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MOLECULAR WEIGHT DISTRIBUTIONS FROM LIGHT SCATTERING STUDIES OF POLYSTYRENE SOLUTIONS DURING PHASE SEPARATION*

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Abstract—Phase separations, brought about by cooling, of very dilute solutions of polystyrenes in a θ-solvent (methylcyclohexane) have been studied using a light scattering instrument. Molecular weight distributions of unfractionated polystyrene samples are presented, evaluated from the experimental data. Two methods of evaluation are described and compared: the conventional method led to poor results, whereas a new method, devised from the consideration of experimental and theoretical evidence, resulted in more accurate estimates of the mol. wt. distributions of the polymer samples.

INTRODUCTION

IN A PREVIOUS paper,(1) the authors have shown that measurements made, with a light scattering instrument, of polystyrene solutions during phase separation can give qualitative information about the breadth of the mol. wt. distribution in the polymer sample under investigation. A description was given(1) of the differential photocurrent measuring system and of the experimental procedure which was used for the light scattering studies of phase separation, brought about by cooling, of very dilute solutions of polystyrene in a θ-solvent (methylcylcohexane). Preliminary light scattering results were presented which show the effect, on the resulting precipitation curves, of changing the mol. wt. and mol. wt. distribution of the polymer, the solution concentration and the rate of cooling. Both the composition and the refractive index of the precipitated phase were determined experimentally at various temperatures. It was then possible to evaluate the light scattering results using a more rigorous theoretical treatment which allowed for the deswelling of the gel phase brought about by decreasing the temperature.

Subsequent measurements, the results of which are presented and discussed here, were directed towards the evaluation of accurate mol. wt. distributions. Since the temperature of precipitation of a polymer species has been shown to be a function of both the mol. wt. and the concentration of the species,(1–3) the investigation of unknown mol. wt. distributions was possibly only after an initial calibration, which related these three variables, had been established.

The two calibration methods which have been described in the literature(2, 3) are based on the common assumption that the precipitation of any given mol. wt. species is not appreciably affected by species of higher or of lower mol. wt. which may be present in the system. Both of these methods relate the precipitation temperature of a species to the mol. wt. and the solution concentration of that species.

The calibration procedure employed initially in this work is that described by Wild,(4) which is based upon the Claesson method.(3) Molecular weight distributions

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are presented which were obtained using this procedure. These results led to an investigation into the validity of the above assumption and a new method of calibration was devised.

The results presented below are compared with the results obtained from gel permeation chromatography (GPC) measurements. However, it should be noted that the GPC method, as used here, tends to give values for the dispersions, $\bar{M}_w/\bar{M}_n$ which are higher than the values found from a combination of light scattering and osmotic measurements.

INTERPRETATION OF EXPERIMENTAL RESULTS

Both the light scattering instrument and the experimental procedure which were used for these measurements have been described elsewhere(1, 5, 6) and require no further comment. Also, an expression has been derived(1) for the relative concentration of precipitated polymer, c_{pt}, at any stage during the phase separation. This is:

$$c_{pt} = \frac{I_{90}^{\circ} v_2'}{P_{90} (D/\lambda')^3 (\Delta n)^2} \tag{1}$$

where I_{90}° is the intensity of the light scattered by the spheres, which constitute the precipitated phase, and is measured relative to the intensity of the incident beam and at a constant distance from the centre of scattering; P_{90} is the particle scattering factor for the spherical model; D is the diameter of the spheres; λ' is the wavelength of the incident light in the scattering medium; v_2' is the volume fraction of polymer in the gel phase and Δn is the refractive index difference between the gel and sol phases. The refractive index difference, Δn, varies approximately linearly with the volume fraction of polymer in the gel phase, v_2', enabling the use of

$$c_{pt} = \frac{I_{90}^{\circ}}{P_{90} (D/\lambda')^3 (\Delta n)} \tag{2}$$

to describe the relative concentration of precipitated polymer.(1)

Initially, the average mol. wt. (M) of a narrow distribution polymer was characterized by $T_{\frac{1}{2}}$, the temperature at the 50 per cent precipitation point and by the increase in the value of c_{pt} found to occur between $(T_{\frac{1}{2}} + \frac{1}{2})$ °C and $(T_{\frac{1}{2}} - \frac{1}{2})$ °C.(4) It was found in this work that the latter parameter, denoted Δc_{pt}, was directly proportional to the concentration of the precipitating species. The calibration procedure for this method involves the precipitation of various narrow distribution polymers, each run at several concentrations. The data obtained from these precipitations may then be used to find a relationship between M, $T_{\frac{1}{2}}$ and Δc_{pt}. The general expression relating M, $T_{\frac{1}{2}}$ and Δc_{pt}, confirmed by this work, has been established as

$$1/T = A + B\mathrm{M}^{-a} - (C + D\mathrm{M}^{-a}) \ln (\Delta c_{pt}) \tag{3}$$

where the temperature, T, is in °K, and it is usually found that $B = 0$ and $a = \frac{1}{2}$. Values of Δc_{pt}, determined for each degree fall in temperature from the precipitation curve given by an unfractionated sample, could be used with the corresponding mean temperatures to give the average mol. wt. of the species that precipitated over each of these 1°C intervals. A normalized cumulative distribution curve was then constructed in the usual manner[10] using the values of Δc_{pl} as the weights of the different "fractions".

