Phase separation of binary copolymers from solution non-solvent mixtures in relation to copolymer structure, and polymer–solvent interactions

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(Received 19 *January* 1981)

Turbidimetric titration is well established as a technique for determining the nature and composition of a polymer in dilute solution by its precipitation behaviour on titration with non-solvent. Although the technique is simple, there are many experimental and theoretical difficulties in obtaining reliable results. Here, a novel technique is described which overcomes some of the experimental difficulties of the titration technique. In particular, the polymer concentration remains constant. Results presented illustrate how clearly pure graft and block copolymers may be distinguished by this technique from constituent homopolymers, their physical mixtures or the corresponding random copolymers of similar molecular weight. The turbidity–precipitant content graphs are sigmoidal in form, but pure graft or block copolymers show a distinct double inflection in the middle of the graph. The effects appear in several different polymer solution systems studied and may be quite general.

INTRODUCTION

Turbidimetric titration is well established as an analytical technique for the determination of the molecular weight distribution of polymers[1], for the recognition of heterogeneity in polymer structure[2] and for the determination of polymer solubility parameters[3]. The technique consists of titrating a dilute polymer solution with a non-solvent for the polymer. The turbidity of the mixture is measured as a function of the volume of non-solvent added.

The quantitative interpretation of results obtained has been the subject of much discussion and criticism in the literature[4]. This has been comprehensively reviewed by Giesekus[5], and, more recently, by Elias[6].

The advantages of the turbidimetric titration technique are its simplicity and rapidity of execution. Compared with the complexity of conventional light scattering techniques and their exacting experimental requirements, turbidimetric titrations are attractive. However, they have serious disadvantages. These stem from the kinetics of formation of the precipitated polymer phase and the variation of polymer concentration and total mixture volume as the titration proceeds. The kinetics of precipitated polymer phase formation and the phase composition are frequently dependent in a complex or ill-defined manner on the precise experimental conditions of the titration, and it is this element which has probably led to most difficulties in interpretation of the results.

In the technique to be described in this paper, we have endeavoured to preserve the essential simplicity and rapidity of the titration technique, whilst removing some of its drawbacks, particularly in the quantitative interpretation of the results.

Initially, the technique was used to detect the presence of homopolymer contamination in preparations of poly(methyl methacrylate) grafts on polystyrene backbones, but was extended to other copolymers as a possible method of 'finger-printing' structure and chemical composition. As a guide to the theoretical interpretation of results, the technique was also applied to styrene homopolymer solutions.

EXPERIMENTAL

Preparations

Homopolymers. Polystyrene, poly(methyl methacrylate) and poly(butyl acrylate) were prepared by free radical polymerization in refluxing toluene under nitrogen. A catalysed monomer feed over 3 h was used. On completion of the feed, the reaction flask was held at reflux for 3 h. Initiators used were t-butyl perbenzoate and azodiisobutyronitrile (ADIB) [poly(methyl methacrylate) only]. Initiator level was 0.4% on monomers. Conversions were greater than 98%.

Random copolymers. These were prepared in similar manner to the homopolymers, using a mixed 1:1 (by weight) monomer feed and ADIB as initiator. Conversion was greater then 90%.

Programmed styrene–methyl methacrylate copolymer. A so-called 'programmed' copolymer was prepared by feeding styrene in a copolymerization process as described above. After 5% of the styrene had been added, a methyl methacrylate monomer feed was started at the same feed rate as the styrene feed. The two monomer feeds were mixed before addition to the reaction vessel. The mixed feed rate was thus twice that of the individual monomer feed rates and, as before, lasted 3 h. The monomer weight ratio was 1:1 and the initiator was ADIB. By this means, a mixed monomer feed was achieved which varied in composition during the course of the polymerization from

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pure styrene initially to pure methyl methacrylate at the end. Conversion was 90%.

Graft copolymers. These were prepared by the method of Waite and Thompson[7,8]. The first step was the preparation of a macromonomer to form the side chains. This is done by polymerizing a suitable monomer with 4,4′-azobis (4-cyanovaleric acid) as initiator in the presence of thioglycolic acid. The resulting polymer, monoterminated with a carboxyl group, was then reacted with glycidyl methacrylate to form a macromonomer which was then copolymerized with the second monomer to form the backbone of the graft copolymer. High yields of graft copolymers of poly(methyl methacrylate) on polystyrene and poly(butyl acrylate) on poly(methyl methacrylate) backbones were obtained.

Block copolymer. A polybutadiene–polystyrene block copolymer was prepared by anionic polymerization in n-hexane at 50°C, using 2% secondary butyllithium solution with 0.4% w/v tetrahydrofuran as the initiator.

Isolation of polymers

This was achieved by precipitation in a large excess of non-solvent. For example, in the case of poly(methyl methacrylate) homopolymer, 500 g of a 10% solution of the polymer in toluene was added by metering pump over a period of 1 h to 5 l of well-stirred n-heptane.

The precipitated polymer was filtered and dried under vacuum at 60°–80°C to constant weight.

Characterization of polymers

G.p.c. data. The molecular weight and weight distribution were determined by gel permeation chromatography (g.p.c.). These determinations were made with a Waters Model 200 instrument, equipped with Styragel columns at 30°C and a refractive index detector. Sample solutions in tetrahydrofuran at 0.3% w/w concentration were injected. All calibrations were made with polystyrene standards and all results quoted in this paper are in terms of these standards.

Acid value determination. Non-aqueous indicator titrations were also used to check the molecular weight of the carboxyl-terminated polymer, as well as for checking completion of the reaction with glycidyl methacrylate in the macromonomer preparation.

Solvent extraction. Small samples of the solid graft copolymers were extracted with appropriate hemi-solvents in a Soxhlet apparatus to determine the presence of homopolymer in the graft preparations. Thus, for example, methanol was used to extract poly(methyl methacrylate) residues.

