Molecular Weight Distributions from Turbidimetric Titration and Related Techniques: Theoretical Evidence for a New Calibration Procedure

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The phase separation of a solution of an unfractionated polymer has been considered theoretically using the Flory–Huggins theory of polymer solutions. Evidence is presented which indicates that a new procedure should be adopted for the evaluation of molecular weight distributions from the experimental results obtained from light scattering or turbidimetric studies of polymer solutions during continuous 'precipitation' processes.

TURBIDIMETRIC titration involves a continuous study of the decrease in transmitted light intensity of a beam during the fractional 'precipitation' of a polymer, brought about by the addition of non-solvent to the polymer solution[1–3]. Alternatively, phase separation may be achieved by the use of a single poor solvent (Θ-solvent[4]) with a continuous lowering of the solution temperature. In a related technique, the precipitation process is studied using a light scattering instrument: more accurate results may be obtained at low concentrations and, in addition, the angular variation of scattering indicates the average size of the particles during precipitation.

This paper refers directly to the use of a single Θ-solvent and the study of phase separation, brought about by cooling the polymer solution, using a light scattering instrument. However, the evidence presented here may also be applied to the related techniques outlined above.

At any stage during the precipitation of a polymer sample, the relative concentration of precipitated polymer, $\underline{c}_{\mathrm{pl}}$, may be found from the light scattering measurements[3,5,6]. The term $\underline{c}_{\mathrm{pl}}$ is directly proportional to the actual concentration of precipitated polymer, which is the weight of precipitated polymer per unit volume of solution. A precipitation curve may be constructed for this sample by plotting $\underline{c}_{\mathrm{pl}}$ versus temperature: it is then necessary to convert this precipitation curve into a molecular weight distribution curve. Since the temperature of precipitation of a polymer species has been shown to be a function of both the molecular weight and the concentration of the species[3,5-9], the investigation of unknown molecular weight distributions is only possible after an initial calibration relating these three variables.

The two calibration methods which have been described in the literature[1,10] are based on the common assumption that the precipitation of any given molecular weight species is not appreciably affected by species of higher or lower molecular weight which may be present in the system. Both of these methods relate the precipitation temperature T_x of a species x to the molecular weight M_x and the relative solution concentration $(\Delta\underline{c}_{\mathrm{pl}})_x$

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reference to the influence of precipitated polymer upon the precipitation of lower molecular weight species.

The effect of the precipitated polymer A4 on the phase separation of the lower molecular weight polymer A5 is demonstrated in *Figures 1* and *2*. From the solution containing equal concentrations of A4 and A5 (*Figure 1*) the 50% 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.

It may be concluded from the above results and from the results of similar experiments presented elsewhere[11] that, if higher molecular weight material is present, the precipitation temperature of lower molecular weight species is a function of the concentration of the precipitated material. This behaviour is in accordance with the experimental results obtained by Cornet[13], 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. Cornet confirmed these experimental results qualitatively by theoretical calculations. He obtained precipitation curves for two solutions containing individual monodisperse polymer fractions and for a solution of a mixture of these two fractions by numerical computations using equations derived from the Flory–Huggins theory of polymer solutions[14,15]. Since satisfactory results were obtained by Cornet using the Flory–Huggins theory, this theory is used here to show how precipitation curves may be interpreted.

THEORY

It has been shown in the preceding section that the precipitation temperature of a polymer species is dependent on the concentration of higher molecular weight species which may be present in the gel phase. As indicated in the introduction, neither of the conventional methods[1,10] which are used for the evaluation of molecular weight distributions from experimental precipitation curves allow for this phenomenon. An approximate solubility equation is therefore derived in this section from theoretical considerations so that a more accurate calibration procedure may be established.

The first step in the derivation of the relevant expressions is to state, in terms of the chemical potentials μ, the conditions for equilibrium between two phases in a polymer–solvent system. For a polymer which is heterogeneous with regard to molecular weight, these conditions are

$$\mu_1 = \mu_1' \text{ (for the solvent)} \tag{1}$$

$$\mu_x = \mu_x' \text{ (for each polymer species, } x) \tag{2}$$

where x is the ratio of the molar volumes of the polymer and solvent and the prime is the designation for the more concentrated phase ('precipitated' or gel phase).

of that species. The term $(\Delta \underline{c}_{\mathrm{p1}})_x$ is directly proportional to the solution concentration of species x and may be determined from the precipitation curves of the narrow distribution polymer calibrants[11].