MATERIALS

The polystyrenes used in this work are listed in Table 1. The solvent, methylcyclohexane, has a θ-temperature for polystyrene of 70·5°C[11] and was purified by passage through columns of activated silica gel before distillation.[12] After this treatment it was shown by gas–liquid chromatographic analysis that the methylcyclohexane contained less than 0·2 per cent of impurities.

RESULTS AND DISCUSSION

In order to establish the relationship between the temperature of precipitation of a species and both the mol. wt. and the concentration of that species, it was necessary to determine many precipitation curves using narrow distribution polystyrenes. The anionic polymers used for this purpose, listed in Table 1, covered as wide a range of mol. wt. as possible and, for each calibrant, measurements were carried out at several concentrations within the range 0·07–1·50 mg/100 ml. Using the calibration procedure employed by Wild,[4] described in the previous section, it was possible to derive the following solubility equation:

TABLE 1. THE POLYSTYRENES

Polymer	Source	Mol. wt. $\bar{M}_v$
S1	Unfractionated polymer: polymerized at 60°C with benzoyl peroxide to 10 per cent conversion of monomer.	350,000
S2	As above, with lower catalyst concentration.	900,000
A1	Anionic polymer, Pressure Chemical Co.	1,800,000
A2	Anionic polymer, Pressure Chemical Co.	842,000
A4	Anionic polymer, Pressure Chemical Co.	411,000
A5	Anionic polymer, Pressure Chemical Co.	160,000
A6	Anionic polymer, Pressure Chemical Co.	98,200

$$1/T = 2\cdot890 \times 10^{-3} + \left[\frac{0\cdot250 - 0\cdot0249 \log (\Delta c_{pl})}{M^{\frac{1}{2}}}\right], \tag{4}$$

where T is in °K. A set of calibration curves, some of which are shown in Fig. 1, could then be constructed using log (Δc_{pl}) as a parameter. Curves were drawn at log (Δc_{pl}) intervals of 0·2: this being a suitable interval for the subsequent interpolation.

Phase separation experiments were performed using the unfractionated polystyrenes S1 and S2, each run at two concentrations, c, within the range 0·24–0·97 mg/100 ml. The cumulative distribution curves obtained from these runs are shown in Figs. 2 and 3 together with the curves obtained from GPC measurements. The corresponding average mol. wts. are listed in Tables 2 and 3.

These results show that the runs performed using higher solution concentrations, i.e. S1.1 and S2.1, led to values of $\bar{M}_n$ and $\bar{M}_w$ which were lower than those values obtained

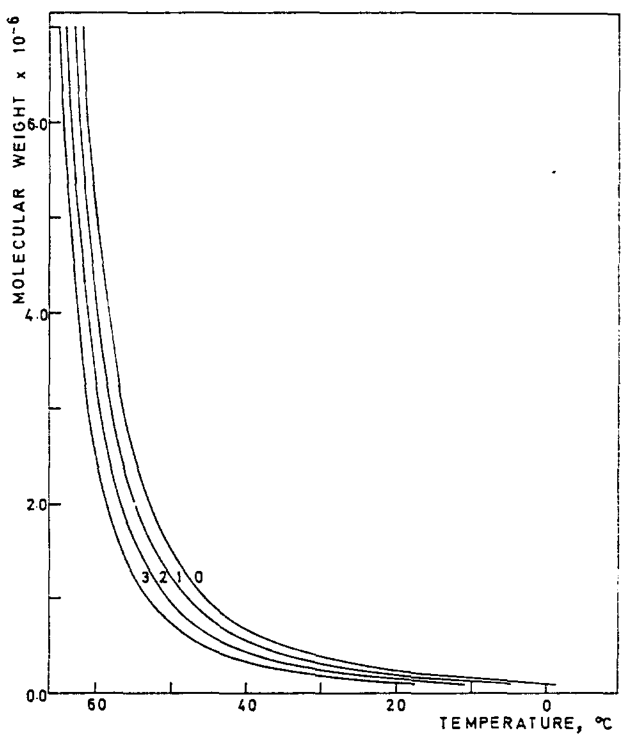

FIG. 1. Molecular weight–temperature calibration curves [$\log_{10}$ (Δc_{pl}) calibration]. Each curve was constructed from Eqn. (4) using the value of $\log_{10}$ (Δc_{pl}) indicated.