Turbidimetric measurements procedure

A nephelometer (manufactured by Evans Electroselenium Ltd.) was used for the measurements. Unlike turbidimetric measurements where the transmitted intensity of light through a turbid solution is measured, this instrument measures the scattered light intensity at 90° to the direction of illumination (Tyndall effect). Readings are on a scale of 0–100%, by comparison with the intensity of light scattered by a standard in the instrument. A 0.2% w/v polymer solution was prepared volumetrically by weighing dry polymer to the nearest 0.1 mg and dissolving completely in a little toluene (AR grade) in a 500 ml volumetric flask before making up to the mark with pure toluene. Ten-fold volumetric dilution in 100 ml flasks was then carried out by pipetting 10.0 ml of the polymer solution into the flask and then adding the requisite volume of AR toluene (solvent) from a burette. AR methanol (non-solvent) was then added to bring the total liquid volume up to the calibration mark on the neck of the volumetric flask. The flasks were allowed to stand 10 min at room temperature after mixing, then shaken by hand and the mixtures used to fill the nephelometer sample tubes to a height of 10 ± 1 cm. The tubes were then corked and kept in a thermostatically controlled bath for 20 min at 25.0 ± 0.1°C, and then the turbidity measurement made. Since the room temperature was always ~25°C and measurements were carried out quickly it was possible to minimize errors even though the equipment was not thermostatically controlled.

A plot of instrument readings against percentage non-solvent was prepared. The final polymer concentration (0.02% w/v) in the sample was sufficient to give a 100% reading at the maximum turbidity encountered.

In certain cases, it was necessary to increase the polymer concentration in order to achieve a maximum turbidity reading of around 100%; in others, the concentration was reduced or turbidity measurements made as a function of time in order, respectively, to eliminate interference due to flocculation of primary precipitate particles or to study the kinetics of this flocculation. As the methanol was used in large quantities, no drying procedure or other precautions were used to counter water absorption by the methanol, other than using methanol from a newly-opened container for each set of experiments.

Calibration of nepheolometer. Colloidal silica dispersions of known particle size and size distribution were prepared by room temperature precipitation from an ethanolic solution of tetraethyl silicate with ammonia by the method of Stober, Fink and Bohm[10]. The resulting precipitated silica dispersion was analysed for total solids and then diluted volumetrically with AR ethanol or distilled water to the required concentration. Particle size of at least fifty particles was determined on an electron micrograph.

Direct precipitated polymer particle size measurements

A few measurements were made with a Nanosizer instrument during precipitation with methanol of dilute styrene homopolymer solution in toluene. In the Nanosizer (Coulter Electronics Ltd.) a pulsed beam from a laser is passed through a dilute sample of the dispersion sample whose particle size is required. As the particles are vibrating due to Brownian motion, the smallest particles, which are moving quickest, give rise to the greatest frequency shift in the scattered light from the frequency of the incident laser light. The instrument measures the intensity of the scattered light at a series of frequency values spanning the incident frequency value. The accumulated data is processed by minicomputer, and the mean particle size (*z*-average) and polydispersity figures are registered in the display panel of the instrument after only a few minutes. The operation of the instrument is entirely automatic.

Unlike conventional light scattering techniques, the only information required is the viscosity and the refractive index of the suspension medium. In particular,

Table 1 G.p.c. characterization data

Polymer type	Polymer composition	M_w	M_n	M_w/M_n
Homopolymer	PS	48300	21500	2.24
	PMMA	53500	21200	2.61
	PBA	35900	6700	5.31
Copolymer				
1 Random	50/50 PS/ PMMA	79600	33900	2.35
2 Programmed	50/50 PS/ PMMA	69400	30600	2.27
Graft copolymer				
1a Whole polymer	50/50 PS/ PMMA	44600	14600	3.05
1b Side chains only	PMMA	3240	1720	1.88
2a Whole polymer	50/50 PBA/ PMMA	18800	5620	3.34
2b Side chains only	PBA	4620	2240	2.06
Block copolymer				
Whole polymer	PS/PB	22625	16700	1.35
Side chains only	PB	9560	7705	1.24

the change in refractive index of the particle material with solvent content (often difficult to obtain and required for conventional light scattering techniques) is not required for this measurement technique. Refractive indices were determined directly from a series of direct measurements (see Discussion and *Figure 10*), whilst viscosities were interpolated from published values.

RESULTS

Characterization of polymers

G.p.c. data. G.p.c. data are given in *Table 1*.

Acid value results. Carboxyl-terminated PMMA, molecular weight 2155; this compares with an M_n of 1720 from g.p.c. data (see above). [Percentage reaction with glycidyl methacrylate 96.5%.]

Carboxyl-terminated PBA, molecular weight 1778; this compares with an M_n of 2240 from g.p.c. data (see above). [Percentage reaction with glycidyl methacrylate 92.6%.]

Extraction. Extraction with hemi-solvents of the polystyrene/poly(methyl methacrylate) grafts showed not more than 10% total homopolymer contamination.

N.m.r. examination of polystyrene/poly(methyl methacrylate) copolymer. The random and the programmed linear copolymers of styrene and methyl methacrylate were examined by n.m.r. in order to determine monomer sequence distribution. An instrument operating at 220 mHz was used and the samples were dissolved in a mixture of *ortho*- and *para*-dichlorobenzene.

The resulting spectra showed that the programmed copolymer had a higher proportion of methyl methacrylate monomer doublets than the random copolymer, but in both cases the number of triplets (and higher order sequences) was insignificant.

