

Molecular Weight Dependence of Precipitation Threshold

Early work on the solubility and fractionation of high polymers by solvent-nonsolvent systems usually involved separation of the polymers according to molecular weight. The earliest work was that of Schulz,¹ who made an attempt to treat the problem of solubility and fractionation from a thermodynamic standpoint. This was followed by Flory,²⁻⁴ Huggins,^{5,6} and Scott.⁷ Later, Morey and Tamblin^{8,9} showed how this could be incorporated with turbidimetric titrations to determine molecular weight distributions. It is the purpose of this paper to describe some experimental studies on the turbidimetric titration of polystyrene fractions of different molecular weight.

The relationship between the concentrations of the polymer of size m in the two phases is given by the well-known basic equation of fractionation theory:⁷

$$\phi_i'/\phi_i = \exp\{Am_i\} \quad (1)$$

where

$$A = 2\chi(\phi_0 - \phi_0') - \ln(\phi_0/\phi_0') \quad (2)$$

with the prime representing the polymer phase, ϕ_0 and ϕ_i representing the volume fractions of solvent mixture and polymer of size m_i , and χ representing the polymer-solvent interaction parameter given by

$$\chi = \chi_{12} + \psi_2(\chi_{23} - \chi_{13} - \chi_{12}) + \chi_{12}\psi_2^2 \quad (3)$$

where

$$\psi_2 = \phi_2/(\phi_1 + \phi_2) \quad (4)$$

$$\chi_{12} = V_0(\delta_1 - \delta_2)^2/RT \quad (5)$$

$$\chi_{i3} = 0.34 + V_0(\delta_i - \delta_3)^2/RT \quad i = 1, 2 \quad (6)$$

$$V_0 = V_1V_2/(\psi_1V_2 + \psi_2V_1) \quad (7)$$

with the subscripts 1, 2, and 3 representing the solvent, nonsolvent, and polymer, respectively, V representing the molar volume, and δ representing the solubility parameter.

The above equations are based on the single-liquid model proposed by Scott.⁷ Equation (3) shows that the polymer-solvent interaction parameter χ is approximately a linear function of ψ_2 at low nonsolvent concentrations ψ_2 . When a polymer dissolved in a solvent is titrated with a borderline nonsolvent whose δ value is about 2 units away from that of polymer (single-liquid model), the nonsolvent concentration ψ_2 is fairly large,^{10,11} and hence, the interaction parameter χ is not linearly related to ψ_2 .

On the other hand, when a polymer dissolved in a solvent is titrated with a strong nonsolvent ("cluster" model)¹⁰⁻¹³ as is the case in most practical industrial applications, the interaction parameter χ is approximately a linear function of ψ_2^2 . In this case, eq. (6) reduces to

$$\chi_{i3} = 0.34 + [V_0(\delta_i - \delta_1)^2/RT] \quad (8)$$

and eq. (3) reduces to

$$\chi \cong 0.34 + \chi_{12}\psi_2^2 \quad (9)$$

Equations (1) and (2) show that for a given solubility of sufficiently large molecular weight material, $\phi_0 \approx 1$, the second term in eq. (2) becomes very small, and $m_i \propto 1/A \propto 1/\chi \propto 1/\psi_2^2$ or $\psi \propto 1/M^{0.5}$. This indicates that the relative volume fraction of

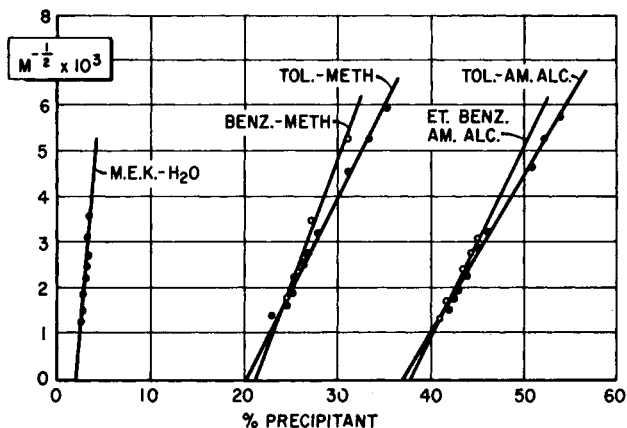


Fig. 1. Turbidimetric titration of polystyrene solutions (0.1 g/100 ml) at 25°C. Data of A. F. Roche.

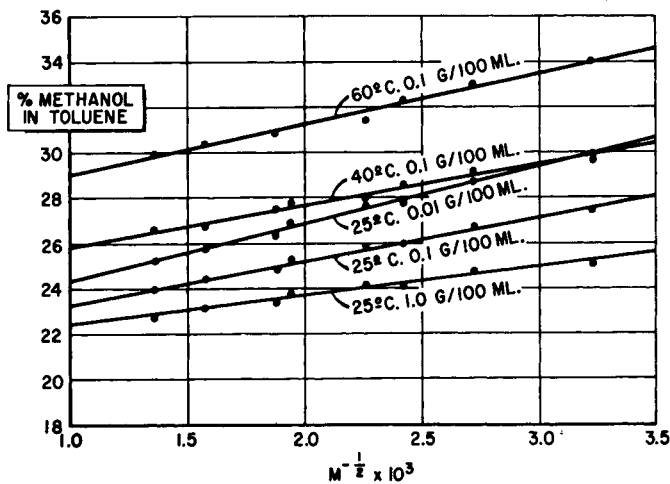


Fig. 2. Turbidimetric titration of polystyrene-toluene with methanol. Data of A. F. Roche.

nonsolvent ψ_2 at the precipitation threshold is linearly related to the square root of molecular weight of the polymer rather than to the first power of the polymer molecular weight, as proposed by Schulz.¹ Figures 1 and 2 illustrate the dependence of the volume per cent of precipitant at the precipitation threshold on molecular weight of the polystyrene fractions at different temperatures and concentrations.

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