TABLE 2. AVERAGE MOL. WTS. FOR S1 [LOG (Δc_{pl}) CALIBRATION]

Source	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Run S1.1 = c = 0·48 mg/100 ml	5·4	6·9	1·3
Run S1.2 = c = 0·24 mg/100 ml	6·2	7·7	1·2
GPC	1·97	4·42	2·24

TABLE 3. AVERAGE MOL. WTS. FOR S2 [LOG (Δ_{pl}) CALIBRATION]

Source	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Run S2.1 = c = 0·97 mg/100 ml	7·2	13·2	1·8
Run S2.2 = c = 0·49 mg/100 ml	8·9	14·6	1·6
GPC	5·42	11·82	2·18

using lower concentrations of solution (runs S1.2 and S2.2). This effect could have been caused by the incomplete precipitation of the polymer at the lowest temperature attained during these runs (10°C) since, if this was the case, a greater proportion of material would have been precipitated, at that temperature, from a solution of higher concentration than from a solution of lower concentration.

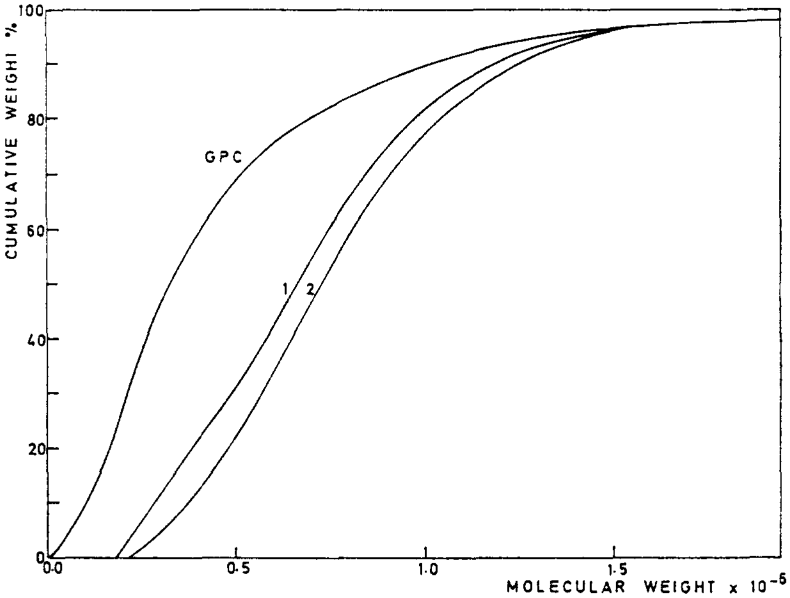

FIG. 2. Cumulative mol. wt. distribution curves for unfractionated polystyrene S1 [log (Δc_{pt}) calibration]. Curve 1: run S1.1, $c = 0{\cdot}48$ mg/100 ml. Curve 2: run S1.2, $c = 0{\cdot}24$ mg/100 ml.

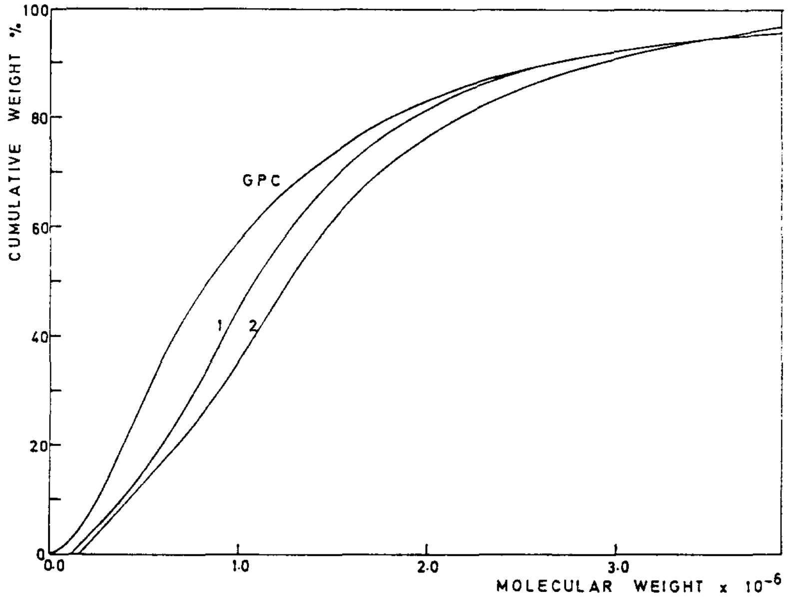

FIG. 3. Cumulative mol. wt. distribution curves for unfractionated polystyrene S2 [log (Δc_{pt}) calibration]. Curve 1: run S2.1, $c = 0{\cdot}97$ mg/100 ml. Curve 2: run S2.2, $c = 0{\cdot}49$ mg/100 ml.