Turbidimetric measurements

Characteristic features of turbidity plots against solvent/non-solvent ratio. The principal finding of this work is shown in *Figure 1*. This is the characteristic maximum and minimum double inflection observed in the plots of turbidity readings against solvent/non-solvent ratio for the graft and block copolymer examples used. Moreover, this is a characteristic of high purity graft copolymer systems. For, as can be seen from *Figure 2*, replacement of 10% by wt of the graft copolymer of methyl methacrylate on styrene by either of the corresponding homopolymers of similar molecular weight to that of the graft leads to complete suppression of the double inflection.

By contrast, both the homopolymers and the random copolymers show simple S-shaped curves with a single inflection. As will be seen from *Figures 3* and *4*, these all show initial and inflection point locations characteristic of the polymer type and solvent/non-solvent system. On this basis, they may be distinguished from each other, and, as can be seen from *Figure 5*, from physical mixtures of the homopolymer pairs corresponding to the copolymers.

It will be seen from *Figure 1* that the characteristic plot for the graft and block copolymers is not confined to any particular polymer of solvent/non-solvent pair; it does seem to be a quite general phenomenon, although one that is readily suppressed by the presence of significant levels of homopolymer contamination in the graft preparation.

Effect of polymer concentration and solvent/non-solvent system on the turbidity against solvent/non-solvent ratio plots. For convenience in theoretical interpretation, the effect of these two variables has been studied using styrene homopolymer in toluene solution. In *Figure 6*, the effect of varying the polymer concentration is shown. Whilst the

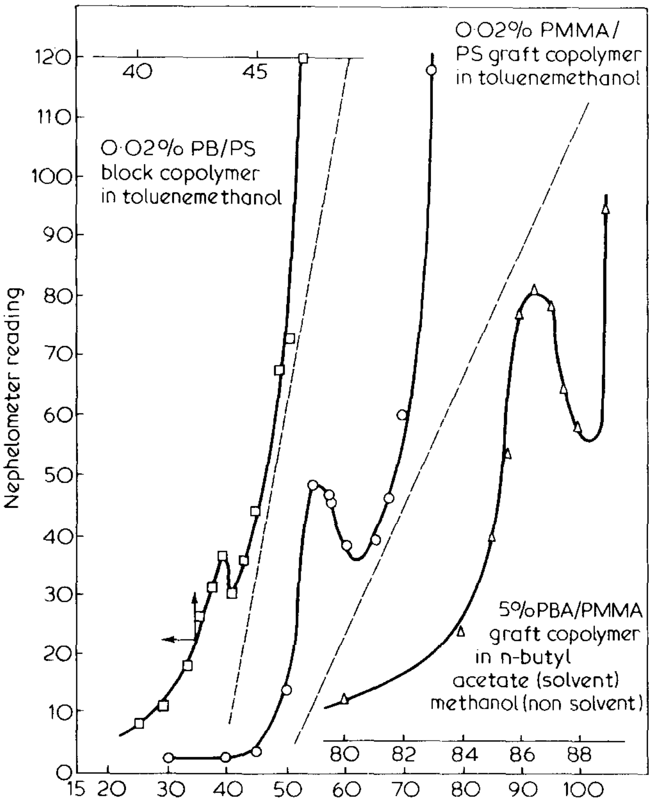

Figure 1 Plot of turbidity *versus* non-solvent content for pure block and graft copolymers dilute solution, showing characteristic double inflection

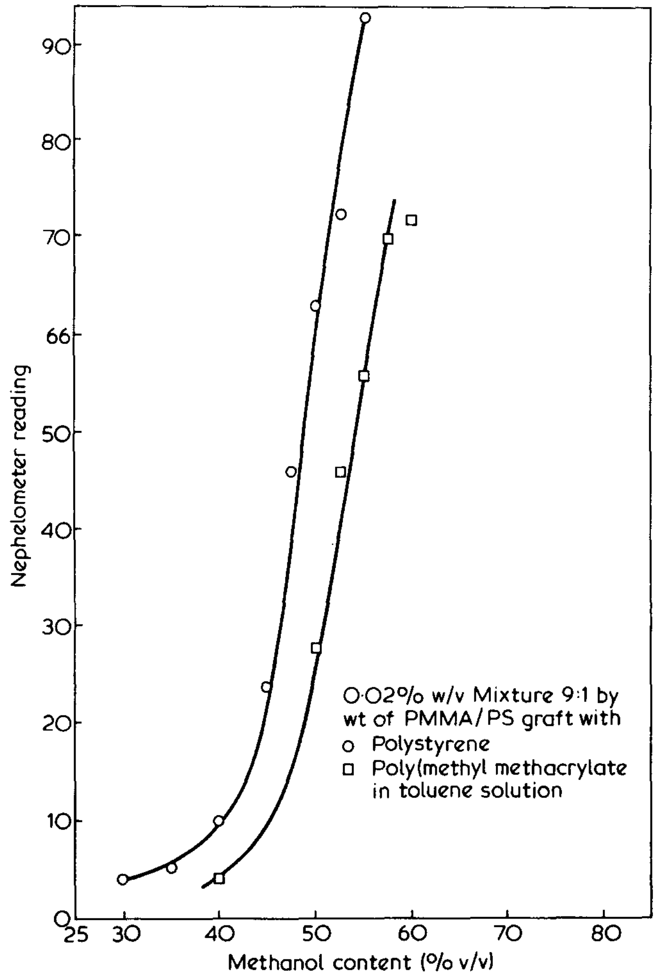

Figure 2 Effect of the addition of a small amount of homopolymer to graft copolymer solution on the characteristic curve shown in *Figure 1*

solvent/non-solvent ratio value, at which initiation of precipitation occurs, remains constant, the rate of turbidity increase as non-solvent content is raised, increases with increasing polymer concentration.

