flory-universal parameter Φ, was calculated using the root mean square end-to-end distance and the value found to be 2.0×10^{21} for the block copolymers.

The extension ratios and the parameters $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ and $(\overline{r_o^2}/M)^{\frac{1}{2}}$ were also calculated. The extension ratio α was found to increase with increasing molecular weight. The unperturbed displacement length parameter $(\overline{r_o^2}/M)^{\frac{1}{2}}$ was larger for each block copolymer sample than the values for each homopolymer. The values showed no marked variation with block copolymer composition, however they did appear to have a slight maximum between 60-80% styrene content. The parameter $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ was almost constant and independent of block copolymer composition in toluene and carbon tetrachloride. In methyl ethyl ketone, however, the values of $(\alpha^5 - \alpha^3)/M^{\frac{1}{2}}$ did change gradually from the value for pure polymethyl methacrylate to that for polystyrene. There appeared to be no marked evidence for the intramolecular phase separation theory put forward by Burnett and co-workers.[14]

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CHAPTER VII.

Experimental.

1. Viscosity.
    - a) The type of viscometer used.
    - b) The kinetic energy correction.
    - c) Purification of solvents and solutions.
    - d) Treatment of the viscosity data.

2. Osmometry.
    - a) The type of osmometers used.
    - b) Calibration.
    - c) The membranes.
    - d) Testing for leaks in the membrane assembly.
    - e) Density and surface tension corrections.
    - f) Solvents.
    - g) Treatment of osmotic pressure data.

3. Light-Scattering.
    - a) The light-scattering apparatus.
    - b) The light-scattering cell.
    - c) Calibration and measurements.
    - d) Clarification of solvents and solutions.
    - e) The specific refractive index increments.
    - f) Treatment of the light-scattering data.

CHAPTER VII.

1. Viscosity.

a) The viscometer used was the suspended level or Ubbelohde type and was designed to have a minimum kinetic energy correction. The flow times of the various solvents used were all in excess of 100 secs., as shown in Table (1-VII).

Table (1-VII). Flow times for the various solvents.

Solvent	Flow time. (secs.)
Toluene	163.80
Butanone	121.47
Carbon tetrachloride	146.20
Nitroethane	159.13

b) The kinetic energy correction was determined from the flow times of water measured at two temperatures, 20° and 25°C. The absolute values[1] of the kinematic viscosity of water at 20° and 25°C were taken as 1.0038 cs. and 0.8928 cs. respectively.

The constants[2] A and B, which incorporate the end-effect and kinetic energy corrections were determined from the equations[3]

$$A = \frac{v_2 t_2 - v_1 t_1}{t_2^2 - t_1^2} \qquad (1\text{-VII})$$

$$\text{and } B = \frac{t_1 t_2(v_2 t_1 - v_1 t_2)}{t_2^{\,2} - t_1^{\,2}} \qquad (2\text{-VII})$$

where v_1 and v_2 are the kinematic viscosities of water having flow times of t_1 and t_2 in the viscometer being calibrated. For the viscometer used in this work, $A = 3.97 \times 10^{-3}$ and $B = 0.0164$. The fractional kinetic energy correction x, for the solvent, is given by the equation[2]

$$x = \frac{B}{A t_o^{\,2}} \qquad (3\text{-VII})$$

where t_o is the flow time for the solvent. For toluene, the fractional kinetic energy correction x, was found to be 1.54×10^{-4} and for butanone, $x = 2.80 \times 10^{-4}$. The kinetic energy correction on the limiting viscosity number ($[\eta]$) was found to be negligible and was not applied as a correction.

Throughout all the viscometric determinations the temperature of the water bath was controlled to within ± 0.005°C, by means of a mercury toluene regulator and a thyratron control.

c) Purification of solvents and solutions.

Toluene and carbon tetrachloride were Analar (B.D.H.) grade solvents. Toluene was dried over sodium and distilled before use. The fraction boiling in the range

110.6 - 110.9°C at 760 mm. pressure was collected and used. Carbon tetrachloride was dried over anhydrous calcium chloride and on distillation the fraction boiling in the range 76.2 - 76.7°C at 760 mm. pressure was collected.

Methyl ethyl ketone (Butanone) and nitroethane were Laboratory (B.D.H.) grade solvents. Methyl ethyl ketone was dried over anhydrous potassium carbonate, filtered from the desiccant and finally fractionated through an efficient column. The fraction boiling in the range 79.2 - 79.8°C at 760 mm. pressure was collected.

