Turbidimetric Determinations of Theta Compositions

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Synopsis

The turbidimetric titration method of determining theta conditions developed by Elias and modified by Cornet and van Ballegooijen has been extended and generalized for different types of polymer–solvent–nonsolvent systems. The modified procedures for the determination of theta compositions have been verified with the following systems: polystyrene–cyclohexane–n-hexane, polystyrene–cyclohexane–n-butanol, and polystyrene–toluene–nonsolvent.

Introduction

The theta compositions of mixed solvents for a polymer can be determined from the turbidimetric titration of a dilute polymer solution with a nonsolvent at constant temperature. This rapid method was introduced in 1959 by Elias and Gruber[1-5] and recently was modified by Cornet and van Ballegooijen.[6] It is the purpose of this paper to present more general procedures for determining theta compositions of different types of solvent–nonsolvent mixture.

Theoretical

A knowledge of the relationship between the polymer–solvent interaction parameter χ, volume fraction ϕ_3 of the polymer, and volume fraction ψ_2 of the nonsolvent added at the cloud point, is necessary for turbidimetric determinations of theta compositions. Cornet and van Ballegooijen have shown that a plot of χ versus $\log \phi_3$ gives approximately a straight line between $\phi_3 = 10^{-2}$ and $\phi_3 = 10^{-5}$ and that the curve can be extrapolated to $\chi = 0.5$ at $\phi_3 = 1$, which corresponds to the theta condition, i.e., theta temperature or theta composition.[6,7] The relationship between the polymer–solvent interaction parameter and the volume fraction of nonsolvent added at the cloud point is given by

$$\chi_{30} = \chi_{13} + \psi_2(\chi_{23} - \chi_{13} - \chi_{12}) + \chi_{12}\psi_2^2 \tag{1}$$

where

$$\psi_2 = \phi_2/(\phi_1 + \phi_2) \tag{2}$$

$$\chi_{12} = V_0(\delta_1 - \delta_2)^2/RT \qquad (3)$$

$$\chi_{i3} = 0.34 + \frac{V_0(\delta_i - \delta_3)^2}{RT}, \qquad i = 1, 2 \qquad (4)$$

$$V_0 = V_1V_2/(\psi_1V_2 + \psi_2V_1) \qquad (5)$$

and the subscripts 1, 2, 3, and 0 represent solvent, nonsolvent, polymer, and mixed solvent, respectively, δ represents the solubility parameter, and V represents the molar volume. These equations are based on the "single liquid" model proposed by Scott.[8] For the solvent–nonsolvent mixture that can be described by the "cluster" model[9,10] eq. (4) reduces to

$$\chi_{13} \approx 0.34 + V_0(\delta_i - \delta_1)^2/RT \qquad (6)$$

and eq. (1) becomes

$$\chi_{30} \approx 0.34 + \chi_{12}\psi_2^2 \qquad (7)$$

Discussion

Equation (1) shows that the Flory-Huggins interaction parameter χ_{30} is approximately a linear function of ψ_2 over a small range of nonsolvent concentration ψ_2. This would be the case when a polymer dissolved in a poor solvent were titrated with a nonsolvent and the solubility parameters of both solvent and nonsolvent were either higher or lower than that of the polymer. For example, the systems; polystyrene–cyclohexane–nonsol-
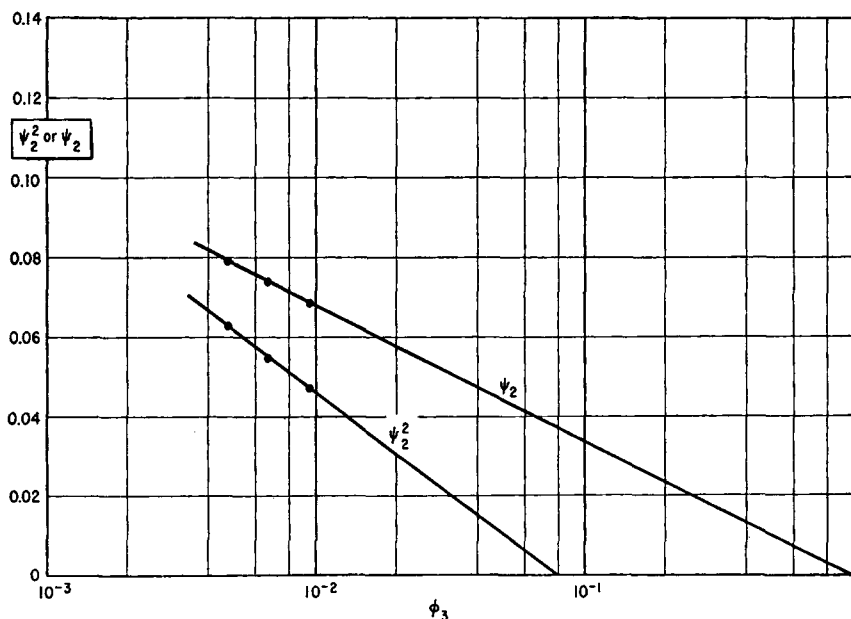