The effect of changing the nature of the non-solvent is shown in *Figure 7.* Whilst holding the polymer concentration constant, a series of four alcohols, ranging from methanol to n-butanol, were used as non-solvent precipitants. Initiation of precipitation moves to higher ratio values as the non-solvent polarity is reduced, but the general shape of the curves for each system remains constant.

Finally, in *Figure 8*, the change in particle size of the precipitated polystyrene particles at low initial concentration in toluene is shown together with the turbidity plot.

Time dependence of turbidity. This was particularly evident with the styrene polymers and copolymers when n-heptane was used as a precipitant with toluene as solvent, or when methanol was used as a precipitant for poly(methyl methacrylate) in butyl acetate solvent. No doubt, this experimental difficulty could be overcome by the use of a recording turbidimeter (see Howard[11]).

Calibration of nephelometer. Two different particle size colloidal silica dispersions were used for the calibration procedure. As will be seen from *Figure 9*, straight line relationships were found between the instrument reading and the silica concentration in both ethanol and water.

RI *measurements on toluene/methanol mixtures. Figure 10* shows results of measurements of refractive index by means of an Abbé Refractometer at 22.3°C for various toluene/methanol mixtures. A straight line relationship between mixture refractive index and composition was found.

DISCUSSION

Previous published results

Hartley[12] used a similar technique to the present work to establish the presence of poly(vinyl alcohol)/poly(vinyl acetate) grafts in poly(vinyl acetate) dispersions in water. However, he used hemisolvent pairs and optical density measurements with a Spekker Absorptiometer at 385 nm. This appears to be the only previous literature reference where a distinct maximum and minimum in the turbidity/solvency plot can be seen for graft copolymer, but, as it is for a hemisolvent pair, rather than a solvent/non-solvent pair, the origin of the phenomenon is likely to be partial resolution.

Howard[11] studied the turbidimetric titration of nylon-6,6 using a recording turbidimeter, and the same basic technique as the present work. A series of determinations in different solvent/non-solvent compositions with constant polymer concentration were recorded, allowing the turbidity to reach a maximum before taking the value.

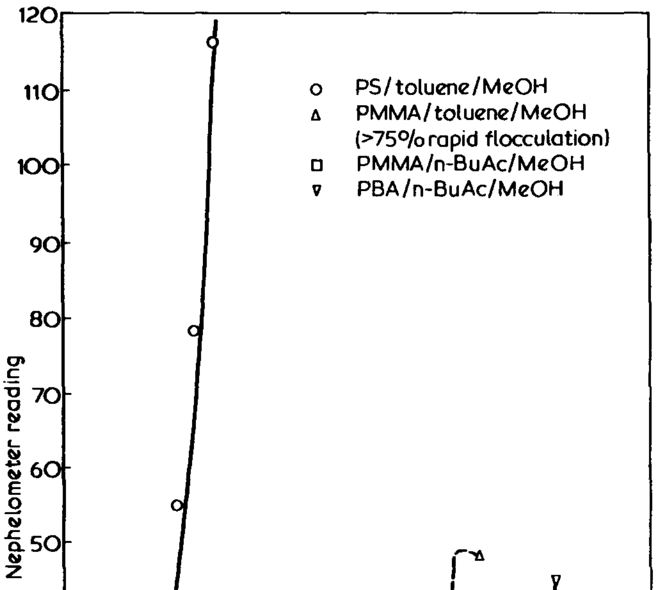

Figure 3 Plot of turbidity *versus* non-solvent content for dilute homopolymer solutions

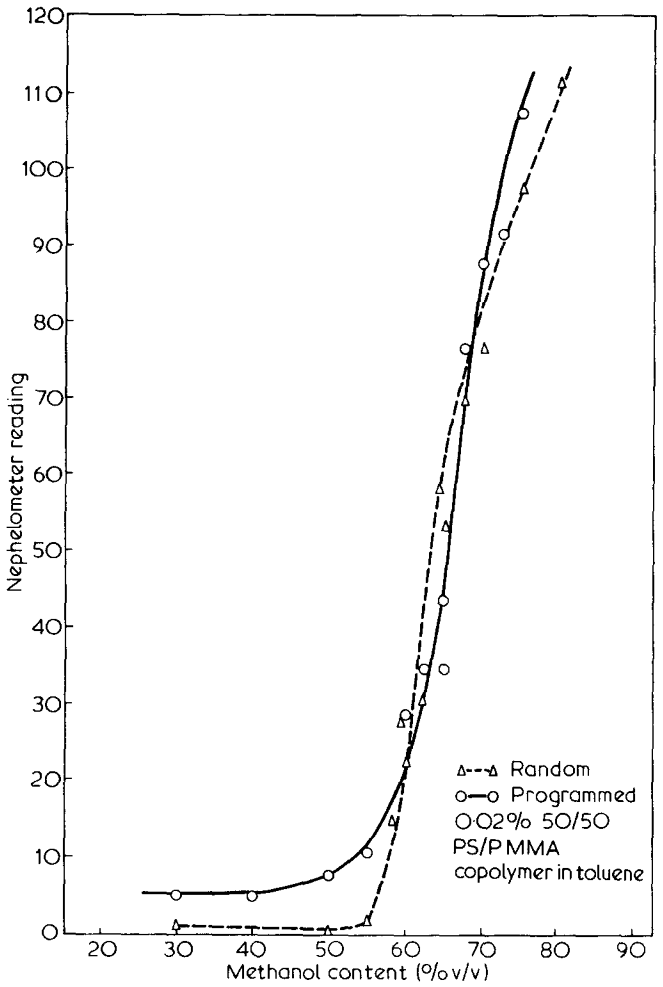

Figure 4 Plot of turbidity *versus* non-solvent content for dilute random copolymer solutions

Theory

The theory of light-scattering has been described many times in textbooks, both from the point of view of the physics of the phenomena[13] and the specific application to polymer solutions[14]. In general, the instruments used for turbidity measurements during the precipitation of polymers from solution are simpler than those used for light-scattering measurements from polymers in solution. In particular, measurements are made at one scattering angle only (in some instances, two), and these are usually 180° (optical density) and 90° (nephelometry, Tyndallometry). In the present case, we are concerned with light scattered at 90°. We are also concerned with very dilute polymer solutions, in order to minimize multiple scattering effects.