Nitroethane was dried over anhydrous calcium sulphate and fractionated at atmospheric pressure. The fraction boiling in the range 114.6 - 114.9°C being collected.

All solvents were filtered under dry nitrogen pressure through a sintered glass filter (No. 4) to remove dust. The solutions were also filtered under dry nitrogen pressure, through a No. 3 glass sintered filter and transferred to the viscometer using dust free pipettes.

Particular care was taken in aligning the viscometer in the bath and it was not removed until one complete determination had been made. The most concentrated solution was tested first and successive dilutions carried out in the viscometer.

d) Treatment of the data.

The data was represented satisfactorily by the equations[4]

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \qquad (4\text{-VII})$$

and

$$\frac{\ln \eta/\eta_0}{c} = [\eta] - k'[\eta]^2 c \qquad (5\text{-VII})$$

The limiting viscosity numbers were obtained from the graphs after extrapolation of the results to zero concentration. The constants k_H and k' were calculated both from the slope of the viscosity plots and from the experimental points, using the method of least squares. The constants k_H and k' could be related by the equation

$$k_H + k' = 0.50 \qquad (6\text{-VII})$$

Particular attention was placed on the exact determination of each point on the graph, especially in the case of the bad solvents. The value for each point was determined from three successive flow times, which did not vary by more than 0.10 secs. The redetermination of some points was necessary, in order to obtain the best line of best fit. Data was obtained at four or five concentrations in each case. The flow times were determined visually using a stopwatch, which could be read to 0.01 of a second.

2. Osmometry.

a) The osmometers used were of the Pinner-Stabin[5] and Immergut-Stabin[6] design. These osmometers are of all glass construction and are particularly useful for high temperature study. The osmometers are modifications of the Zimm-Meyerson[7] apparatus but have the added advantage that equilibrium is approached more rapidly.

Four osmometers were used in a special rotating holder, which was carefully mounted in a large thermostat bath fitted with an observation window. All operations were carried out on the osmometers while they were mounted in the bath and removal was only necessary to replace membranes from time to time. Particular care was taken in aligning each osmometer assembly to ensure that the reference and solution capillaries were vertical.

b) Calibration.

The osmometers were checked to ensure that the reference and solution capillaries were matched pairs in each apparatus. This was done by gradually adding solvent to the outer jacket and measuring the rise in solvent level in each capillary. The levels were measured with a cathetometer, capable of measuring to 0.001 cm. Differences in each capillary level were found to be negligible over the entire capillary length in all the osmometers. When the osmometers had been assembled in a leak-free condition (see section d), identical concentrations of the one polymer sample were added to each apparatus. The osmotic pressure developed in each apparatus was found to be the same.

c) The membranes used were PECEL 600 Grade cellulose membranes supplied by Polymer Consultants Ltd., England. The membranes were supplied packed in aqueous acetone and it was necessary to condition them to toluene before use. The procedure outlined by Pinner[8] for conditioning the membranes to benzene was found to be too severe in the case of toluene and was thus modified. The membranes were transferred from their polythene packets and at 24 hour intervals were transferred to solutions of 75% acetone-water, pure acetone (twice), 75% acetone-toluene, 50% acetone-toluene, 25% acetone-toluene and finally pure toluene. The membranes were left for 48 hours in pure toluene before use. Some membranes exhibit a positive osmotic pressure, which arises due to surface inequalities and unsatisfactory conditioning. Observations on all membranes tested did not yield a positive osmotic pressure greater than 0.05 cms. If the difference in the two capillary levels was small and constant, then it was applied as correction to subsequent measurements on the polymer solutions. If the capillary difference was found to be non-reproducible then the membranes were removed and replaced with fresh ones.

d) Testing for leaks in the membrane assembly.

The method for testing for leaks was the same as that outlined by Pinner.[8] The testing was carried out with solvent in the osmometer cell and with the most concentrated solution of one of the low molecular weight polymers used. If a leak was detected, then the membrane assembly was dismounted and carefully reassembled again.

e) Density and surface tension corrections.

The osmotic pressure measurements were corrected for the density of the polymer solutions using the values of Matheson and co-workers.[9] The densities of the block copolymer solutions were obtained from the values of polystyrene and polymethyl methacrylate assuming a linear relationship between density and homopolymer composition of the block copolymer. The densities of the block copolymer (B4) at 15° and 50°C were determined assuming a linear relationship between temperature and density. The molecular weights of the samples tested did not exceed 500,000 and hence significant errors due to surface tension were deemed negligible.