Fig. 1. Turbidimetric titration of PS–cyclohexane with n-hexane at the theta temperature of the PS–cyclohexane mixture (34°C.).
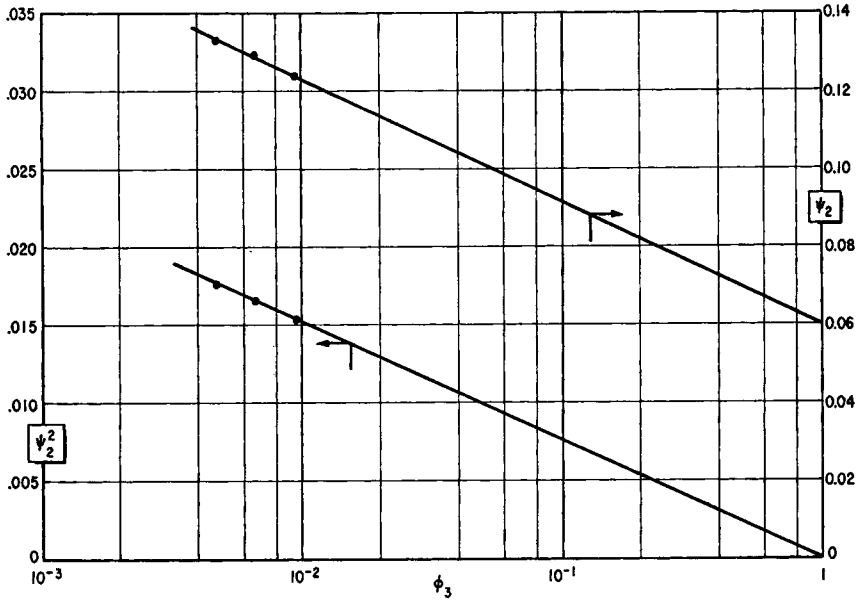
Fig. 2. Turbidimetric titration of PS–cyclohexane with n-butanol at the theta temperature of the PS–cyclohexane mixture (34°C.).
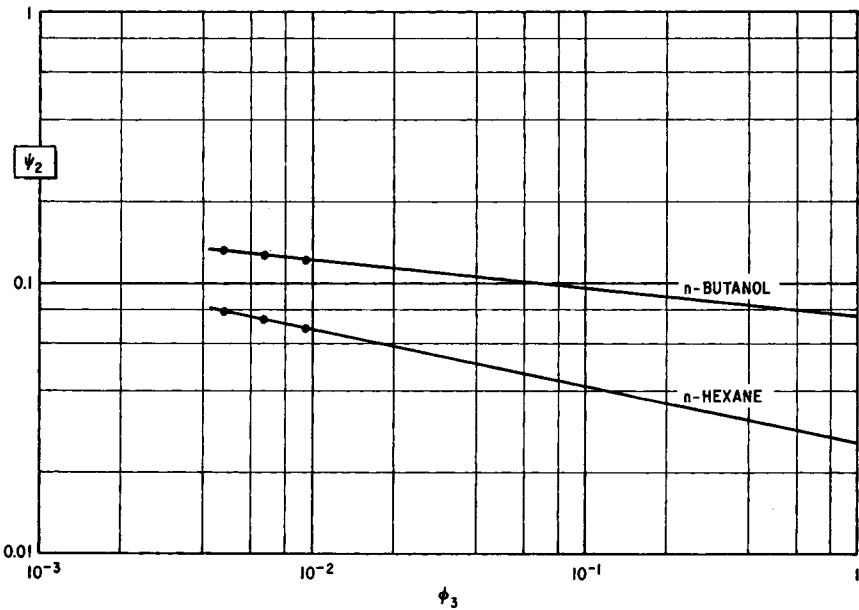

