ed to be inadequate when the contour length of any of the blocks is not sufficiently long in comparison with its Kuhn length. We are developing a theory, based on a more appropriate model, for the dynamics of such block copolymers in solution.

Acknowledgment. The author is grateful to the Academic Computing Center, the University of Wisconsin, Madison, for its making available the software described in ref 17 of the text.

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Notes

On the Narrow Miscibility Gap in Polymer 1–Polymer 2–Solvent Ternary Systems

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Received August 13, 1974

Koningsveld, *et al.*,[1] reported in 1970 on the very narrow one-phase temperature region between the lower and upper two-phase regions in the ternary mixture of isotactic polypropylene, polyethylene, and diphenyl ether. They suggested that this occurrence was caused by some effect from the tacticity of the polypropylene molecule, since this occurrence was not found in the atactic polypropylene system with similar components. Recently the author found quite a similar phenomenon in other ternary systems containing two polymers and one solvent: the polystyrene (PS)–polydimethylsiloxane (PDMS)–ethyl acetate system (Figure 1) and the PS–PDMS–methyl acetate system (Figure 2). As seen in the figures the narrow miscibility gap appears close to the cloud point curve of one of the corresponding binary polymer solvent systems. The fact that a similar phenomenon was observed in the three different ternary systems and not in the binary system suggests the existence of certain special features which are common in ternary (or multicomponent) systems. One of the noteworthy features common to these three systems is that the critical solution temperatures of the two binary polymer–solvent systems corresponding to each ternary system are close. On this basis, the PDMS–polyisobutene–phenetole system was also examined, since the Flory temperatures of the two corresponding binary systems lay within 83 to 86°,[2,3] and gave the results illustrated in Figure 3. Although this system did not show the narrow miscibility gap, it would appear that the cloud point curve suggests the interpenetration of the lower and upper cloud point curves.

A similar behavior of the spinodal curve on the temperature was found (Figure 4a) from the computer analysis of the Scott theory[4] on condition that the values of the interaction parameters between the solvent and the two polymers (χ_{01}, χ_{02}) are the same and decrease with increasing temperature, and that the polymer–polymer interaction parameter χ_{12}, which is very small, increases with increasing temperature (Figure 4b). The analysis under many different conditions was tried, but the very small value (around 0.02) and the positive temperature dependence of χ_{12} seem to be essential in order to obtain the narrow miscibility gap.[5]

The necessity of considering the positive temperature dependence of χ had been suggested already by Koningsveld, *et al.*,[1] and cases of positive temperature dependence of χ parameters have been found in many polymer–solvent or polymer–polymer binary systems, and are well interpreted by means of the concept of the free volume dissimilarity between the components.[6] Our particular binary mixture of styrene and dimethylsiloxane oligomers (both approximately hexamers) has, however, an "upper" critical solution temperature which we noticed to be above 35°. This indicates that the χ_{12} value of this system which is higher than 0.3 decreases with increasing temperature. This fact seems to indicate that, as solvent is added as a third component to a binary mixture of two polymers, the magnitude of χ_{12} decreases drastically and the temperature dependence is reversed from negative to positive.

At the lower polymer concentration, the polymer molecules form segment clouds around the center of gravity of the molecules. This behavior prevents the occurrence of intermolecular segment–segment contacts. The probability of making this contact must be reflected in the apparent value of the polymer–polymer interaction parameter χ_{12} in dilute ternary systems, and this apparent value must be far

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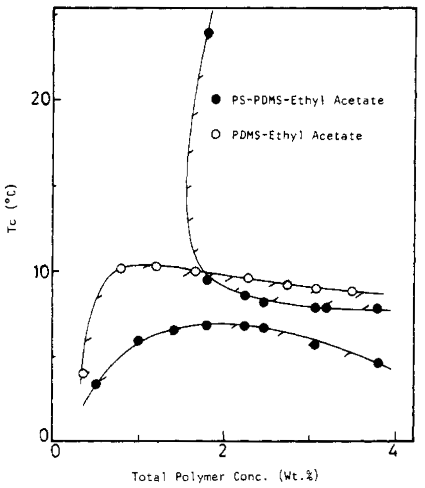

Figure 1. Experimental cloud-point curves for the PS–PDMS (1:1)–ethyl acetate ternary system (●) and the PDMS–ethyl acetate binary system (○): $\bar{M}_n$(PS) = 67 × 10^4, $\bar{M}_v$(PDMS) = 39 × 10^4.