Temperature control to ± 0.005°C was achieved with a mercury toluene regulator and a thyratron relay.

f) Solvents.

Toluene was the only solvent used. This was supplied as analar (B.D.H.) grade, which was dried over sodium and distilled before use. The fraction boiling in the range 110.6° - 110.9°C at 760 mm. pressure was collected and used for all subsequent osmotic pressure measurements.

g) Treatment of the osmotic pressure data.

The osmotic pressure, measured as a height (h in cms. of solution) was converted to atmospheres (Π) by the expression,

$$\Pi \text{ (atmos.)} = \frac{hd}{1033.3} \qquad (7\text{-VII})$$

where d is the density of the solution and 1 atmosphere = 1033.3 g/cm.^{2}

The gas constant R was taken as 82.06 cm^3 atmospheres per degree per mole.

The osmotic pressures of the polymer solutions were represented by the equations

$$\frac{\Pi}{cRT} = \frac{1}{M} + A_2c + A_3c^2 + \dots \qquad (8\text{-VII})$$

$$\frac{\Pi}{cRT} = \frac{1}{M}\left[1 + \Gamma_2c + \Gamma_3c^2 + \dots\right] \qquad (9\text{-VII})$$

and $$\left(\frac{\Pi}{cRT}\right)^{\frac{1}{2}} = M^{-\frac{1}{2}}\left[1 + \tfrac{1}{2}\Gamma_2c\right] \qquad (10\text{-VII})$$

where $\Gamma_3 = g\Gamma_2$ and $g = \frac{1}{4}$

Equation (10-VII) was used with the approximation that higher terms in equation (9-VII) could be ignored. Equation (10-VII) gave almost straight lines for both polystyrene and the block copolymers. The second virial coefficients A_2 and Γ_2 were calculated from the slope of the experimental plots using equation (10-VII). The value of $(\overline{M_N})$ was obtained from the extrapolation of these same points to zero concentration.

3. Light Scattering.

a) The light-scattering apparatus was a commercially available P.C.L. - Peaker light-scattering instrument,[10,11] which was modified to eliminate the large fluctuations in signal, resulting from the "hot-spotting" of the mercury arc lamp used as light-source. The modifications to this instrument have been described previously.[12]

b) The light-scattering cell was of rectangular design, inside dimensions being 4 mm. x 33 mm. (length) x 46 mm. (height). The cell was constructed from glass 3.5 mm. thick. The cell had a capacity of approximately 4 ml. of solution, and could be covered by a small piece of microscope slide glass during an experiment. The cell was mounted in an outer cell of blackened brass, which contained the same solvent used in preparing the solutions. The outer cell was fitted with a piece of red glass, which absorbed the light after it traversed the inner rectangular cell. The scattered light was observed through a semi-circular glass window, cemented to the outer cell. The angular observation range was 27 - 140°. The actual cell was designed[12] to reduce Fresnel[13] corrections to a minimum.

c) Calibration and measurements. The symmetry of the system was checked by measuring the fluorescence from dilute solutions of sodium dichlorofluoresceinate, employing a yellow filter (Ilford, 109 Delta: Chromatic 3, Deep Yellow) to eliminate the scattered light. It was found, as was previously reported,[12] that 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 a slight dependence on θ. The values were found to be reproducible[12] and were thus used to determine correction factors $x(\theta)$ to the usual $\sin\theta$ volume factor.[13] The values of $x(\theta)$ are listed in table (2-VII)

Table (2-VII). The correction factor $x(\theta)$ for each angle of observation.

θ°	$x(\theta)$	θ°	$x(\theta)$
30	1.020	75	1.010
35	1.024	90	-
40	1.024	105	0.986
45	1.027	120	0.994
60	1.030	140	0.995

The apparatus was calibrated using purified dust free benzene. The R_{90} value for benzene was taken[14] as 16.4×10^{-6} at a wavelength of 5460Å.

The reduced intensity of scatter, $R(\theta)$ for the unknown solutions was determined using the equation,

$$R(\theta) = Cc\,n^2\, r(\theta).x(\theta)\ \frac{\sin\theta}{1+\cos^2\theta} \qquad (11\text{-VII})$$

where Cc is the calibration constant for the instrument, n is the refractive index of the solvent and $r(\theta).x(\theta)$ $(\sin\theta/1+\cos^2\theta)$ the corrected ratio of photocurrents due to the scattered and incident light at the angle θ .

d) Clarification of solvents and solutions.

