

Coexistence Curve of a Star-Shaped Polymer Solution. Comparison with the Hybrid Theory

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In a dilute polymer solution, polymer segments are not uniformly distributed in space because they are connected with chemical bonds. Such non-uniform distribution of local polymer segment density is of essential importance to thermodynamic properties of a dilute solution, while in a concentrated solution connectivity of segments reduces its influence on thermodynamic properties and the mean-field approximation is applicable to theoretical treatment of the solution. Phase equilibrium of a binary polymer solution is a phenomenon extending over these two concentration regimes and consequently the mean-field type theory such as the Flory–Huggins theory fails in quantitative description of phase diagram of a binary polymer solution. On the other hand, theories of dilute polymer solutions such as the virial expansions deteriorate their validity with increasing polymer concentration and cannot afford to give a phase diagram. To evade this difficulty, Koningsveld *et al.*¹ proposed a theory in which the Flory–Huggins theory and the dilute polymer solution theory are combined so that the Flory–Huggins free energy crosses over to the free energy given by the virial expansion as concentration is decreased. Their theory, referred as the hybrid theory, was applied to linear polymer solutions and gave a good agreement with experimental results.

Recent experimental studies on phase diagrams of star-shaped polymer solutions revealed that phase diagram of a star-shaped polymer solution differs from that of the homologous linear polymer of the same molecular weight.^{2–4} Such solubility difference caused by molecular architecture cannot be explained either by the Flory–Huggins theory. However, it is expected that the hybrid theory reproduces the observed difference of phase diagrams of these polymer solutions, if the difference in free energy of dilute phase is a principal origin of the difference in phase diagram. Since explicit expressions of the second virial coefficients of star-shaped polymer solutions have been given by the perturbation theories, extension of the hybrid theory to star-shaped polymer solutions is straightforward.

In this note, we calculated phase diagram of a binary star-shaped polymer solution based on the hybrid theory

and compared with experimental results in order to examine validity of the hybrid theory.

RESULTS AND DISCUSSION

A binary polymer solution at temperature T and polymer volume fraction ϕ_2 is considered. The solution consists of a solvent and an f -arm star-shaped polymer of the total segment number N . According to the hybrid theory¹ chemical potentials of solvent $\Delta\mu_1$ and polymer $\Delta\mu_2$ are given by

$$\Delta\mu_1/kT = \log \phi_1 + (1 - 1/N)\phi_2 + \xi_1\phi_2^2 \quad (1)$$

$$\Delta\mu_2/kNT = (1/N)\log \phi_2 + (1 - 1/N)\phi_1 + \xi_2\phi_1^2 \quad (2)$$

respectively, where $\phi_1 = 1 - \phi_2$, k is the Boltzmann constant and

$$\xi_1 = \alpha + \beta(1 - \gamma)(1 - \gamma\phi_2)^{-2} + (1/2 - \chi_1)[1 - h(z)] \times (1 + \lambda)^{-1}(1 + \lambda\phi_1) \exp(-\lambda\phi_2) \quad (3)$$

$$\xi_2 = \alpha + \beta(1 - \gamma\phi_2)^{-2} + (1/2 - \chi_1)[1 - h(z)] \times (1 + \lambda)^{-1}(1 - \lambda\phi_2) \exp(-\lambda\phi_2) \quad (4)$$

In eq 3 and 4, α , β , γ are coefficients of temperature and concentration dependence of the interaction parameter χ in sufficiently concentrated solutions:

$$\chi = \alpha + \beta(1 - \gamma\phi_2)^{-1}, \quad \beta = \beta_0 + \beta_1 T^{-1} \quad (5)$$

and χ_1 is given with these coefficients by

$$\chi_1 = \alpha + (1 - \gamma)\beta \quad (6)$$

The coefficient λ is a parameter proportional to $N^{1/2}$ and is set to the inverse of the overlap concentration ϕ_2^* in this study as first proposed by Einaga *et al.*⁵

$$\lambda = 1/\phi_2^* \quad (7)$$

The function $h(z)$ of the excluded volume parameter z is related to the second virial coefficient A_2 as

$$A_2 V_1/v_2^2 = [(1/2) - \chi_1]h(z) \quad (8)$$

where V_1 the molar volume of the solvent and v_2 the specific volume of the polymer. For normal star-shaped polymer with f arms $h(z)$ was calculated to the first order of z by Casassa⁶:

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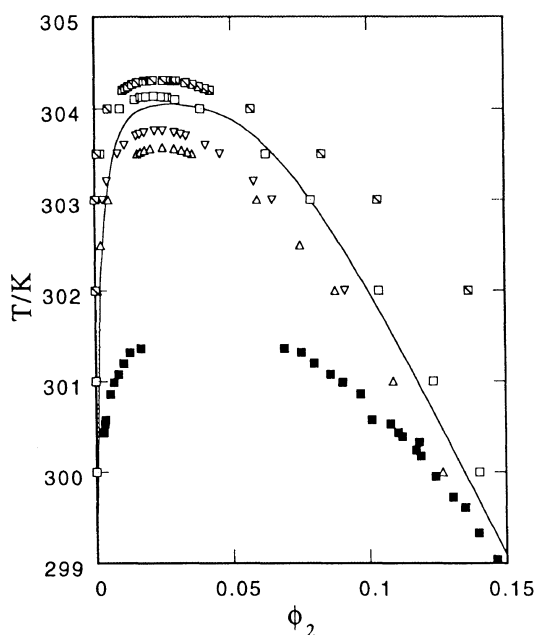


Figure 1. Theoretical and experimental coexistence curves of 11-arm star-shaped polystyrene/cyclohexane solution and linear polystyrene/cyclohexane solution. Molecular weight of polymers is 2.05×10^6 : Theoretical with ϕ_2^* defined by eq 10a (\square) star, (\triangle) linear; with ϕ_2^* defined by eq 10b (\blacksquare) star, (∇) linear; experimental (\blacksquare) star, (∇) linear.

$$h(z) = 1 - Cz + \dots,$$

$$C = \frac{32}{15f^{1/2}} [7 - 4 \cdot 2^{1/2} + (f-1)(17 \cdot 2^{1/2} - 9 \cdot 3^{1/2} - 8)] \quad (9)$$

Figure 1 shows experimental and theoretical coexistence curves of 11-arm ($f=11$) star-shaped polystyrene/cyclohexane and linear ($f=1$) polystyrene/cyclohexane solutions. Weight average molecular weight of star-shaped polystyrene was 2.05×10^6 and experimental curve for linear polystyrene of the same molecular weight was obtained by the interpolation of the experimental data by Nakata *et al.*⁷ The theoretical curves were calculated from eq 1–9: the parameters for polystyrene/cyclohexane solutions were evaluated to be^{1,8}

$$\alpha = -0.1597, \quad \beta_0 = 0.4987, \quad \beta_1 = 111.74 \text{ K}, \quad \gamma = 0.2365$$

$$V_1 = 108 \text{ cm}^3 \text{ mol}^{-1}, \quad v_2 = 0.925 \text{ cm}^3 \text{ g}^{-1}$$

$$z = 0.305(0.5 - \chi_1)N^{1/2}$$

The segment size l^3 was chosen equal to the solvent volume, which leads to $N = 1.76 \times 10^4$. The overlap concentration ϕ_2^* is conventionally defined by using the radius of gyration of a polymer chain R_g to be

$$\phi_2^* = \frac{Nl^3}{(4\pi/3)R_g^3} \quad (10a)$$

Experimental values of R_g of star-shaped³ and linear⁹ polystyrenes at the theta temperature were obtained to be $R_g = 23.9 \text{ nm}$ and 41.8 nm , respectively, and their temperature dependence was neglected.

In case of linear polystyrene (PS), good agreement between theoretical and experimental curves was obtained. However, in case of star-shaped PS, agreement was not good. The difference between experimental and

theoretical upper critical solution temperatures (UCST) T_c was roughly 2.5 K in star-shaped PS in contrast to 0.5 K in linear PS. A more serious problem is a discrepancy observed in the direction of a shift of phase diagram by branching of the component polymer. The theory predicted that the coexistence curve of star-shaped PS was located at higher temperatures than the curve of linear PS, being opposite to the experimental results.

It is known that there are several ways of defining the overlap concentration other than eq 10a. We calculated coexistence curves based on a different definition

$$\phi_2^* = \frac{Nl^3}{R_g^3} \quad (10b)$$

in order to know the influence of definition of ϕ_2^* or the dependence on the parameter λ . The results were shown in Figure 1. Though ϕ_2^* was increased about four times by the change of definition, the coexistence curve of linear PS scarcely changed over a wide concentration range, which confirmed the weak λ -dependence already reported by Koningsveld *et al.*¹ Coexistence curve of star-shaped PS was more sensitive to λ especially on the concentrated-phase side. However, the change of λ resulted in enlarging the two-phase region and deteriorated the agreement with the experimental result.