In a dilute solution of polymer in a thermodynamically 'good' solvent, the polymer molecule coils are expanded. As precipitant is added to the solution, the coils contract into the minimum dimensions possible before coalescing into particles of a new phase. Such particles will consist of polymer, solvent and precipitant (non-solvent). Interfacial tension forces will tend to constrain the particles to a spherical shape.

If a distribution of polymer molecular weights is present in the solution, then it is predicted by the thermodynamic theory that the highest molecular weight polymer will come out of solution first as precipitant is added, followed progressively by the lower molecular weights as more and more precipitant is added. This is the basis of polymer fractionation processes. The theory of such processes originated with Flory; it has been described in great detail in a textbook by Tompa[15], and reviewed recently by Flory[16].

As the proportion of non-solvent in the solvent medium becomes greater, the medium becomes a thermodynamically 'poorer' solvent for the polymer and the saturation concentration will fall, until finally it becomes just less than the actual polymer concentration and precipitation commences. The number of nuclei formed will depend on the difference between the actual and the saturation polymer concentration and, consequently, will increase with increasing proportion of non-solvent in the mixture. Once precipitation is initiated, the nuclei may grow by two possible mechanisms. First (analogous to crystal growth), the difference in concentration between the continuous phase and the saturation concentration leads to continuous deposition of polymer on the surfaces of the nuclei until the concentrations become equal (growth rate at any moment will be proportional to the instantaneous value of this concentration difference and, therefore, initially will be fast and will fall off with time). Secondly, collision and coalescence of growing particles will lead to growth in particle size, again with growth rate being large initially and falling off with time as the number of particles in suspension becomes smaller with consequent collision rate decrease. Whatever mechanism is operative for any

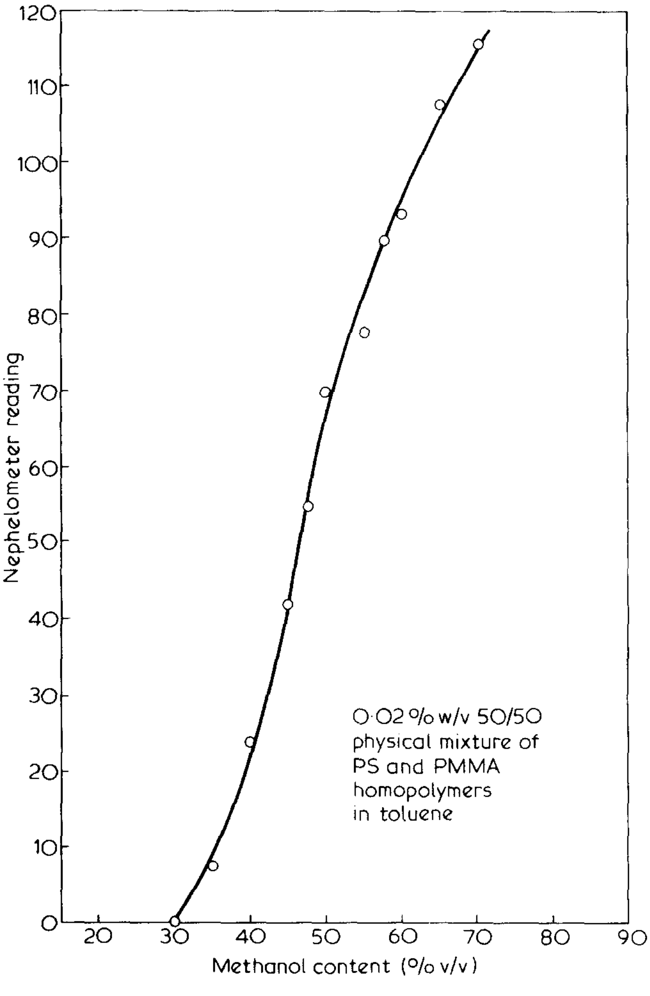

Figure 5 Plot of turbidity *versus* non-solvent content for dilute mixed homopolymer solutions