If these results are compared with those obtained from GPC measurements, it can be seen that there was an underestimation of the low mol. wt. species present. This inability to determine fully the amount of material of low mol. wt. may have been due to the incomplete precipitation of the polymer species at 10°C and/or to the assumptions inherent in the method used to evaluate the experimental data.

Experiments were then designed to test the validity of the assumption used above, namely that the precipitation temperature of a species depends only on the concentration of that species and that it is independent of the concentrations of other species which may be present in the gel or sol phases.

In order to determine whether the precipitation of a low mol. wt. anionic polymer was affected by the presence of an unfractionated sample of higher average mol. wt., a preliminary experiment was performed by cooling a solution containing 0·38 mg of S1/100 ml ($\bar{M}_v$ = 350,000) and 0·10 mg of A6/100 ml ($\bar{M}_v$ = 98,200). It was found that the temperature at which the anionic polymer was 50 per cent precipitated from the mixture was about 7°C higher than that predicted from the above calibration. This higher temperature corresponded to an apparent mol. wt. of 130,000 for A6, in the mixture, which is considerably higher than the true value of 98,200 (Table 1). This behaviour is in accordance with the results obtained by Cornet,(9) who found that the temperature at which a species precipitates is higher when precipitated polymer is present in the system, than when this species is precipitated on its own.

To investigate this phenomenonon further, two runs were performed on solutions containing mixtures of polymers A4 ($\bar{M}_v$ = 411,000) and A5 ($\bar{M}_v$ = 160,000). The

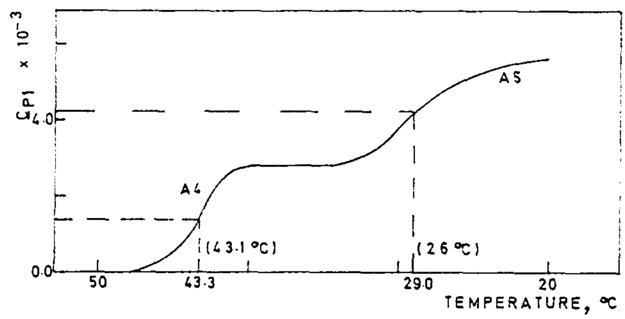

FIG. 4a. Phase separation of a solution containing equal concentrations of anionic polystyrenes A4 and A5. The temperatures given in brackets are those predicted from the calibration curves (Fig. 1).

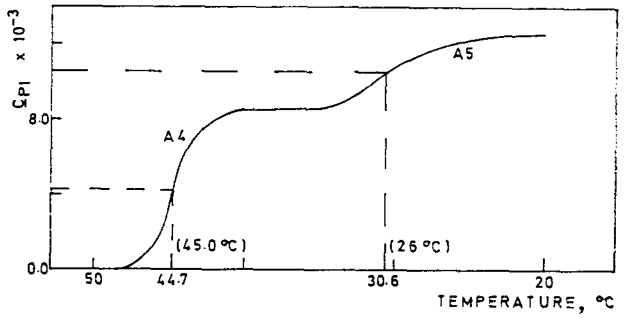

FIG. 4b. As above, but with a three fold increase in the concentration of anionic polystyrene A4.

first solution, which contained equal concentrations of A4 and A5, i.e. 0·24 mg/100 ml, gave the precipitation curve shown in Fig. 4 a. Figure 4b was obtained using the second solution, which contained the same concentration of A5 and a three fold increase in the concentration of A4.

The temperatures obtained from these curves, corresponding to the 50 per cent precipitation point of the higher mol. wt. polymer A4, were found to be within 0·3°C of the temperatures predicted from the calibration curves (shown in brackets in the figures). Thus, the precipitation characteristics of a species are not influenced by the presence of lower mol. wt. material in the solution. Klein and Patat(13) also reached this conclusion but made no reference to the influence of precipitated polymer upon the precipitation of lower mol. wt. species.