Toluene was obtained as Analar (B.D.H.) grade reagent. The solvent was dried over sodium and fractionated through an efficient column. The fraction boiling in the range 110.70 - 110.90°C at 760 mm. pressure was collected and used for preparing all the solutions examined. The toluene fraction was also distilled several times in a dry clean apparatus. The receiving vessel was rinsed each time with purified toluene, which in turn was returned to the distilling flask. After several redistillations the toluene was filtered under dry nitrogen pressure through a sintered glass filter porosity No. 5. The solvent was then centrifuged at 20,000 g. in 1" x 3" stainless steel tubes using a Servall SS-1 angle head centrifuge.

The benzene was also obtained as Analar (B.D.H.) grade reagent. This solvent was also sodium dried and fractionated. The collected fraction boiled in the range 79.9° - 80.5°C at 760 mm. pressure. The clarification was the same as outlined above for toluene.

The preparation of the solutions was carried out using the purified dust free toluene. Before transferring to the light-scattering cell the solutions were carefully filtered through a sintered glass filter No. 4 using dry nitrogen pressure and finally centrifuging for 1 hour at 20,000 g. The pipette and cell were carefully rinsed with clarified solvent and finally the cell was rinsed three times with clarified solution before finally filling. The presence of large impurities such as dust could be detected by visual inspection of the solutions at low scattering angles. It was found necessary to remove the light filter and darken the room for this procedure.

e) <u>The specific refractive index increments</u> were determined using a double-prism differential refractometer of the type previously described by Cecil and Ogston.[15] The instrument was calibrated using solutions of sodium chloride. The standard deviation of a refractive increment was 4 x 10^{-6}. The values of the specific refractive increments measured at $\lambda = 5460\mathring{A}$ were found to be independent of polymer concentration in the range studied. The refractive index increments for the block copolymers were determined from the values obtained for pure polystyrene and pure polymethyl methacrylate assuming a linear relationship between refractive index increment and percentage homopolymer composition of the block copolymer.[16] The refractive index increment for polystyrene in toluene at 25°C and λ = 5460Å was found to be 0.111 (ml.g^{-1}), which is in good agreement with previously reported values.[20,21] The refractive index increment for polymethyl methacrylate under the same experimental conditions was found to be 0.014 (ml.g^{-1}) and for block copolymer sample B4, the refractive index increment was found to be 0.061 (ml.g^{-1}). This data, together with the refractive index increments of several other block copolymer samples of polystyrene and polymethyl methacrylate, measured under identical experimental conditions,[19] is shown in Fig. (1-VII).

f) Treatment of data.

The light-scattering data was presented as a plot of (Kc/R_θ) against $\sin^2\theta/2 + kc$ according to the method proposed by Zimm.[17] The factor K is defined by the relationship,

$$K = \frac{2\pi^2 n^2}{N\lambda^4}\left(\frac{dn}{dc}\right)^2 \qquad (12\text{-VII})$$

where n is the refractive index of the solvent in light of wavelength λ, N is Avogadro's number and (dn/dc) the refractive index increment of the solution. The factor k is an arbitrary constant, chosen to give a convenient spread of the experimental data when plotted on a grid-like curve, and c is the concentration of the solution.

