Phase Equilibrium in Polymer + Polymer + Solvent Ternary Systems
III. Polystyrene + Polyisoprene + Cyclohexane System Revisited

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ABSTRACT: The polystyrene (PS)+polyisoprene (PIP)+cyclohexane ternary system was further studied by light scattering and phase separation experiments, using for the PS component a sample whose molecular weight was about ten times higher than that used before. Cloud point curves and binodals of the present system were appreciably displaced toward the solvent apex and highly distorted, compared with the previous ones. The light scattering data were analyzed using our recent expression for the interaction function χ

$$\chi = \xi_1^2 \chi_{11}^b(\phi_1) + \xi_2^2 \chi_{22}^b(\phi_2) + 2\xi_1\xi_2\chi_{12}'(\phi_1, \phi_2)$$

where $\chi_{ii}^b(\phi_i)$ is the χ function for solvent 0+polymer i, with ϕ_i the volume fraction of polymer i and $\xi_i = \phi_i/(\phi_1 + \phi_2)$, and χ_{12}' represents the contribution due to the interaction between polymers 1 and 2. The χ function determined was found to be able to describe the observed binodals almost quantitatively. The present result for χ_{12}', along with that from our previous work, clearly demonstrates that χ_{12}' must be treated as molecular-weight dependent.

KEY WORDS   Phase Equilibrium / Polymer + Polymer + Solvent Ternary
System / Cloud Point Curve / Binodal / Light Scattering / Polystyrene /
Polyisoprene /

For a ternary system consisting of two chemically different polymers and a solvent, phase equilibrium behavior depends in a subtle way on such factors as polymer–polymer interaction, affinity of the solvent to the polymer components, and chain lengths of the constituent polymers. The usual approach to this behavior takes advantage of the Flory–Huggins lattice theory in which the interaction function χ is expressed as a quadratic form of the concentrations of the components,[1–3] with the assumption that the coefficients characterizing the interactions of different components are composition-independent. However, the results of many trials[4–8] along this line of formalism were far from satisfactory in a quantitative sense. This may be expected from the fact that the χ function for binary systems of a polymer and a solvent

usually exhibits a significant concentration dependence.[2,9–11]

In a recent paper,[12] we have shown that χ for the ternary system concerned can be put in the form

$$\chi = \xi_1^2 \chi_{11}^b(\phi_1) + \xi_2^2 \chi_{22}^b(\phi_2)$$
$$+ 2\xi_1\xi_2\chi_{12}'(\phi_1,\phi_2) \quad (1)$$

where $\chi_{ii}^b(\phi_i)$ is the χ function for the solvent 0+polymer i binary system, with ϕ_i being the volume fraction of polymer i and $\xi_i = \phi_i/(\phi_1 + \phi_2)$, and $\chi_{12}'(\phi_1,\phi_2)$ represents the interaction between polymers 1 and 2 in the ternary solution. It was found[13,14] for a polystyrene (PS)+polyisoprene (PIP)+cyclohexane (CH) ternary system that this expression evaluated from light scattering data successfully explained observed phase separation be-

havior. The success implies that our χ function properly took into account the influences of composition and temperature on phase equilibria. However, we left the examination of a possible chain length dependence of χ for further work.

In the present work, similar light scattering and phase separation experiments were carried out on another PS + PIP + CH ternary system, in which the PS component had the molecular weight about ten times higher than the previous one. Our main aim was to examine whether the phase equilibrium behavior of this ternary system is affected by the change in molecular weight of the PS component.

EXPERIMENTAL

The new PS sample chosen was the standard sample F40 supplied by Toyo Soda Co. Its weight-average molecular weight $\bar{M}_w$ was determined to be 447000 by light scattering in cyclohexane at 34.5°C. For PIP the same sample P-5, whose $\bar{M}_w$ is 53300, was used. The preparation of test solutions and the calculation of their composition were made as described before.[13,14]

Scattering intensities of light and cloud points were measured and analyzed in the same way as in the previous work.[13,14]

RESULTS AND DISCUSSION

Cloud Point Curves and Binodals

Observed cloud point curves for PS(F40) + PIP(P-5) + CH ternary solutions are illustrated in Figure 1, where the volume fraction ξ_{PS} ($=\xi_1$) of PS in the polymer mixture is fixed at different values ranging from 0.0865 to 1. The features of these curves are essentially similar to those found in the previously studied PS(F4) + PIP(P-5) + CH system.[14] The curve for the PS-rich solution tends to merge with the curve for the PS + CH binary system as the temperature and concentration are lowered. This behavior is expected because the

PS(F40) + CH binary solution undergoes phase separation below 27.2°C. At temperatures higher than 35°C, the cloud point curves for different ξ_{PS} are almost parallel with each other.