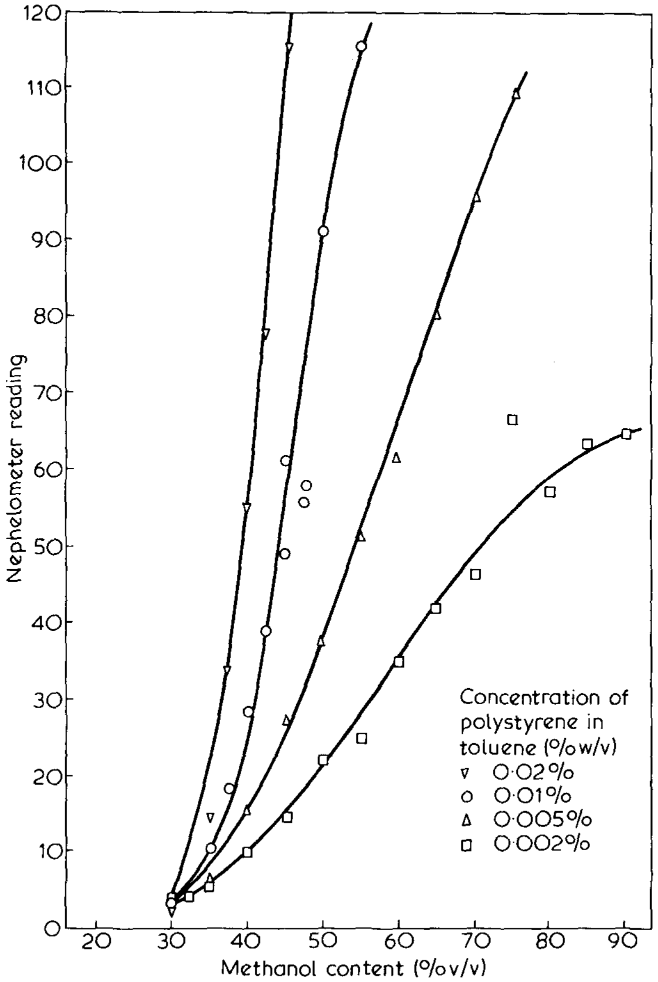

Figure 6 Effect of polymer concentration on the turbidity/non-solvent plot

given solvent/non-solvent mixture the particle size will grow rapidly initially and then slow down with time. Alternatively, particle number will initially fall quickly and then more slowly as time after initiation of precipitation increases. Thus, unless sedimentation or some other mechanism such as Ostwald ripening becomes significant, we can expect both the size and number of precipitated polymer particles to become more or less constant after an initial period of time and this was found to be the case with a number of the systems examined in this work.

The saturation concentration will also be molecular weight dependent. For a given solvent composition, the number of nuclei formed will depend not only on the total polymer concentration but also on how the concentration is distributed amongst the molecular weights.

Thus, initially few nuclei will be formed and these will grow rapidly due to the large difference between saturation concentration and polymer concentration remaining in solution, whilst the contribution to particle size and number from coalescence will be negligible because of the few nuclei and particles formed and consequent low collision rate. As the solvent mixture becomes a very poor solvent for the polymer, a given increment in non-solvent content will lead to a relatively small increase in the large number of nuclei formed so that the contribution to particle number and size from coalescence will remain relatively constant, whilst the small polymer concentration remaining in solution will result in a smaller particle growth rate from the solution. The overall particle size will thus decline whilst the number remains fairly constant in this solvency region. In the intermediate solvency region, the number of nuclei will increase sharply for a given increment in non-solvent content, whilst the growth rate of individual particles from solution will decline. Thus, unless coalescence becomes a dominant factor, particle size will decline steadily as non-solvent content increases, whilst particle number will increase in such a way as to give a sigmoidal plot of particle number against non-solvent content. If the turbidity value measured by the instrument is directly proportional to particle number, then a sigmoidal plot of turbidity against non-solvent content can be expected, providing this is not masked by the effect of the decline in particle size as non-solvent content increases. This latter effect has been confirmed by Klenin and his coworkers[17], who made measurements of turbidity at a number of light wavelength values, as well as by the limited number of particle size measurements we have made using the Nanosizer.

Light scattering theory

The direct measurements of precipitated polymer phase particle size by the Nanosizer show that the particle diameters are of the same order as the wavelength of the light (tungsten filament light peak intensity is ~560 nm). Consequently, calculation of light scattering intensities or turbidities requires the use of the full Mie theory.