The effect of the precipitated polymer, A4, on the phase separation of the lower mol. wt. polymer A5, is demonstrated in Fig. 4a and b. From the solution containing equal concentrations of polymers A4 and A5, Fig. 4a, the 50 per cent precipitation point of polymer A5 was found to occur at 29·0°C. With a three fold increase in the concentration of polymer A4, the precipitation of A5 occurred at a higher temperature (30·6°C). These temperatures may be compared with that at which precipitation occurred from a solution containing the same concentration, 0·24 mg/100 ml, of polymer A5 only, i.e. about 26°C.

Additional evidence is supplied in Figs. 5 and 6 which refer to a further experiment. The solution used contained equal concentrations of polymers A1, A2, A4 and A5, i.e. 0·24 mg/100 ml. The temperatures given in brackets in Fig. 5 are those which were derived from the calibration curves: only the highest mol. wt. polymer A1 precipitated at the predicted temperature. The solid line given in Fig. 6 shows the order of this effect on the resulting cumulative distribution obtained for this solution of four components using the above calibration.

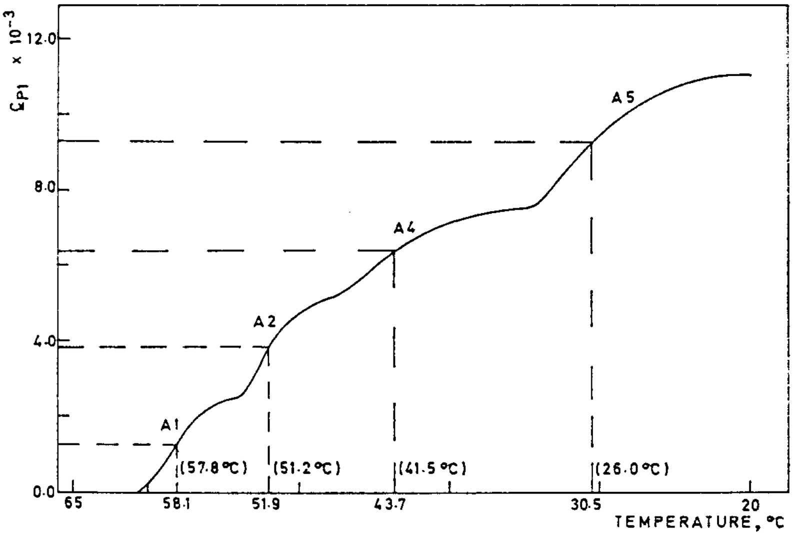

FIG. 5. Phase separation of a solution containing equal concentrations of anionic polystyrenes A1, A2, A4 and A5. The temperatures given in brackets are those predicted from the calibration curves (Fig. 1).

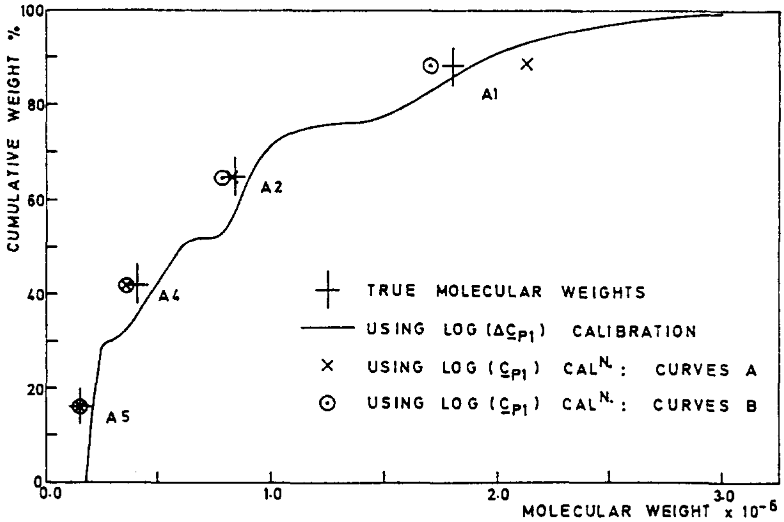

FIG. 6. Cumulative mol. wt. distribution for mixture of four anionic polystyrenes.

It may be concluded from these experiments that, if higher mol. wt. material is present, the precipitation temperature of lower mol. wt. species is a function of the concentration of the precipitated material.

The phase separation of a solution of an unfractionated polymer has been considered theoretically using the Flory–Huggins theory of polymer solutions.(14, 15) It has been shown(16, 17) that, for a given polymer–solvent system over the range of concentration used in this work, the temperature at which a species precipitates is determined by the amount of polymer in the gel phase, rather than by the concentration of the precipitating species, and by the mol. wt. of that species. The amount of polymer in the gel phase is proportional to c_{pl}, whereas Δc_{pl} is proportional to the concentration of the precipitating species. Thus, this theoretical treatment indicates that log (c_{pl}) should be used in place of log (Δc_{pl}) as the parameter in the construction of the calibration curves relating temperature of precipitation and mol. wt. This conclusion is in accordance with the results of the experiments, described above, which were performed using solutions containing mixtures of anionic polymers.