By reading the cloud point concentrations for different ξ_{PS} at fixed temperature and plotting them on a phase triangle, we can construct the binodal curve at a given temperature. The results for the present system are shown in Figure 2. It is seen that the miscible region is confined to very low concentrations of the polymer mixture and becomes even smaller with decreasing temperature. The binodal curve at 27°C intersects the PS–CH edge, corresponding to the observation that the PS–CH binary system is phase separated at this temperature. The binodal curves are asymmetric and distorted toward the PIP–CH edge, since CH is more favored by PIP than by PS.

Figure 3 compares the binodal data for the present system with those for the previous system PS(F4) + PIP(P-5) + CH. It is found that the binodal curve is greatly displaced toward the solvent apex and becomes more asymmetric as the molecular weight of PS gets higher. This observation is in qualitative agreement not only with the experimental findings for many polymer + polymer + solvent systems examined so far[8,15,16] but also with the theoretical calculations for model systems.[17]

Light Scattering Data

In Figure 4, the light scattering data for $\xi_{PS} = 0.8870$ at 28, 30, 32, and 34.5°C are shown in the form of $KV_0\phi/\Delta R_0$ plotted against ϕ. Here, K is an optical constant, V_0 the molar volume of the solvent, ϕ the total polymer volume fraction, and ΔR_0 the excess Rayleigh ratio at zero scattering angle. The data points at each fixed temperature follow a curve convex upward, which intersects the abscissa at a relatively low concentration, giving a spinodal point. The spinodal concentration becomes lower as the temperature is lowered.
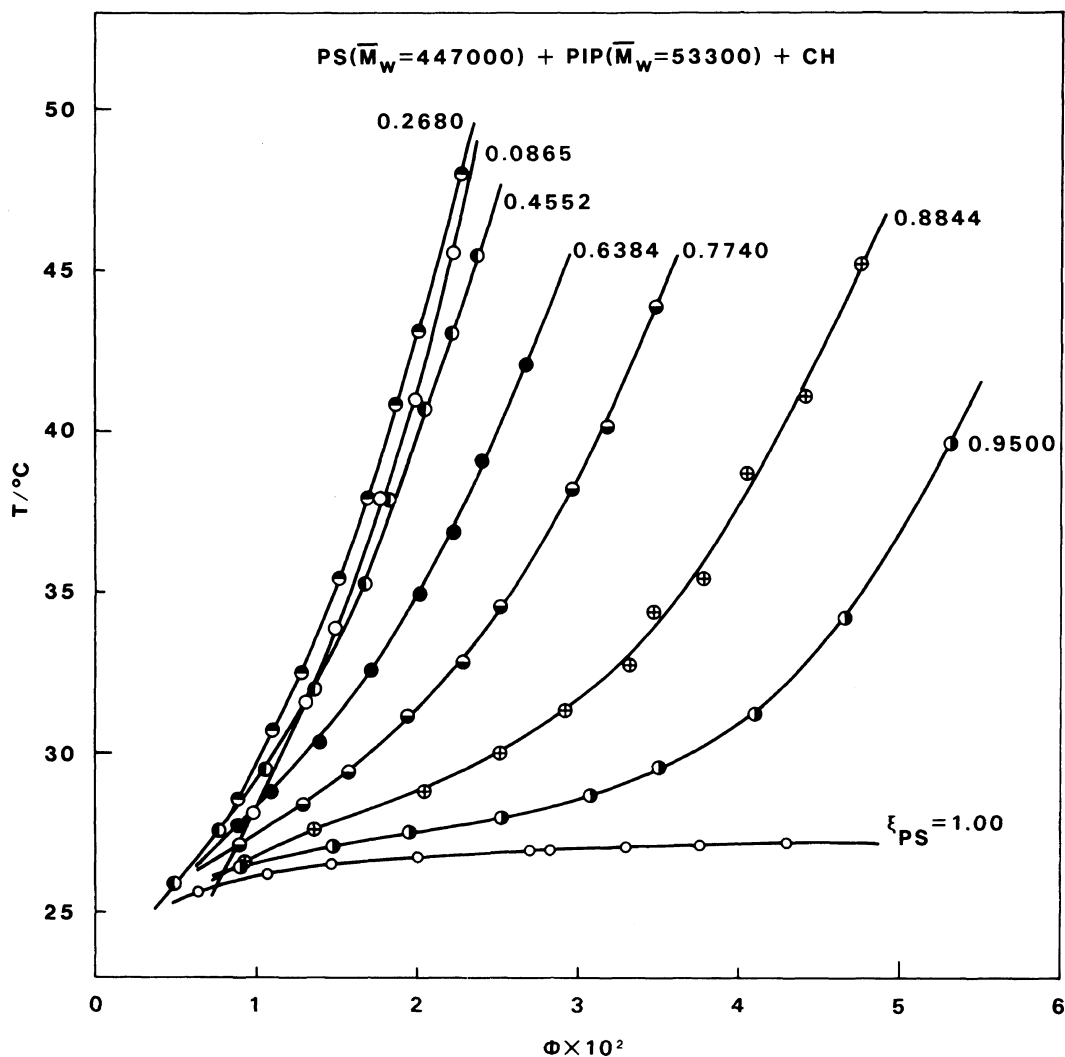
Figure 1. Cloud point curves for PS(F40)+PIP(P-5) mixtures of indicated compositions in CH.

