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Phase Equilibrium in Polymer + Polymer + Solvent Ternary Systems. 4. Polystyrene + Polyisobutylene in Cyclohexane and in Benzene

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ABSTRACT: Light-scattering and phase-separation experiments were done on polystyrene + polyisobutylene mixtures in cyclohexane and in benzene. The observed phase diagrams revealed that the compositions of the two equilibrated phases were highly dependent on the solvent. They were almost quantitatively described by using our recent expression for the interaction function χ, i.e., $\chi = \xi_1^2\chi_{11}^b(\phi_1) + \xi_2^2\chi_{22}^b(\phi_2) + 2\xi_1\xi_2\chi_{12}^t(\phi_1,\phi_2)$, with χ_{ii}^b and χ_{12}^t determined from light scattering or osmotic pressure for the associated binary and ternary solutions. Here, $\chi_{ii}^b(\phi_i)$ is the χ function for the polymer i + solvent binary solution and $\chi_{12}^t(\phi_1,\phi_2)$ the interaction function between polymers 1 and 2 in the ternary solution, with ϕ_i being the volume fraction of polymer i and $\xi_i = \phi_i/(\phi_1 + \phi_2)$. The estimated χ_{12}^t functions were found to include the repulsive interactions of the two polymer components as well as the solvent affinities to them.

The phase equilibrium behavior of a ternary solution containing two chemically different polymers and a pure solvent is greatly affected by two thermodynamic factors, i.e., incompatibility between the polymer components and solvent affinity to them. In part 2[1] of this series, we examined phase relations for a ternary system polystyrene (PS) + polyisoprene (PIP) + cyclohexane (CH), in which PS and PIP are incompatible with each other and CH is good for PIP but poor for PS. The observed binodal curves spread from a point near the CH apex toward the PS–PIP edge of the composition triangle, as is generally the case with systems consisting of an incompatible polymer pair dissolved in a common good solvent.[2–8] Therefore, it seemed that the repulsive interaction of the incompatible polymer components is the main cause of phase separation. However, the tie lines were significantly tilted to the PS–CH edge owing to distinct difference in affinities of CH to PIP and to PS, in marked contrast to the fact that they were nearly parallel with the polymer–polymer edge in the systems of an incompatible polymer pair in a common good solvent.[2–8]

In the present work, we examine another incompatible polymer pair PS + polyisobutylene (PIB) in CH and in benzene for further clarification of the solvent effect. The two solvents were chosen for the reason that CH is good for PIB but poor for PS, while benzene is good for PS but poor for PIB. Owing to such solvent properties, the phase diagrams of these two ternary systems would reveal solvent effects clearly.

Recently, we[9] have formulated the interaction function χ for ternary polymer systems as

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

where ξ_i and ϕ_i are the volume fractions of polymer component i in the solvent-free polymer mixture and in the ternary solution, respectively, and ϕ is the total polymer volume fraction in the solution ($\phi = \phi_1 + \phi_2$). χ_{ii}^b and χ_{12}^t represent the interaction between polymer components i and that between polymer components 1 and 2 in the solvent, respectively. The phase diagrams of the PS + PIP + CH system were almost quantitatively described by this χ expression with χ_{ii}^b and χ_{12}^t evaluated from light-scattering data on the related binary and ternary systems.[1,10] The same procedure is here adopted to calculate phase relationships. Another aim of this work is to examine solvent effects that are expected to appear in χ_{ii}^b and χ_{12}^t.

Experimental Section

Polymer Samples. The standard polystyrene (PS) sample F4′ in part 1[10] of this series was again used for the present work. Gel permeation chromatography (GPC) measurement confirmed its sufficiently narrow molecular weight distribution. Its weight-average molecular weight M_w was 53 600 when determined by light scattering in benzene at 25 °C.

A commercial polyisobutylene (PIB) sample was fractionated by fractional precipitation with benzene and methanol as solvent and precipitant, respectively. The fractionation was repeated six times, and two central fractions U-1 and U-2 were chosen for this work. The M_w value determined by light scattering in CH at 25 °C was 154 000 and 152 000 for U-1 and U-2, respectively. The values of the ratio of M_w to the number-average molecular weight M_n, i.e., M_w/M_n, evaluated by GPC were smaller than 1.06 for both samples.