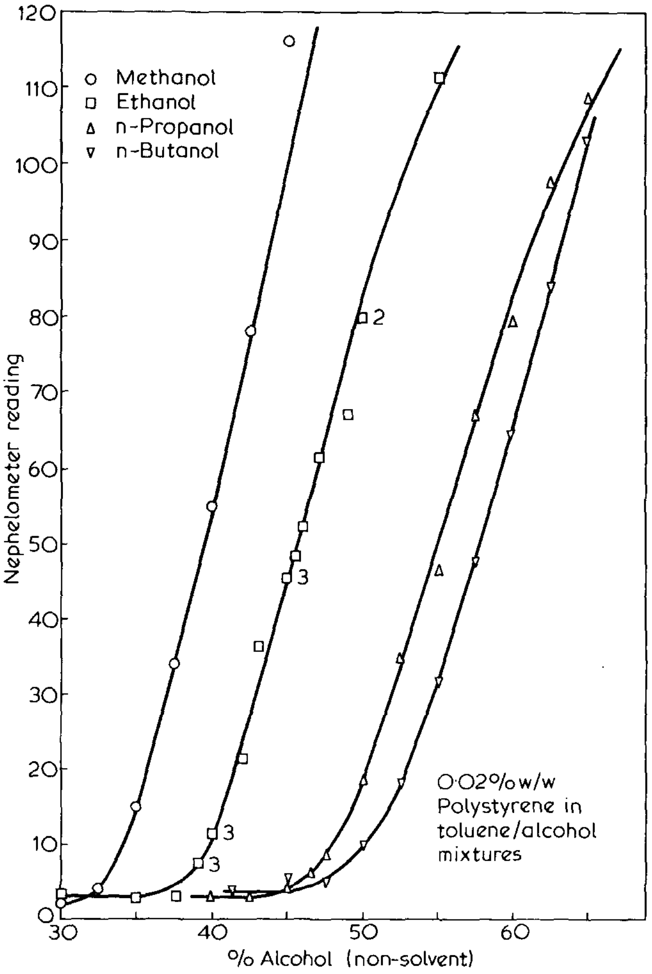

Figure 7 Effect of non-solvent type on the turbidity/non-solvent plot

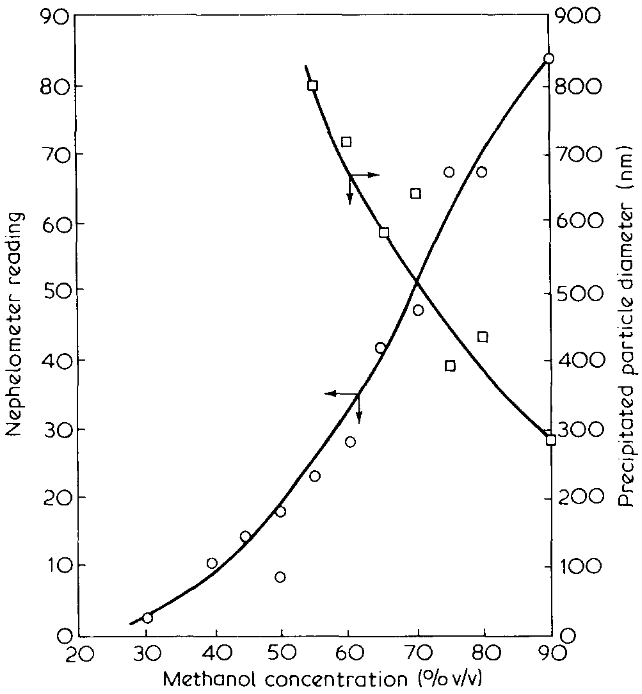

Figure 8 Particle size and turbidity as a function of non-solvent content

However, the calculations of the Mie theory are too cumbersome for use in a practical analytical method, and thus the simpler, approximate Rayleigh–Gans theory must be used. Experimental justification for this procedure has been provided by Gooberman[18], whilst studying the polystyrene–benzene–methanol system. The equations of the theory are as follows[19,20].

$$I_u(\theta)=[n\pi^4d^6(m-1)^2P(\theta)/18\lambda^4](1+\cos^2\theta) \qquad (1)$$

where $I_u(\theta)$ is the reduced (unpolarized) light intensity at a scattering angle θ, n is the number of scattering particles per unit volume of suspension, d is the particle diameter (assumed to be spherical), λ the wavelength of the incident light in the suspension medium, and m is the ratio of the particle refractive index (μ) to that of the continuous phase (μ_0).

The particle scattering function $P(\theta)$ is given by

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

where $x=(2\pi d/\lambda)\sin(\theta/2)$. The reduced light intensity is defined as the intensity scattered per unit of incident light intensity, unit solid angle received and unit volume of scattering material. As we are concerned only with a scattering angle of 90°, and assuming that the nephelometer reading is proportional to the reduced light intensity, the reading R is given by:

$$R=5.412Knd^6(m-1)^2P(90°)/\lambda^4 \qquad (3)$$

where K is an instrument constant, while, from equation (2), the particle scattering function becomes:

$$P(90°)=\{[3.421\lambda^3/100d^3](\sin x-x\cos x)\}^2 \qquad (3a)$$

and

$$x=4.443d/\lambda \qquad (3b)$$

Equation (3) is for a light source of uniform wavelength whereas the tungsten filament lamp used in practice has a range of wavelengths, each of different intensity. So, equation (3) should be rewritten:

$$R=5.412Knd^6(m-1)^2\Sigma P(90°)/\lambda^4 \qquad (3c)$$

where m is assumed to be independent of wavelength. Equations (3) and (3c) show that for a given polymer–solvent–non-solvent system and a given particle size, the instrument reading (R) is directly proportional to the number of particles, i.e.:

$$R=Cn \qquad (4)$$

where C is a constant. This is confirmed by the calibration results with colloidal silica (see *Figure 9*), where particle size was constant and R was plotted as a function of particle concentration.

Further development of these equations is not worthwhile because of the wavelength spread in the light source, as well as the variation of particle number concentration (n) and diameter (d) during the course of polymer precipitation, whilst the complicated mathematical form of the $P(90°)$ function renders this development difficult.

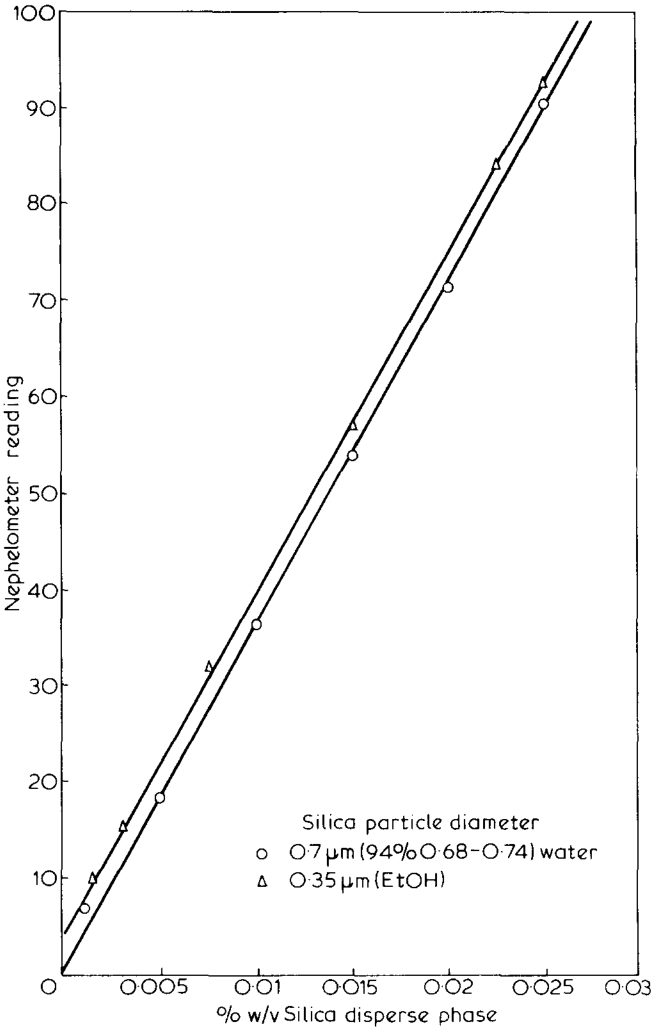

Figure 9 Calibration curves for the nephelometer using colloidal silica of known particle size in water