Recently,[13] we have derived an expression for $KV_0\phi/\Delta R_0$ on the basis of our generalized Flory–Huggins theory.[12] It reads:

$$KV_0\phi/\Delta R_0 = [1 + \phi(1-\phi)^{-1}P_w$$
$$- \phi(P_w L + Y)]/WX \quad (2)$$

where

$$W = (\tilde{\gamma}_1{}^2 P_1 \xi_1 + \tilde{\gamma}_2{}^2 P_2 \xi_2)/(1-\phi)^2 \quad (3)$$

$$X = 1 + (\tilde{\gamma}_1{}^2 P_1 \xi_1 + \tilde{\gamma}_2{}^2 P_2 \xi_2)^{-1}$$
$$\times \xi_1 \xi_2 \{(\tilde{\gamma}_1 - \tilde{\gamma}_2)^2 P_1 P_2 [1 + (P_n{}^{-1} - 1)\phi]\phi$$
$$- 2(\tilde{\gamma}_1 - \tilde{\gamma}_2)(\tilde{\gamma}_1 P_1 - \tilde{\gamma}_2 P_2)\phi$$
$$- (\tilde{\gamma}_1 - \tilde{\gamma}_2)^2 P_1 P_2 (1-\phi)^2 \phi L$$
$$+ 2(\tilde{\gamma}_1 - \tilde{\gamma}_2)(\tilde{\gamma}_1 \xi_1 + \tilde{\gamma}_2 \xi_2)P_1 P_2 (1-\phi)\phi M$$
$$+ (\tilde{\gamma}_1 \xi_1 + \tilde{\gamma}_2 \xi_2)^2 P_1 P_2 N \} \quad (4)$$

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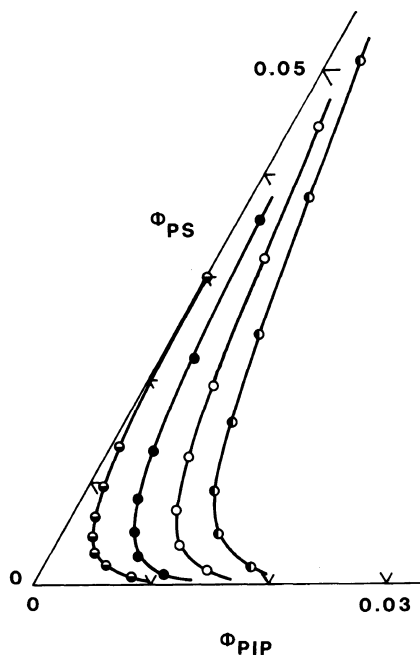PS($\overline{M}_W$=447000) + PIP($\overline{M}_W$=53300) + CH