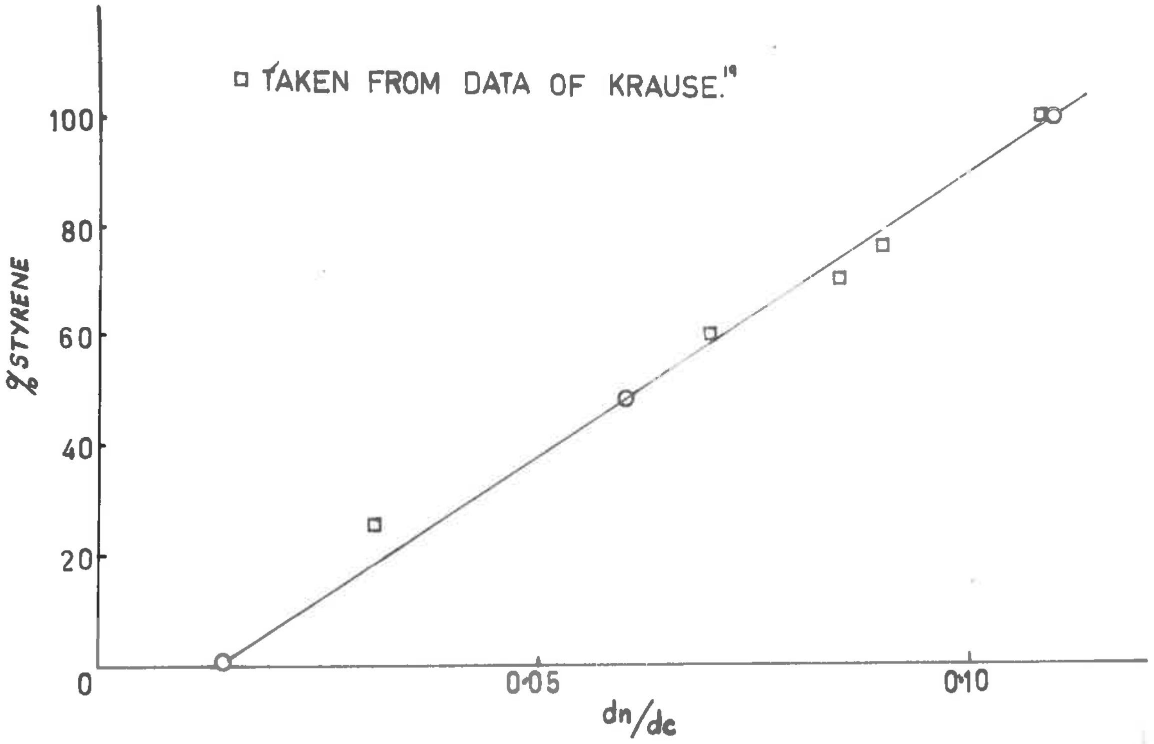

Fig.(1-VII). Refractive index increment values for polystyrene, polymethyl methacrylate and block copolymer samples in toluene at 25°C.

The measurements were all determined at $\lambda = 5460\text{Å}$.

The molecular weight ($\overline{Mw}$) was determined according to the equation,

$$Kc/R\theta = \frac{1}{\overline{Mw}\,P(\theta)} + 2A_2c + \ldots.. \qquad (13\text{-VII})$$

where $P(\theta)$ is the particle scattering factor and A_2 the second virial coefficient. The factor $P(\theta)$ by definition becomes one when $\theta = 0$.

The mean square z-average radius of gyration $(R_Gz)^2$ was determined from the ratio of the initial slope of the $c = o$ line to the intercept, according to the relationship,

$$\text{Initial slope/Intercept} = 16\pi^2(R_Gz)^2/3\lambda^2 \qquad (14\text{-VII})$$

The second virial coefficients A_2 and Γ_2 were obtained from the slope of the $\theta = 0$ line according to equation (13-VII) above.

No correction for depolarization was found necessary, as it was too small to be measured with any accuracy.

All measurements were made at a temperature of $25 \pm .2^\circ C$.

4. Turbidimetric Titrations.

a) Purification of solvents and solutions.

Methyl ethyl ketone was used as solvent and isopropanol as the precipitant. Methyl ethyl ketone was obtained as Laboratory (B.D.H.) grade solvent. This was dried over anhydrous potassium carbonate, filtered from the desiccant and finally fractionated through an efficient column. The fraction boiling in the range 79.2 - 79.8°C at 760 mm. pressure was collected and used to prepare the subsequent solutions.

The isopropanol was obtained as analar (B.D.H.) grade solvent. This solvent is often contaminated by peroxides. The test for peroxides was carried out according to that listed by Vogel.[18] If the peroxide test was positive, then purification was effected as described.[18] If the test was negative, then the isopropanol was dried over calcium oxide and fractionally distilled. The fraction boiling in the range 81.9 - 82.5°C was collected.

The solvents were filtered through porous glass filters, porosity No. 5, using dry nitrogen pressure. This filtration process was repeated several times and the solvents finally stored in dust free containers. All solutions were prepared using the purified dust free solvents.

The scattering cell used in the turbidimetric titration studies was carefully rinsed with dust free solvent and finally with dust free solution before finally filling with the solution to be studied. The solutions were actually filtered under dry nitrogen pressure directly into the cell through a sintered glass filter No. 4.

b) Since the intensity of the scattered light at 90° is dependent on the voltage supplied to the photomultiplier, it was necessary to obtain the coefficient of the plot of τ vs. (i_{90}/It) measured as a function of voltage. Thus τ is related to the measured (i_{90}/It) value by an equation of the form,

$$\tau = K(i_{90}/It)\text{ meas.} \qquad (15\text{-VII})$$

where K is the slope of the plot of τ vs $(i_{90}/It$ meas. The value of K as a function of voltage is shown in Fig. (2-VII). The perspex standard (Chapter IV) was used in the calibration of each voltage to ensure reproducibility from run to run.