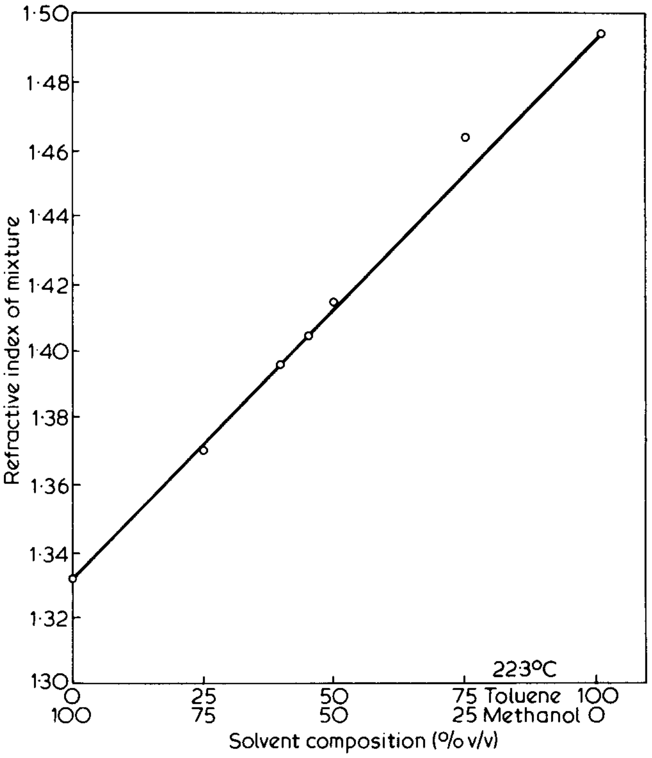

Figure 10 Refractive index *versus* solvent mixture ratio for toluene/methanol mixtures

Qualitatively, providing the polymer solution is very dilute so as to minimize interference from coalescence, a Gaussian or similarly-shaped polymer molecular weight distribution must lead to a sigmoidal precipitation curve, whose median slope will be directly proportional to polymer concentration. This was found to be the case from the random copolymer and homopolymer systems examined (*Figures 4* and *6*).

Qualitatively the results for different alcohol precipitants (*Figure 7*) are also as might be expected for the refractive indices of toluene/alcohol mixtures. Our experimental measurements (see Results above) show that the refractive index of binary toluene/alcohol solvent mixture may be calculated from the refractive indices of the pure solvents and the volume fraction of alcohol in the mixture (straight line relation between refractive index of mixture and the volume fraction of alcohol in the mixture). Calculation of the mixture refractive indices corresponding to toluene/alcohol mixture compositions read from *Figure 7* for an instrument reading of 50 show a reasonable constancy (*Table 2*).

In addition, qualitative agreement of the results with changes in solubility parameters of the mixtures can also be found.

The main experimental observation remains to be explained; namely, the appearance of a double inflection in the precipitation curve of pure block or graft copolymer solutions. As this appears to happen quite generally with these copolymer solutions and is associated with rigorous segregation of the component monomer units in the structure of the copolymer chains, we must attribute this to collapse of the backbone chain from an expanded coil to a microglobule, in which the side chains, still solubilized, help to stabilize the microglobule. In the case of the block copolymers, presumably collapsed blocks of one kind micellize together with much the same effect. Such stabilization will, over a limited concentration range of non-solvent, hinder or prevent coalescence, thus causing the particle size to decrease much more sharply with increase in non-solvent content than if coalescence was present, so that it dominates over the effect of increased particle number and, consequently, the instrument reading declines until the side chain polymer starts precipitating (cf *Figures 1* and *3*). Presumably, the presence of free homopolymer of either kind in solution hinders this stabilization process or masks it by forming alternative nucleation sites that can grow from solution. In view of this possible explanation, it would be interesting to study the precipitation of a graft copolymer of polystyrene side chains on polymethyl methacrylate backbone from toluene solution with methanol. This would be the reverse of the present example, in that in this new experiment, the side chains would be less soluble in a given solvent/non-solvent blend than the backbone a stabilized microglobule would be more difficult to rearrangement postulated between an expanded coil and a stabilised microglobule would be more difficult to achieve.

CONCLUSIONS

An improved turbidimetric method for studying the precipitation of polymers from dilute solution has been described. Whilst maintaining the simplicity of apparatus and technique associated with turbidimetric titration, it avoids some of the difficulties (both experimental and theoretical) inherent in the titration technique.

As such, it may be used as a method for 'fingerprinting' homopolymers and copolymers in solution. In particular, graft and block copolymers (when pure) show a characteristic double inflection in the precipitation curve, which is quite distinct from the sigmoidal curves obtained with the corresponding homopolymer or their physical mixtures or random copolymers of similar molecular weight and monomer composition.

It is thought that this double inflection may correspond to a change of the graft copolymer from an expanded coil configuration to a stabilized microglobule (a corresponding stabilized micelle in the case of block copolymers being formed) as the solvency for the copolymer is reduced. A possible means of testing this conclusion is indicated.

ACKNOWLEDGEMENTS

I would like to acknowledge helpful discussions with my colleagues Mr F. A. Waite and Mr A. Doroszkowski, as well as with Professor C. H. Bamford (Liverpool University).

Table 2

Solvent mixture	Refractive index* (for mixture at R = 50)
Toluene–methanol	1.43206
Toluene–ethanol	1.43081
Toluene–propanol	1.43174
Toluene–butanol	1.43666

* These values are calculated from *RI* values for the Na–D line at 25°C of 1.49413 for toluene, 1.32652 for methanol, 1.35941 for ethanol, 1.28270 for n-propanol and 1.3873 for n-butanol (ref. 21)

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