Figure 2. Binodals for the PS(F40)+PIP(P-5)+CH ternary system. ◑, 40; ○, 34.5; ●, 30; ◒, 27°C.
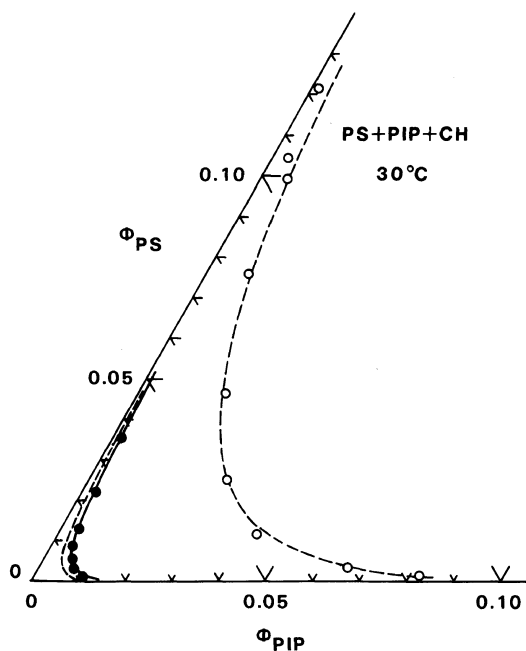

Figure 3. Binodals for the PS+PIP+CH ternary system. ○, PS(F4)+PIP(P-5)+CH; ●, PS(F40)+PIP(P-5)+CH. ----, calculated with k_1=0.44; ——, calculated with k_1=0.455.
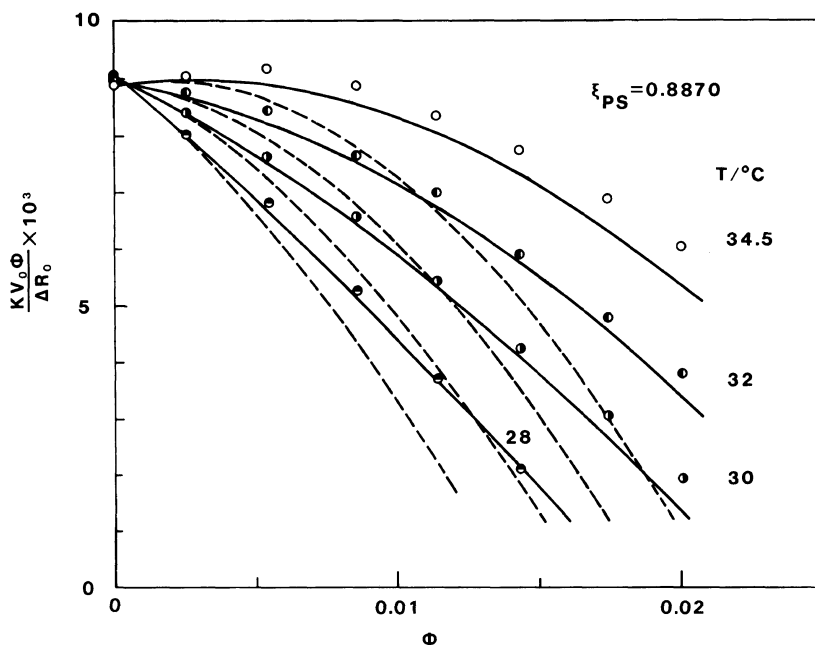

Figure 4. Concentration dependence of $KV_0\phi/\Delta R_0$ for the PS(F40)+PIP(P-5) mixture with ξ_{PS}=0.8870 in CH at indicated temperatures. ----, calculated with k_1=0.44; ——, calculated with k_1=0.455.

$$Y = \xi_1 \xi_2 \{ 2(P_1 - P_2)M - P_1 P_2 [(1 - \phi)^{-1}$$
$$+ (P_n \phi)^{-1} - L]N + P_1 P_2 \phi M^2 \} \qquad (5)$$

with

$$\tilde{\gamma}_i = \gamma_i - \sum_{j=1}^{2} \gamma_j \phi_j, \quad \gamma_i = (\partial n / \partial \phi_i)_{\phi k} \qquad (6)$$

$$P_w = P_1 \xi_1 + P_2 \xi_2, \quad P_n^{-1} = \xi_1 / P_1 + \xi_2 / P_2,$$

$$P_i = M_i v_i / V_0 \qquad (7)$$

$$L = 2\chi + \phi (\partial \chi / \partial \phi)_{\xi_1} \qquad (8)$$

$$M = (\partial \chi / \partial \xi_1)_{\phi} \qquad (9)$$

$$N = -(\partial^2 / \partial \xi_1^2) \int_0^{\phi} \chi(u, \xi_1) \, du \qquad (10)$$