In the present work, we designate PS as component 1, PIB as component 2, and the solvent cyclohexane (CH) or benzene as component 0. The relative chain length P_i of polymer component i was calculated by

$$P_i = M_i v_i / M_0 v_0 \quad (i = 0, 1, 2) \qquad (2)$$

where M_i and v_i are the molecular weight and specific volume of component i, respectively. The value used for v_i in cubic centimeters per gram was 0.9343 for PS,[11] 1.0906 for PIB,[12] 1.2923 for CH,[13] and 1.1446 for benzene,[13] all of which refer to 25 °C. With these v_i values, eq 2 gives P_1 values of 460 and 560 for PS sample F4′ in CH and in benzene, respectively, and P_2 values of 1540 and 1850 for PIB sample U-1 in CH and for U-2 in benzene, respectively.

Light-Scattering Measurements. The binary and ternary solutions for light-scattering measurements were prepared in the same way as described before.[10,14] The total polymer volume fraction ϕ in the ternary solution was calculated from the total polymer weight fraction w by

$$\phi = [1 + v_0/(\omega_1 v_1 + \omega_2 v_2)(w^{-1} - 1)]^{-1} \qquad (3)$$

where ω_i is the weight fraction of polymer i in the polymer mixture. The volume fraction ξ_1 of PS in the polymer mixture is related to ω_1 by

$$\xi_1 = [1 + v_2/v_1(\omega_1^{-1} - 1)]^{-1} \qquad (4)$$

Scattering intensities were measured with a Fica 50 photometer and vertical incident light of 436-nm wavelength for the binary systems PIB(U-1) + CH and PS(F4′) + benzene as well as for the ternary system PS(F4′) + PIB(U-2) + benzene and with incident light of 546-nm wavelength for the PS(F4′) + PIB(U-1) + CH system. As described in part 1[10] of this series, the excess

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Rayleigh ratio ΔR_0 at zero scattering angle for a polymer i + solvent binary system can be expressed by

$$K_\phi/\Delta R_0 = 1/(1-\phi) + 1/(P_i\phi) - L_{ii} \tag{5}$$

with

$$L_{ii} = 2\chi_{ii}^{\mathrm{b}} + \phi(\partial\chi_{ii}^{\mathrm{b}}/\partial\phi) \tag{6}$$

Here, K_ϕ is the optical constant $4\pi^2n^2\gamma_i^2V_0/N_\mathrm{A}\lambda_0^4$, with n being the refractive index of the solution, γ_i the refractive index increment ($\gamma_i = \partial n/\partial\phi_i$), V_0 the molar volume of the solvent, N_A the Avogadro constant, and λ_0 the wavelength of incident light in the vacuum. Equation 5 allows L_{ii} to be evaluated at a given ϕ from the data for $K_\phi/\Delta R_0$ along with a known value of P_i. The light-scattering data $KV_0\phi/\Delta R_0$ on the ternary systems PS + PIB + CH and PS + PIB + benzene were processed to estimate the χ_{12}^{t} function, with use of the χ_{ii}^{b} equations determined in advance as described below, where K is the optical constant $4\pi^2n^2/N_\mathrm{A}\lambda_0^4$.

The refractive index increment γ_i for the polymer i + solvent binary solution was measured as a function of temperature T (in kelvin). The γ_i equations derived are as follows:

For PIB + CH

$$\gamma_2 = 0.0285 + 2.08 \times 10^{-4}T \quad (436\ \mathrm{nm}) \tag{7a}$$

$$\gamma_2 = 0.0198 + 2.29 \times 10^{-4}T \quad (546\ \mathrm{nm}) \tag{7b}$$

For PS + benzene

$$\gamma_1 = 0.0495 + 2.20 \times 10^{-4}T \quad (436\ \mathrm{nm}) \tag{8}$$

For PIB + benzene

$$\gamma_2 = -0.0070 \quad (25\ {}^\circ\mathrm{C},\ 436\ \mathrm{nm}) \tag{9}$$

(This γ_2 value was used for the PS + PIB + benzene ternary system by neglecting the temperature dependence of γ_2.) For PS + CH, the infinite-dilution value

$$\gamma_1 = 0.0960 + 2.77 \times 10^{-4}T \quad (546\ \mathrm{nm}) \tag{10}$$

was obtained from Scholte's equation.[15]