Fig. 3. Turbidimetric titration of PS–cyclohexane with n-hexane and with n-butanol at the theta temperature of the PS–cyclohexane mixture (34°C.) (extrapolation according to Elias gives an erroneous theta composition).

vent with lower δ value and polyisoprene–methyl isobutyl ketone–nonsolvent with higher δ value give a linear relationship between χ_{30} and ψ_2 over a small range of ψ_2. In this case ψ_2 is plotted against $\log \phi_3$, and a straight line is extrapolated to $\log \phi_3 = 0$, as suggested by Cornet and van Ballegooijen.[6]

On the other hand, when a polymer dissolved in a good solvent ($\delta_1 \approx \delta_3$) is titrated with a nonsolvent, eq. (1) reduces to eq. (7) and, hence, the interaction parameter χ_{30} is approximately a linear function of ψ_2^2. This indicates that the systems consisting of a poor solvent with lower δ and a nonsolvent with higher δ and of a poor solvent with higher δ and a nonsolvent with lower δ give approximately a linear relationship between χ_{30} and ψ_2^2 beyond $\chi_{30} = 0.5$. In this case ψ_2^2 is plotted against $\log \phi_3$, and a straight line is extrapolated to pure polymer, to give the theta composition.

Figures 1–3 illustrate the difference between these two types of solvent–nonsolvent system. For the PS–cyclohexane–n-hexane system ($\Theta = 34°$C.) the turbidimetric titration data must be plotted, not according to Elias' method ($\log \psi_2$ versus $\log \phi_3$), but according to the method described by Cornet and van Ballegooijen (ψ_2 versus $\log \phi_3$); see Figure 1. For the PS–cyclohexane–n-butanol system the titration data must be plotted according to our method, described above, namely ψ_2^2 versus $\log \phi_3$; see Figure 2. When turbidimetric titrations are made at temperatures far from the theta temperature, the three extrapolation methods give identical results, as is shown in Table I. These values are in agreement with the reported values.[11]

TABLE I

Determination of Theta Compositions for Polystyrene–Toluene–Nonsolvent Systems[a] at 25°C.

Nonsolvent	Theta composition ψ_2 of nonsolvent		
	$\log \psi_2$ vs. $\log \phi_3$	ψ_2 vs. $\log \phi_3$	ψ_2^2 vs. $\log \phi_3$
Methanol	0.200	0.204	0.200
n-Butanol	0.330	0.330	0.330
n-Hexane	0.503	0.505	0.503

[a] A thermally polymerized polystyrene of 350,000 weight-average molecular weight was used in this experiment.

In conclusion, the turbidimetric titration method of determining theta conditions, developed by Elias and recently modified by Cornet and van Ballegooijen, has been generalized for different types of polymer–solvent–nonsolvent system. The relative volume fraction ψ_2 of nonsolvent is linearly related to the logarithm of the volume fraction of the polymer in a dilute polymer solution at the precipitation threshold. This linear relationship can be extrapolated to the pure polymer to give the theta compositions for the following systems: (*1*) polymer, poor solvent with lower δ

value, and nonsolvent with lower δ value, and (*2*) polymer, poor solvent with higher δ value, and nonsolvent with higher δ value.

The square of the relative volume fraction ψ_2 of nonsolvent is linearly related to the logarithm of the volume fraction of the polymer in a dilute polymer solution at the precipitation threshold. This linear relationship can be extrapolated to the pure polymer to give the theta composition for the following systems: (*1*) polymer, good solvent, nonsolvent, (*2*) polymer, poor solvent with lower δ value, nonsolvent with higher δ value, (*3*) polymer, poor solvent with higher δ value, nonsolvent with lower δ value, and (*4*) polymer, solvent, very effective nonsolvent (cluster model).

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