In view of the above experimental and theoretical evidence, a calibration was constructed based upon log (c_{pl}) rather than upon log (Δc_{pl}). The value of c_{pl} at the 50 per cent precipitation point was found for each of the precipitation curves obtained using the anionic polymer calibrants. It was then possible to derive two extreme solubility equations which would encompass all the calibration data. These are

$$1/T = 2\cdot903 \times 10^{-3} + \left[\frac{0\cdot242 - 0\cdot0231 \log (c_{pl})}{M^{\frac{1}{2}}}\right] \qquad \text{(A)}$$

and

$$1/T = 2\cdot880 \times 10^{-3} + \left[\frac{0\cdot259 - 0\cdot0240 \log (c_{pl})}{M^{\frac{1}{2}}}\right] \qquad \text{(B)}$$

where T is in °K. Figure 7 shows the calibration curves, where the mol. wt.–temperature relationships are plotted for several values of log (c_{pl}) for each of the Eqns. (A) and (B).

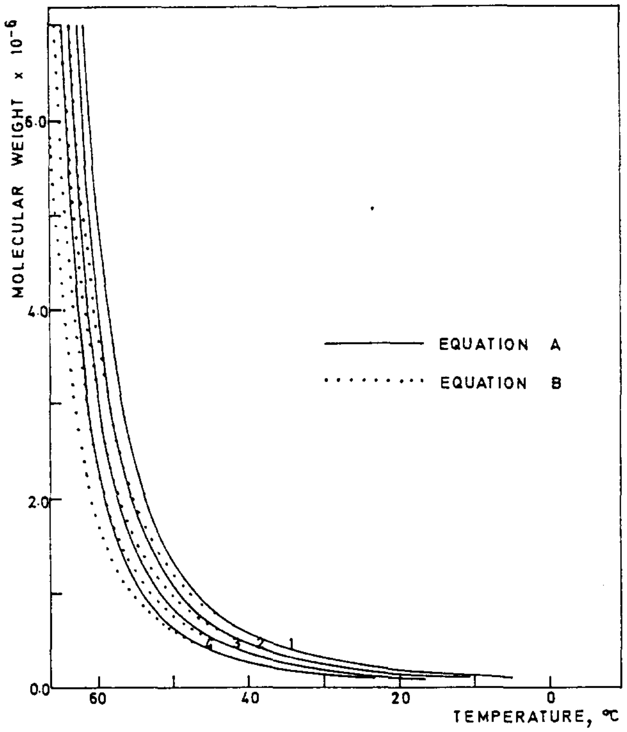

FIG. 7. Molecular weight–temperature calibration curves [$\log_{10} (c_{pl})$ calibration]. Each curve was constructed from Eqn. (A) or (B) using the value of $\log_{10} (c_{pl})$ indicated.

Before considering the mol. wt. distributions obtained for unfractionated samples, an estimation was made of the ability of the calibration curves A and B to yield the correct mol. wts. Thus, the results obtained by cooling a solution containing four anionic polymers (Fig. 5) were evaluated using calibration curves A and B. Since these calibration curves were only applicable for a species which was 50 per cent precipitated,(16, 17) the mol. wt. of each anionic polymer was determined at this point only. The improvement obtained using this calibration is illustrated in Fig. 6: the mol. wt. found for the lowest mol. wt. polymer A5 corresponded to its true value.

For very high mol. wt. material (polymer A1) it was apparent that calibration B gave the more accurate results. However, since calibration A gave a more accurate estimate of the mol. wt. of polymer A2 ($\bar{M}_v = 842{,}000$), the mol. wt. distributions presented below were evaluated, for each sample run, using both sets of calibration curves, A and B. The two cumulative distribution curves thus obtained from a single precipitation, performed using an unfractionated polymer sample, represent the limits of the experimental error involved in the calibration procedure. The true distribution would be expected to lie between these curves.

Figures 8 and 9 and Tables 4 and 5 give the cumulative distribution curves and the average mol. wts. evaluated for polymers S1 and S2 using these two sets of calibration curves, A and B (Fig. 7).