Osmotic Pressure Measurements. For PIB(U-2) + benzene solutions, osmotic pressures were measured at 20, 24.5, and 30 °C on a modified Knauer membrane osmometer fitted with a Sartorius membrane SM11536 of 0.005–0.01-μm pore size made from regenerated cellulose. The delivered membranes soaked in 25% aqueous ethanol were transferred into pure benzene via pure water and acetone. The transfer was carried out step by step with increasing content of the next solvent by 25% in volume and by taking about 1 day at each step for conditioning the membrane. The value of χ_{22}^{b} for this system was calculated from osmotic pressure data by the conventional method.

Phase-Separation Experiments. Test solutions for the PS + PIB + CH and PS + PIB + benzene systems were prepared following the procedure described previously.[1] Their cloud-point temperatures were determined by monitoring the intensity of the laser beam transmitted through the solution. The method, however, failed in PIB-rich solutions of the PS + PIB + benzene system, since the refractive index of PIB was so close to that of benzene that the second incipient phase gave no turbidity detectable by this method. Hence, the cloud point for such a solution was determined visually by comparing very slight turbidity with the transparency of pure solvent in a reference cell. The cloud-point temperatures so determined differed no more than ±0.05 °C from those by the method using a laser beam when the comparison was feasible.

Phase-separation experiments were carried out on the above ternary systems at 20 and 30 °C in the same way as for the PS + PIP + CH system.[1] The compositions of separated phases were determined as follows: Parts of the solutions in the two equilibrated phases were carefully drawn out with syringes and freeze-dried after weighing. The total polymer weight fraction w of each phase was calculated from the weight of the solution sucked out and that of the polymer mixture recovered from it by freeze-drying. Then, the weight fraction ω_1 of PS in the solvent-free PS + PIB mixture recovered from the CH solution was evaluated from the 262-nm ultraviolet (UV) absorbance for a CH solution of a known amount of the mixture. A Shimadzu UV-200 double-beam spectrophotometer was used with the following linear relation between absorbance A_UV and weight fraction w of PS in the PS + CH binary solution:

$$A_\mathrm{UV} = 1.54 \times 10^3 w \quad (w \le 8.5 \times 10^{-4},\ 25\ {}^\circ\mathrm{C}) \tag{11}$$

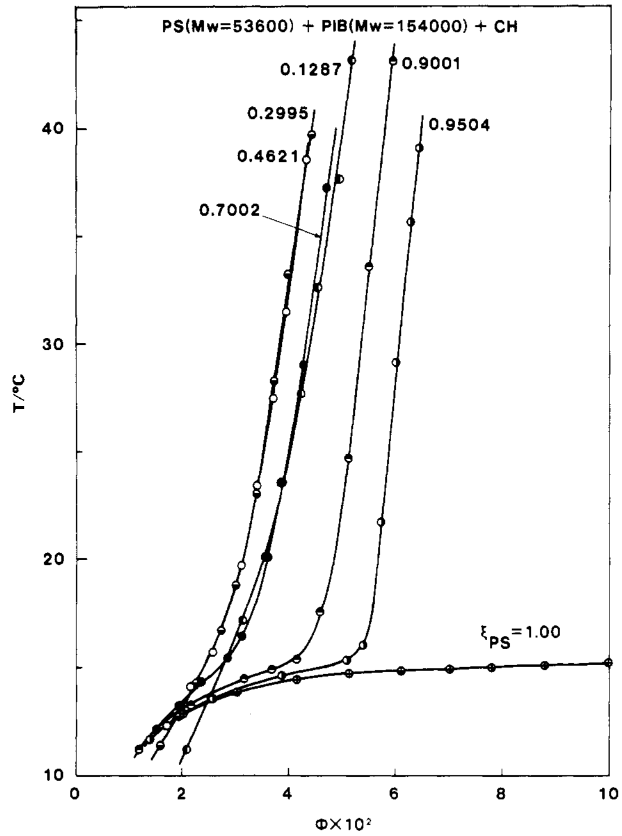

Figure 1. Cloud-point curves for PS + PIB mixtures of the indicated compositions in CH.