In a previous study,[13] we analyzed the light scattering data for the PS(F4) + PIP(P-5) + CH

system by using eq 2 with eq 1 and determined $\chi_{12}{}^t$ to be

$$\chi_{12}{}^t = k_1 + (k_2 \xi_1 + k_3 \xi_2)\phi \qquad (11)$$

with

$$k_1 = 0.44 \qquad (12)$$

$$k_2 = -6.1 + 2000/T \quad (T \text{ in K}) \qquad (13)$$

$$k_3 = -4.8 + 1300/T \quad (T \text{ in K}) \qquad (14)$$

when we substituted for $\chi_{11}{}^b$ and $\chi_{22}{}^b$ the empirical expressions obtained from separate light scattering experiments on the PS + CH and PIP + CH binary systems. The χ function so determined was found to describe rather accurately the phase equilibrium data for the ternary system studied.[14]

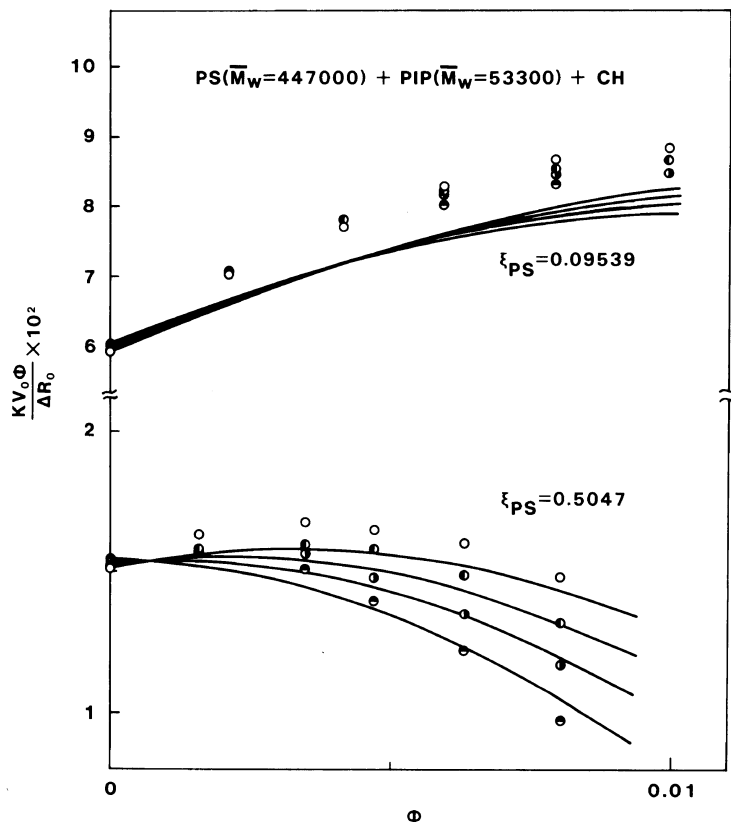We attempted to apply the above expression

Figure 5. Concentration dependence of $KV_0\phi/\Delta R_0$ for PS(F40) + PIP(P-5) mixtures with indicated ξ_{PS} in CH. ○, 34.5; ◑, 32; ◔, 30; ◕, 28°C. Solid line, values calculated with $k_1 = 0.455$.

for $\chi_{12}{}'$ to the present system, ignoring the difference between the molecular weights of the PS samples. As seen in Figure 4, the calculated $KV_0\phi/\Delta R_0$ values are significantly smaller than the experimental data, when compared at fixed ϕ. The calculated binodal curves also deviate from the observed ones as exemplified in Figure 3. These discrepancies are clear evidence of the molecular weight dependence of $\chi_{12}{}'$, since the molecular weight effect on $\chi_{11}{}^b$ was already taken into account and since the PIP samples used in the present and previous experiments were the same. Thus, we modified $\chi_{12}{}'$ and found after some trials that a change in k_1 sufficed to improve agreement between the calculated and observed results for $KV_0\phi/\Delta R_0$. For $\xi_{PS}=0.8870$, the agreement (see Figure 4) was most satisfactory when k_1 was chosen to be 0.455. Figure 5 compares the calculated $KV_0\phi/\Delta R_0$ with the experimental data for two other compositions $\xi_{PS}=0.5047$ and 0.09539. These calculated curves predict the observed feature that $KV_0\phi/\Delta R_0$ decreases with increasing T at dilute concentrations lower than a certain ϕ value while it increases with T at higher ϕ. However, the quantitative agreement is only moderate. The calculated values progressively deviate downward from the observed ones as ξ_{PIP} and ϕ are increased, indicating that our expression for $\chi_{12}{}'$, i.e., eq 11, is not always adequate to describe the effect of the composition of the polymer mixture. The discrepancy is largest at $\xi_{PS}=0.09539$, but it remains less than 10% and does not lead to significant deviations from measured phase composition as described below.