Experiments, designed to test the validity of the above assumption, have been performed in this work. In these experiments a study was made of the phase separation from solution of mixtures of narrow distribution anionic polystyrenes ($\overline{M}_w/\overline{M}_n \leqslant 1{\cdot}06$)* using methylcyclohexane as solvent. Methylcyclohexane has a Θ-temperature for polystyrene of 70·5°C[12]. The results obtained from one of these experiments are described below.

Precipitation runs were performed on two solutions containing mixtures of anionic polystyrenes A4 ($\overline{M}_v = 411\,000$) and A5 ($\overline{M}_v = 160\,000$). The first solution, which contained equal concentrations of A4 and A5 (0·24 mg of each polymer per 100 ml of methylcyclohexane), gave the precipitation curve shown in *Figure 1*. *Figure 2* was obtained using the second solution, which contained the same concentration of A5 and a three-fold increase in the concentration of A4.

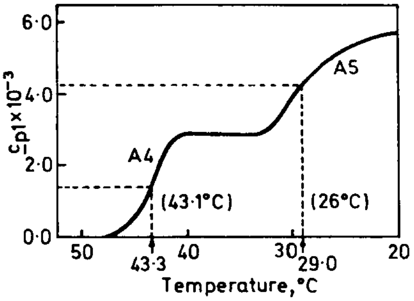

Figure 1—Relative concentration of precipitated polymer, $\underline{c}_{\mathrm{p1}}$, as a function of temperature for a solution containing equal concentrations of narrow distribution anionic polystyrenes A4 and A5, i.e. 0·24 mg of each polymer per 100 ml of methylcyclohexane. The temperatures given in brackets are those found to correspond to the 50% precipitation points of solutions containing the same concentrations of the individual polymers

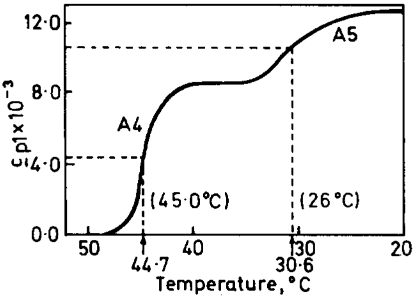

Figure 2—Relative concentration of precipitated polymer, $\underline{c}_{\mathrm{p1}}$, as a function of temperature for a solution containing 0·72 mg of polystyrene A4 and 0·24 mg of polystyrene A5 per 100 ml of methylcyclohexane. The temperatures given in brackets are those found to correspond to the 50% precipitation points of solutions containing the same concentrations of the individual polymers.

The temperatures obtained from the curves in *Figures 1* and *2*, corresponding to the 50% precipitation point of the higher molecular weight polymer A4, were found to be within 0·3 deg C of the temperatures (shown in brackets in the *Figures*) at which precipitation occurred from solutions containing the same concentrations (0·24 and 0·72 mg/100 ml respectively) of polymer A4 only. Thus, the precipitation characteristics of a species are not influenced by the presence of lower molecular weight material in the solution. Klein and Patat[9] also reached the same conclusion but made no

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Expressions for the chemical potentials of polymer species x in both the sol and gel phases, i.e. μ_x and μ_x' respectively, may be derived using the Flory–Huggins theory of polymer solutions[4] and then substituted into equation (2). Suitable rearrangement of the equation thus produced yields the polymer–solvent interaction parameter χ_1[16]:

$$\chi_1 = \frac{v_2'(1-1/\bar{x}_n') - v_2(1-1/\bar{x}_n) + [\ln (v_x'/v_x)]/x}{2(v_2'-v_2) - [(v_2')^2 - (v_2)^2]} \tag{3}$$

In equation (3) v_2 is the volume fraction of polymer in the sol phase, v_x is the volume fraction of polymer species x in the sol phase and $\bar{x}_n$ is the number average value of x in the sol phase. Primed symbols denote the corresponding values in the gel phase.

The interaction parameter χ_1 is related to the temperature T by the equation

$$-\psi_1(1-\Theta/\mathrm{T}) = \chi_1 - 1/2 \tag{4}$$

where Θ is the Θ-temperature of the polymer–solvent system and ψ_1 is the entropy of dilution parameter[4].