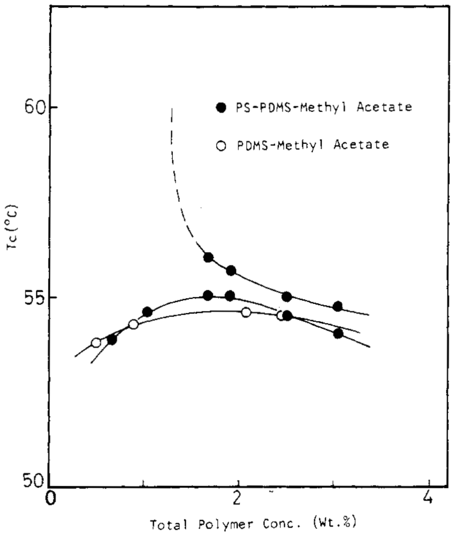

Figure 2. Experimental cloud-point curves for the PS–PDMS (1:1)–methyl acetate ternary system (●) and the PDMS–methyl acetate binary system (○): $\bar{M}_n$(PS) = 67 × 10^4, $\bar{M}_v$(PDMS) = 63 × 10^4.

smaller than the actual value in the polymer–polymer binary system. Since the total polymer concentration employed in our experiments is less than 10%, at which the chain conformation effect on the χ parameter is observable even in binary systems,[7] this effect might be playing a significant role in the behavior of χ_{12} parameter in our ternary systems.

At infinite dilution, the free energy of mixing for polymer 1–polymer 2–solvent ternary systems can be expressed in the form

$$\Delta F_{\mathrm{M}} = -kT\left[(N_1 + N_2)\ln V - \frac{1}{V}\{(N_1 - 1)N_1u_{11}/2 + N_1N_2u_{12} + (N_2 - 1)N_2u_{22}/2\} + \ldots\right] \quad (1)$$

where N_i's are the number of molecules of i components, V is the volume of the system, and u_{ij}'s are the excluded volume of polymer molecules between i and j components. It was of interest to evaluate the value of u_{12} which is the excluded volume between two polymer chains of different species. In general, one can use the conventional theories

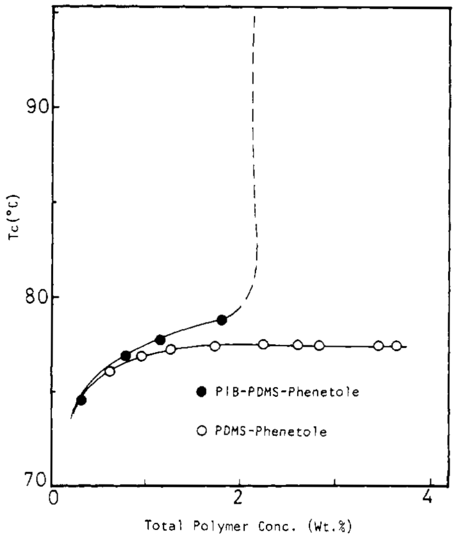

Figure 3. Experimental cloud-point curves for the PIB–PDMS (1:1)–phenetole ternary system (●) and the PDMS–phenetole binary system (○): $\bar{M}_v$(PIB) = 14 × 10^4, $\bar{M}_v$(PDMS) = 39 × 10^4.