Calculated Binodals

The compositions of conjugate separated phases are determined by the phase equilibrium conditions, i.e., $\Delta\mu_0{}'=\Delta\mu_0{}''$ and $\Delta\mu_i{}'=\Delta\mu_i{}''$ ($i=1, 2$), where single and double primes signify the pair of separated phases. When eq 1 for χ is used, the solvent chemical potential difference $\Delta\mu_0$ is represented by
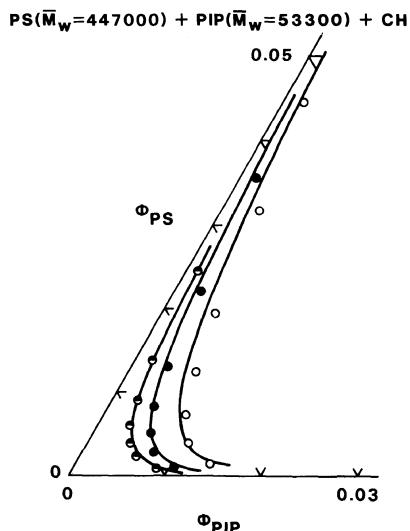
Figure 6. Comparison of calculated and observed binodals for the PS(F40)+PIP(P-5)+CH ternary system. Solid lines, calculated binodals with $k_1=0.455$. Circles, observed binodals; ○, 34.5; ●, 30; ◓, 28°C.

$$\Delta\mu_0/RT=\ln(1-\phi)+(1-P_n{}^{-1})\phi$$
$$+[\xi_1{}^2\chi_{11}{}^b(\phi_1)+\xi_2{}^2\chi_{22}{}^b(\phi_2)$$
$$+2\xi_1\xi_2\chi_{12}{}'(\phi,\xi_1)]\phi^2 \qquad (15)$$

The equilibrium condition for the solute component i leads to the following expression of the separation factor σ_i

$[\equiv P_i{}^{-1}\ln(\phi_i{}''/\phi_i{}')]$:

$$\sigma_i=\Delta\Bigg\{\ln(1-\phi)+\phi_i\chi_{ii}{}^b(\phi_i)$$
$$+\int_0^{\phi_i}\chi_{ii}{}^b(u)\mathrm{d}u+2\xi_1\xi_2\chi_{12}{}'(\phi,\xi_1)$$
$$+2(1-\xi_i)^2\int_0^\phi[\chi_{12}{}'(u,\xi_1)$$
$$+\xi_i\partial\chi_{12}{}'(u,\xi_1)/\partial\xi_i]\mathrm{d}u\Bigg\}$$
$$(i=1, 2) \qquad (16)$$

where ΔX denotes $X''-X'$.

With eq 15 substituted into the relation $\Delta\mu_0{}'=\Delta\mu_0{}''$, along with eq 16, three equations

are set up for two sets of unknown composition variables (ϕ', ξ_1') and (ϕ'', ξ_1'') corresponding to the dilute and concentrated phases, respectively. Three of the four variables can be solved at each given value of the remaining one. Thus, the use of our experimental $\chi_{ii}^b(\phi_i)$ and $\chi_{12}^t(\phi,\xi_1)$ allows us to determine binodals for the present system, with the results shown in Figure 6. The agreement between calculated and observed binodals is seen to be almost quantitative, in contrast to the light scattering results shown in Figure 5. This finding implies that the precise information about χ_{12}^t is not needed for quantitative prediction of phase behavior of the ternary system studied, though this function plays a role far from being ignored.

CONCLUSION

In this paper, we have shown again that our formulation for χ can be applied to a quantitative prediction of the phase equilibrium behavior of the PS+PIP+CH ternary system when χ_{ii}^b and χ_{12}^t are separately determined by light scattering. The χ_{12}^t function associated with the interaction between PS and PIP was found to depend on molecular weight of the polymer component. However, no systematic study of chain length effect on χ_{12}^t was attempted here. In addition, a possible dilute-solution effect on χ_{12}^t was ignored in the present treatment. Thus, more work is needed

for elaboration of χ_{12}^t.

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