In the hybrid theory, χ parameters applicable to limited concentration ranges, namely dilute or concentrated solution, are linearly combined to express the interaction parameter for arbitrary concentration:

$$\chi = P\chi_{\text{dil}} + (1-P)\chi_{\text{conc}} \quad (11)$$

$$P = \exp(-\lambda\phi_2)$$

It seems more straightforward to combine chemical potentials and we attempted to calculate the critical temperature T_c based on this approach.

$$\Delta\mu_1 = P\Delta\mu_{1,\text{dil}} + (1-P)\Delta\mu_{1,\text{conc}} \quad (12)$$

where

$$\Delta\mu_{1,\text{dil}}/kT = -\phi_2/N - (1/2 - \chi_1)h(z)\phi_2^2$$

$$\Delta\mu_{1,\text{conc}}/kT = \log \phi_1 + (1 - 1/N)\phi_2 + \chi_1\phi_2^2$$

The critical temperatures of star-shaped PS ($f=11$) solution and of linear PS solution were evaluated to be 303.6 K and 300.9 K, respectively, and modification of the theory brought about no improvement.

As stated in the introductory section, phase equilibrium of a binary polymer solution is a phenomenon extending over dilute and semidilute (or concentrated) regimes. Hence, the difference of coexistence curves of a star-shaped polymer solution and a linear polymer solution is caused by a difference of chemical potential of the concentrated phase as well. Because of the higher segment density around the center of a star-shaped polymer, average number of intermolecular contacts in a semidilute solution is reduced near its center compared with the outer region, which leads to the difference in the mixing enthalpy from linear polymer solutions. We showed that such enthalpy effect actually resulted in an appreciable change of coexistence curve by carrying out a simple theoretical calculation.¹⁰ The theoretical

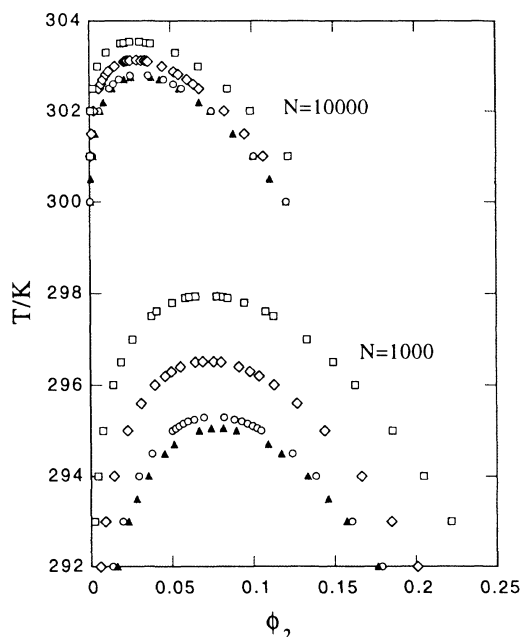


Figure 2. Coexistence curves, calculated by the hybrid theory, of cyclohexane solutions of star-shaped polystyrene with arm numbers $f=3$ (\circ), 6 (\diamond), and 11 (\square) and linear (\blacktriangle) polystyrene for segment numbers $N=1000$ and $N=10000$.

calculation correctly gave a result that the upper critical solution temperature (UCST) of 11-arm star-shaped PS/cyclohexane solution was lower than the UCST of linear PS/cyclohexane solution of the same molecular weight though it quantitatively overestimated the difference ΔT_c of these two critical temperatures (theoretical $\Delta T_c=8$ K, experimental $\Delta T_c=3$ K).¹⁰

However, this enthalpy effect in the semidilute regime is considered to appear only in the case of relatively large number of arms f , and contribution of the effect is expected to be negligibly small for a 3-arm star-shaped

polymer solution. Experimental results showed that even for $f=3$ the UCST is slightly lower than that of linear polymer solution.² This observed difference must consequently arise from the free-energy difference in the dilute phase. As shown in Figure 2, application of the hybrid theory to 3-arm star-shaped PS solutions gave results opposite to the experimental observations, and the present calculation (eq 1–10) could not correctly describe the contribution of free energy of the dilute phase. Since the basic idea of the hybrid theory, *i.e.*, connecting free energies of dilute and concentrated solutions with using a function that abruptly changes from unity to zero around the overlap concentration, seems reasonable, it is considered that the expression used for chemical potential of the dilute phase is not appropriate. Probably the higher virial terms should be taken into account.

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