Comparison of these results with those evaluated using the calibration based upon log (Δc_{pl}) shows that the calibration used here, which is based upon log (c_{pl}), yields

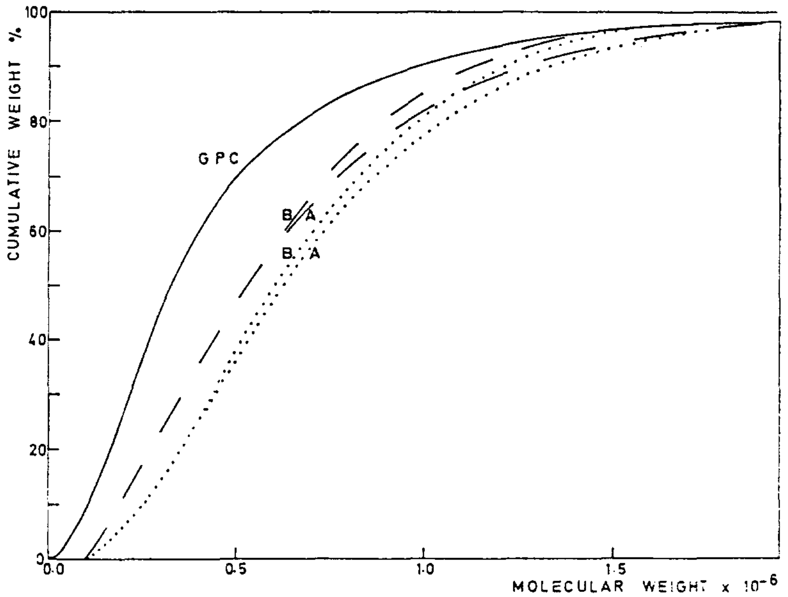

FIG. 8. Cumulative mol. wt. distribution curves for unfractionated polystyrene S1 [log (c_{pt}) calibration]. Dashed curves: run S1.1, c = 0·48 mg/100 ml. Dotted curves: run S1.2, c = 0·24 mg/100 ml. The curves were constructed using the calibration curves A and B, as indicated.

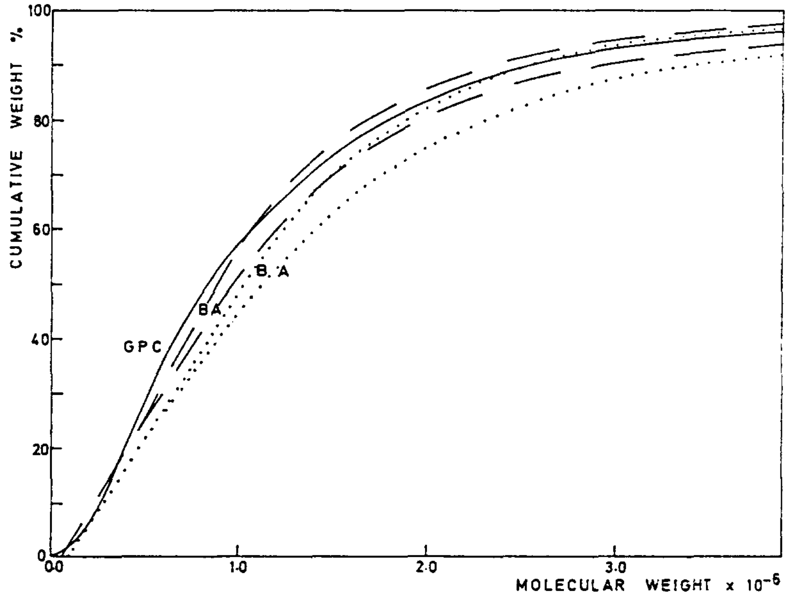

FIG. 9. Cumulative mol. wt. distribution curves for unfractionated polystyrene S2 [log (c_{pt}) calibration]. Dashed curves: run S2.1, c = 0·97 mg/100 ml. Dotted curves: run S2.2, c = 0·49 mg/100 ml. The curves were constructed using the calibration curves A and B, as indicated.

TABLE 4. AVERAGE MOL. WTS. FOR S1 [LOG (c_{pl}) CALIBRATION]

Source		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Run S1.1: $c = 0{\cdot}48$ mg/100 ml	A	3·9	6·3	1·6
	B	3·9	6·0	1·5
Run S1.2: $c = 0{\cdot}24$ mg/100 ml	A	4·8	7·2	1·5
	B	4·7	6·7	1·4
GPC		1·97	4·42	2·24

TABLE 5. AVERAGE MOL. WTS. FOR S2 [LOG (c_{pl}) CALIBRATION]

Source		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Run S2.1: $c = 0{\cdot}97$ mg/100 ml	A	4·9	13·4	2·7
	B	4·9	11·1	2·3
Run S2.2: $c = 0{\cdot}49$ mg/100 ml	A	6·3	14·9	2·4
	B	6·2	12·3	2·0
GPC		5·42	11·82	2·18

considerably lower values for the average mol. wts. For example, for sample S2, run at $c = 0{\cdot}97$ mg/100 ml, the value of $\bar{M}_n$ is reduced from 720,000 to 490,000. The greater ability of the present calibration to estimate the lower mol. wt. species may also be seen by comparison of the cumulative distribution curves obtained for polymer S2 (Figs. 3 and 9).