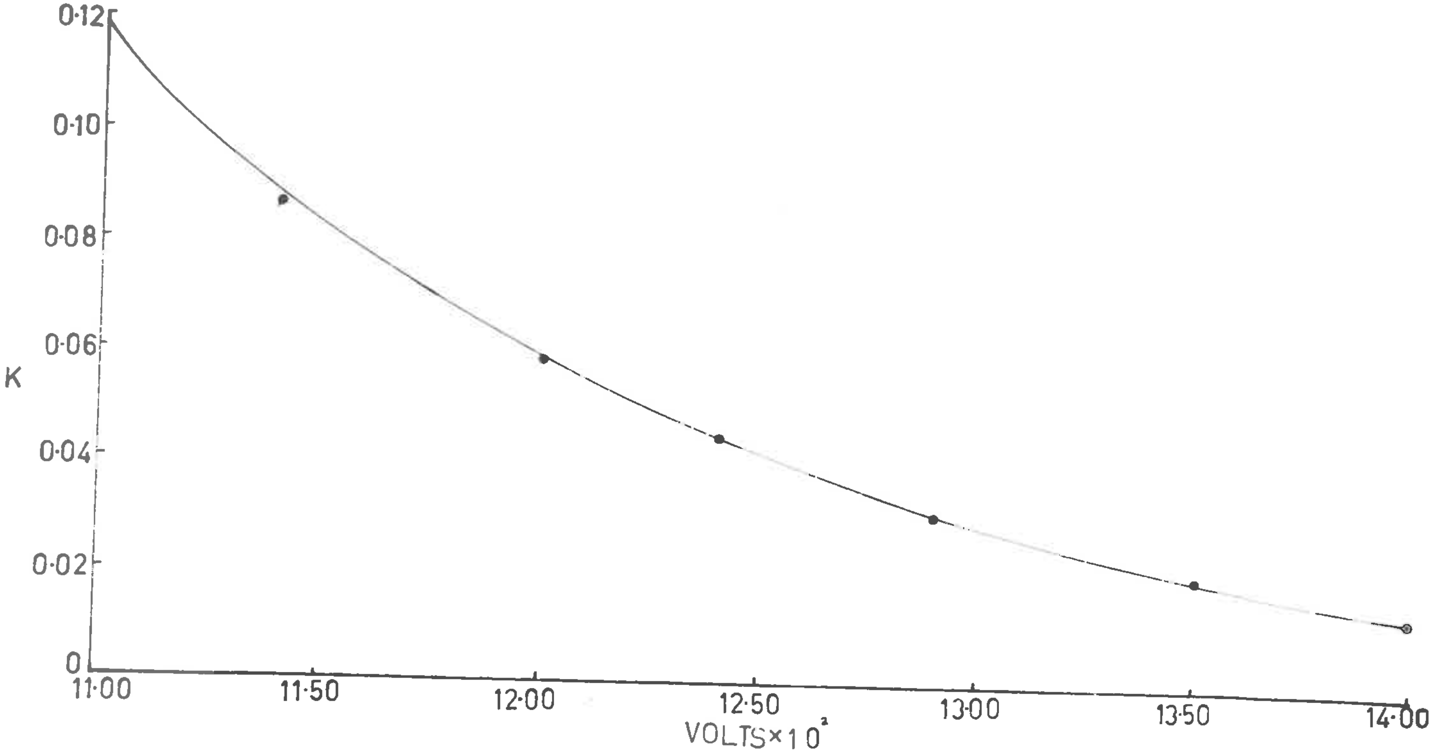

Fig.(2-VII). The variation of the constant K with voltage of the photomultiplier power-unit.

5. The Ultracentrifuge.

a) The instrument used was a Spinco (Model E) ultracentrifuge designed for analytical experimentation.

The purpose of the analysis was of a purely qualitative kind, to illustrate the difference in polymer heterogeneity, resulting from the modification of a preparative technique.

b) Toluene was used as the solvent and was purified as for the viscosity and osmometry experiments, mentioned in this chapter.

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APPENDIX

Publications.

Turbidimetric Titrations. Part I. The Automatic Turbidimeter.

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