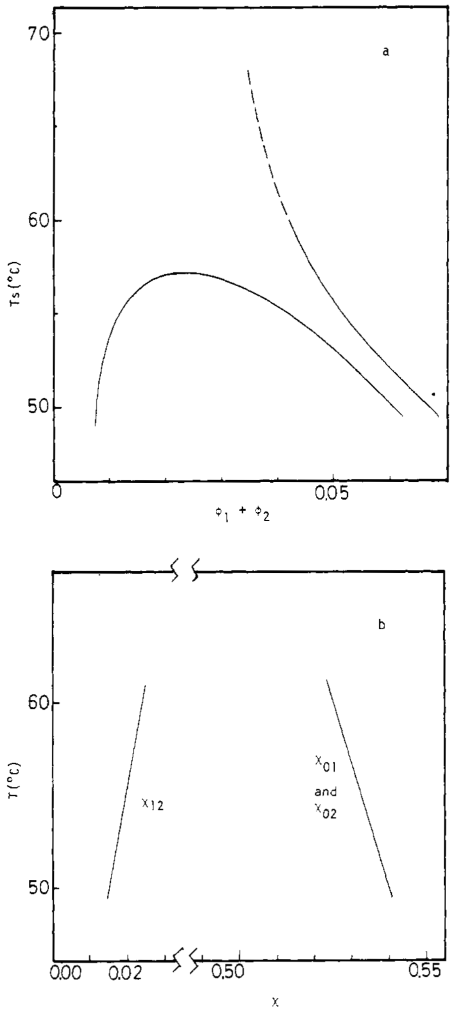

Figure 4. Computed spinodal curve: (a) using the values of χ_{ij}'s shown in (b) and $r_1 = r_2 = 2000$.

for the binary systems. The application of the method by Flory and Krigbaum[8] to the ternary system leaves u_{12} in the same form as in the binary system. The advantage of this method is the possibility for estimating the binary cluster integral

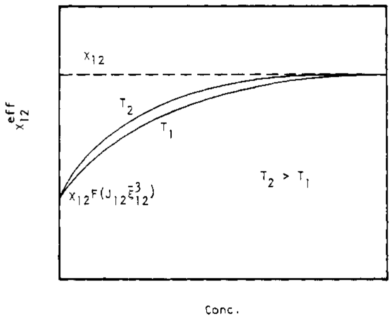

Figure 5. Schematic illustration of the concentration dependence of χ_{12} parameter at different temperatures T_1 and T_2 ($T_2 > T_1$).

$$u_{12} = 2J_{12}m_1m_2F(J_{12}\bar{\xi}_{12}^3)$$

here

$$J_{12} = 0.5(1 - \chi_{01} - \chi_{02} + \chi_{12})\bar{v}_1\bar{v}_2/v_0$$

Unlike the binary system, the value of J_{12} which is related to the binary cluster integral is very large due to the chemical difference between the two polymer chains (exhibited in χ_{12}). This causes the value of the function $F(J_{12}\xi_{12}^3)$ to be close to zero and insensitive to change of the J_{12} value. Hence the effective value of χ_{12} must be far smaller than its actual value at higher concentrations. The value of u_{12} will increase with temperature, since the values of χ_{01} and χ_{02} decrease with increasing temperature even when χ_{12} is independent of temperature. The above discussion is limited to the infinite dilution of the two polymers. In the intermediate concentration, the efficient value of χ_{12} may approach its actual value with increasing concentration due to the interpenetration of the polymer coils. The effect on the cloud point curve of binary systems has been discussed by Koningsveld, *et al.*[9] using the decay function P of concentration. That is

$$\chi_{\mathrm{eff}} = \chi_{\mathrm{conc}} + P(\varphi)(\chi_{\mathrm{dil}} - \chi_{\mathrm{conc}})$$
$$P(\varphi) = \exp(-\lambda_{\mathrm{w}}\varphi)$$