Each of the distribution curves, obtained from phase separation measurements, which are shown in Figs. 8 and 9, has a finite intercept on the mol. wt. axis, corresponding to mol. wts. between 70,000 and 100,000. These diagrams demonstrate that the polymer samples were not completely precipitated at 10°C. The calibration curves, Fig. 7, confirm that a lower temperature was required for the more complete precipitation of these samples under the conditions of concentration employed here. The underestimation of polymer species having mol. wts. less than about 100,000 had, of course, a greater effect on the cumulative curves obtained for the lower mol. wt. polymer S1 than on those found for S2.

The effect of solution concentration on the resulting cumulative distribution curve, which is discussed above, may be seen in Figs. 8 and 9. These figures show that runs performed at higher solution concentrations yield cumulative distributions indicating greater proportions of low mol. wt. material. This evidence also indicates incomplete precipitation of the polymer samples at 10°C.

The two phase separation experiments performed using the higher mol. wt. unfractionated polymer ($\bar{M}_v = 900{,}000$) led to mol. wt. distributions (Fig. 9) and to values for the mol. wt. averages (Table 5), which are in good agreement with the results obtained from GPC measurements. Of these two runs, the one performed using the higher initial solution concentration (S2.1, $c = 0{\cdot}97$ mg/100 ml) gave results which were closer to the GPC results. It is believed that, compared with run S2.2 ($c = 0{\cdot}49$ mg/100 ml), a smaller proportion of material remained in solution at the end of this run (S2.1).

CONCLUSIONS

The importance of using the correct calibration procedure is illustrated by the results presented in this paper. Low mol. wt. material was underestimated when the conventional method, which relates the precipitation temperature of a species to the mol. wt. and the solution concentration of that species, was adopted. Experimental and theoretical evidence was used to predict that the amount of polymer in the gel phase, rather than the solution concentration of the precipitating species, determines the precipitation temperature. The validity of a calibration, based upon this prediction, was confirmed by the results. Thus, the mol. wt. distribution of the unfractionated polymer S2 ($\bar{M}_v = 900{,}000$) has been found to follow closely the distribution obtained from GPC measurements.

However, there are limitations to this phase separation method. Over the range of concentration used in this work for the polystyrene–methylcyclohexane system, it is believed that polymer is incompletely precipitated from solution at the lowest temperature attained here, i.e. 10°C. This was indicated by the underestimation of low mol. wt. material present in the unfractionated polymer S1 ($\bar{M}_v = 350{,}000$). Also, incomplete precipitation of polymer may well have caused the observed dependence of the cumulative distribution curves, obtained from a precipitation run using an unfractionated polymer, on the initial solution concentration of polymer used in that run. Therefore, the technique employed in this work cannot give an accurate estimation of the mol. wt. distribution of a polystyrene sample which contains a significant proportion of material having mol. wts. below 100,000.

There is also an upper limit of mol. wt., since a polystyrene of higher average mol. wt. than polymer S2 ($\bar{M}_v = 900{,}000$) would give higher intensities of scattering from the initial solution of this polymer than the intensities found from a solution of polymer S2. The change in the background scattering from solution to pure solvent during the course of the precipitation would then be greater, thus increasing this source of error in the resulting mol. wt. distribution curve. Also, for higher mol. wt. species, the resolution obtained between species of similar mol. wt. was less than the resolution between lower mol. wt. species. This is inherent in the form of the solubility equation.

It has been demonstrated elsewhere(16) from the angular distribution of scattering, measured at 2° intervals between 44° and 136°, that the spheres, which constitute the precipitated phase, were heterogeneous with regard to size. In addition, from similar measurements, it was found that the form of the size distribution changed as the temperature of a two phase system was reduced. Also, the post-precipitation values of the relative concentration of the precipitated polymer, evaluated as c_{pt} from runs using anionic polymers, were found to increase with decreasing temperature. It was shown(16) that these post-precipitation increases in the relative concentration of precipitated polymer may well have been caused by the changing particle size distribution. This arises because changes in the form of the particle size distribution cannot be detected by a single dissymmetry measurement (the dissymmetry ratio $Z_{70/110}$ has been used throughout this work).

The authors conclude that the light scattering method, as applied here, may be used to give semi-quantitative estimates of mol. wt. distributions. A more rigorous study would include the determination of the particle size distribution at various stages during a precipitation run. However, this would greatly lengthen the analysis time of a polymer sample since both the experimental and the computational procedures would increase in complexity.

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