It is instructive to consider the relative sizes of the terms contained in equation (3). For typical experimental conditions used in this work we find:

$$v_2' = 0{\cdot}4$$

$$v_2 = 0{\cdot}4 \times 10^{-5}$$

$$(v_x'/v_x) = 10^5$$

where x, $\bar{x}_n$ and $\bar{x}_n'$ are approximately 3×10^3. If these numerical values are substituted into equation (3), it may be seen that several terms have a value less than $0{\cdot}2 \times 10^{-3}$ and hence may be omitted. Neglecting these terms we find

$$\chi_1 \simeq \frac{v_2' + [\ln(v_x'/v_x)]/x}{2v_2' - (v_2')^2} \tag{5}$$

It should be noted that, during the precipitation of a species x, the value of $[\ln (v_x'/v_x)]/x$ changes to an extent which is far greater than the terms that have been omitted.

A polymer sample having a continuous molecular weight distribution is now considered in which c_x^0 is the initial solution concentration of species x, and the density of polymer is ρ_2. At any temperature during the precipitation process, it may be assumed that there is some species x which is 50% precipitated. Then

$$v_x = c_x^0/2\rho_2$$

$$\text{and } v_x' = v_2' \times \frac{\text{(volume of species } x \text{ in the gel phase)}}{\text{(total volume of polymer in gel phase)}} \tag{6}$$

$$= v_2' \times \frac{c_x^0 V/2\rho_2}{\text{(total concentration of precipitated polymer) } V/\rho_2}$$

where V is the volume of the solution and the total concentration of precipitated polymer is the weight of precipitated polymer per unit volume of solution. Thus

$$v_x' = v_2' \times c_x^0/2 \times L/\underline{c}_{\mathrm{p1}} \tag{7}$$

where $\underline{c}_{\mathrm{p1}}$ is the relative total concentration of precipitated polymer and L is a constant, given by $\underline{c}_{\mathrm{p1}}$/(total concentration of precipitated polymer). Dividing equation (7) by equation (6) we find

$$v_x'/v_x = Lv_2'\rho_2/\underline{c}_{\mathrm{p1}} \tag{8}$$

Equation (8) may now be substituted into the approximate expression (5), which, combining with equation (4), yields

$$\tfrac{1}{2} + \psi_1(\Theta/T - 1) \simeq \frac{v_2' + (1/x)\ln(L\,v_2'/\rho_2) - (1/x)\ln(\underline{c}_{\mathrm{p1}})}{2v_2' - (v_2')^2} \tag{9}$$

It should be remembered that, apart from the assumptions made above, this relationship is only approximate because of the imperfections of the Flory–Huggins theory which was used to obtain the expressions for μ_x and μ_x'[4].

For precipitations performed using solutions of polystyrenes in methylcyclohexane having initial concentrations within the range used in this work (i.e. 0·07 to 1·50 mg/100 ml), the volume fraction of polymer in the gel phase, v_2', has been found experimentally to be a function of temperature only[17]. Thus, it may be seen that equation (9) predicts that the precipitation temperature of a species should be related to the molecular weight of that species and to the value of log ($\underline{c}_{\mathrm{p1}}$), not to the value of log ($\Delta\underline{c}_{\mathrm{p1}}$) as previously used[1,10]. That is, the temperature at which a species precipitates is determined by the concentration of the precipitated polymer (i.e. the weight of precipitated polymer per unit volume of solution) rather than by the solution concentration of the precipitating species, and by the molecular weight of that species.

CONCLUSIONS

The theoretical evidence presented above indicates that a new procedure should be adopted for the evaluation of molecular weight distributions from the precipitation curves obtained from light scattering or turbidimetric studies of polymer solutions during phase separation. This evidence shows that the precipitation temperature of a species is governed by the molecular weight of that species and by the concentration of the precipitated polymer, which is the weight of precipitated polymer per unit volume of solution. Thus, in order to convert a precipitation curve into a molecular weight distribution curve, a calibration should be established which relates these three variables.

These conclusions are in accordance with the results of experiments, described in the introduction, which were performed using solutions containing mixtures of anionic polystyrenes. Molecular weight distribution curves, obtained using the proposed calibration procedure, are presented and discussed elsewhere[11]. These experimental results provide further support for the above conclusions.

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