Here φ is the volume fraction of the solute and λ_{w} is the reciprocal of the volume fraction of the solute at which the sum of the coil volumes equals the volume of the entire solution. The value of λ_{w} must be temperature dependent, since the dimension of the coil expands with increasing temperature. Hence, the function P must decay more rapidly at higher temperature with φ. Figure 5 shows the expected behavior of $\chi_{12_{\mathrm{eff}}}$ *vs.* φ of the ternary system based on the above discussion, assuming that χ_{12} is independent of temperature. At infinite dilution, $\chi_{12_{\mathrm{eff}}}$ equals $\chi_{12}F(J_{12}\xi_{12}^3)$ and because of insensitivity of the function $F(J\xi^3)$ to temperature at high values of $J\xi^3$, $\chi_{12_{\mathrm{eff}}}$ does not change very much with temperature. With increasing concentration, $\chi_{12_{\mathrm{eff}}}$ increases and approaches its actual χ_{12} value, the process being faster at higher temperature T_2 than at lower temperature T_1. Hence, the value of $\chi_{12_{\mathrm{eff}}}$ apparently increases with increasing temperature in the intermediate concentration region. This effect does not appear in binary systems and is unique in ternary systems.

This consideration interprets the small value and the temperature dependence of χ_{12} used in the computer analysis. Also, the absence of the higher two-phase region in the atactic polypropylene–polyethylene–diphenyl ether system[1] can be understood from the difference of the chain dimension due to the difference of the tacticity between two polypropylene samples. Kinsinger, *et al.*,[10] reported that the unperturbed radius of gyration of isotactic polypropylene is 10% higher than that of the atactic polypropylene and that the Flory temperature in diphenyl ether of the isotactic sample is eight degrees lower than the atactic sample. Thus the probability of making intermolecular segment–segment contacts is less in atactic than in isotactic polypropylene.

The change in the chemical potential of the solvent upon mixing at infinite dilution can be derived from eq 1 for free energy in the form

$$\begin{aligned}\Delta\mu_0 = -RT[\varphi_1r_1^{-1} + \varphi_2r_2^{-1} + {}\\ \{\varphi_1^2(1/2 - \chi_{01})F(J_{11}\xi_{11}^3) + \varphi_2^2(1/2 - \chi_{02})F(J_{22}\xi_{22}^3) + {}\\ \varphi_1\varphi_2(1 - \chi_{01} - \chi_{02} + \chi_{12})F(J_{12}\bar{\xi}_{12}^3)\} + \ldots]\end{aligned} \quad (2)$$

The lattice theory by Scott, in which concentrated solution is considered, shows

$$\begin{aligned}\Delta\mu_0 = -RT[\varphi_1r_1^{-1} + \varphi_2r_2^{-1} + \{\varphi_1^2(1/2 - \chi_{01}) + {}\\ \varphi_2^2(1/2 - \chi_{02}) + \varphi_1\varphi_2(1 - \chi_{01} - \chi_{02} + \chi_{12})\} + \ldots]\end{aligned} \quad (3)$$

The chemical potential of the solvent in the intermediate concentration region is not available because the explicit form of the decay function, P, of ternary systems, especially for the cross-term, is not known. Osmometry in ternary systems may give information on the function $P(\varphi_1\varphi_2)$. The values of χ_{12} and $F(J_{12}\xi_{12}^3)$ in the two expressions (eq 2 and 3) for the chemical potential can be evaluated by using the values of χ_{0i} and $F(J_{ii}\xi_{ii}^3)$, which can be given by the separate measurement of the corresponding binary systems. Thus the temperature dependence of the apparent χ_{12} value at the intermediate concentration may also be given by osmometry.

This discussion appears speculative due to the lack of basic information. It is, however, worthwhile to study further this problem, not only because of the special importance of the chain conformation on the thermodynamic properties of ternary systems, but because of the very high value of the binary cluster integral which would appear to be the preferred feature for examining the closed-form expressions for the $F(J\xi^3)$ function in dilute polymer solution theories.

Acknowledgment. The author is greatly indebted to Professors D. D. Patterson and W. H. Stockmayer for their interest and important suggestions regarding this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and also to the National Research Council of Canada for their continuing support of this laboratory.

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