The composition of the PS + PIB mixture recovered from its benzene solution was determined from the refractive index increment $\partial n/\partial w$ for a benzene solution of the mixture at 436 nm and at 25 °C. This method was employed since the UV absorbance was affected by a trace amount of benzene remaining in the polymer mixture. The value of ω_1 for the PS component was computed by

$$\partial n/\partial w = \omega_1(\partial n/\partial w_1) + (1-\omega_1)(\partial n/\partial w_2) \tag{12}$$

where $\partial n/\partial w_i$ is the refractive index increment for the component i in benzene and evaluated from eq 8 and 9 with $\partial n/\partial w_i = (v_i/v_0)\gamma_i$. The $\partial n/\partial w_2$ value for PIB in benzene was so small that this method led to a gross error in ω_1 when the amount of PS in the polymer mixture was small. In this case, the UV absorption method described above was utilized after benzene was thoroughly removed by careful freeze-drying. The ω_1 values were converted to ξ_1 by eq 4.

Results and Discussion

Cloud-Point Curves. Cloud-point curves at different compositions ξ_PS ($=\xi_1$) are depicted for the ternary systems PS(F4′) + PIB(U-1) + CH and PS(F4′) + PIB(U-2) + benzene in Figures 1 and 2, respectively. Each curve represents the temperature of incipient phase separation as a function of the concentration of the polymer mixture of a given ξ_PS. The dashed line in Figure 2 shows the calculated cloud-point curve for the PIB + benzene binary system, which cannot be experimentally determined since PIB is almost transparent in benzene. The cloud-point curves reveal universal features essentially similar to those found in the PS + PIP + CH system,[1] as expected from the fact that these three ternary systems have the following thermodynamic features in common, i.e., the polymer

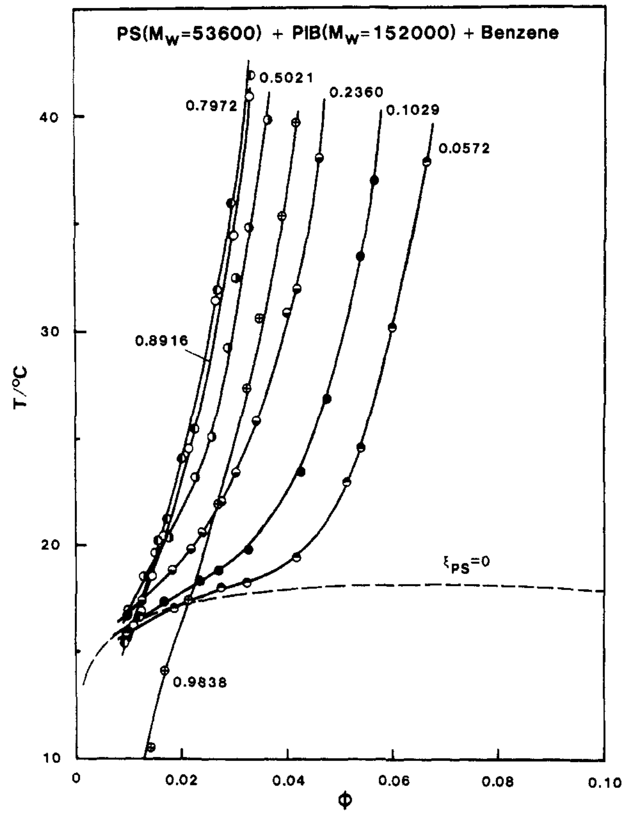

Figure 2. Cloud-point curves for PS + PIB mixtures of the indicated compositions in benzene. Dashed line: calculated cloud-point curve for the PIB + benzene system.

components are incompatible and the solvent is good for one polymer component but poor for the other.

In all the systems studied, the cloud-point curves for different ξ_{PS} are nearly parallel with the T axis at temperatures sufficiently higher than the critical point of the binary system, PS + CH or PIB + benzene. At low temperatures close to or below this critical point, the cloud-point curves can be divided into two groups depending on the composition of polymer mixture. They penetrate into the demixing region for the PS + CH or PIB + benzene binary system when the polymer, for which the solvent is good, is a major component in the ternary solution. On the other hand, the curves for the ternary solutions rich in the polymer component for which the solvent is poor tend to merge with the cloud point curve for the binary system as the temperature is lowered.

Binodals. Figures 3 and 4 illustrate three-dimensional representations of the binodal surfaces for the ternary systems PS + PIB + CH and PS + PIB + benzene; these were constructed from the cloud-point data. The cloud point curve for each ξ_{PS} in Figure 1 or 2 is the intersection of the binodal surface by the constant-polymer composition plane, on which the composition of a given polymer mixture is fixed but the temperature and overall polymer concentration in the solution are varied. The symbols ϕ_{PS} and ϕ_{PIB} are used instead of ϕ_1 and ϕ_2 for easy understanding of the graphs. *It can be seen that every binodal surface has a shelf in the low-temperature region near the plane defined by the T axis vs polymer concentration axis for the poor solvent + polymer binary.* The same behavior was also found for the PS + PIP + CH system previously.[1] This finding implies that phase equilibrium of a ternary system is not determined by the polymer–polymer repulsive interaction only. The solvent property is also an important factor, especially when phase separation occurs in the binary solution consisting of the solvent and one of the two polymers included in the ternary system.

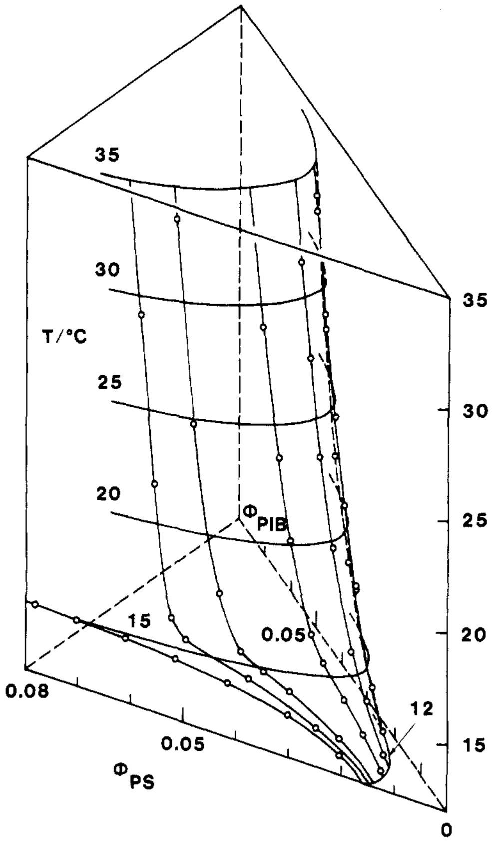

Figure 3. Three-dimensional representation of the binodal surface for the PS + PIB + CH system. Circles: experimental data.

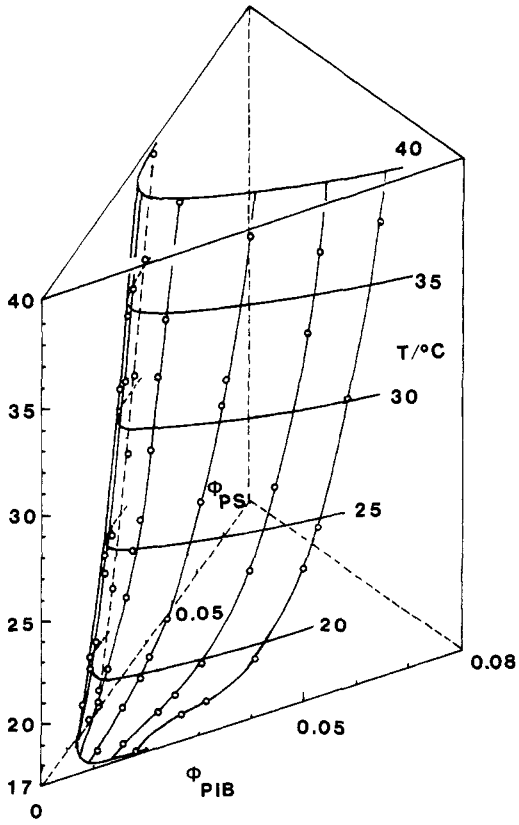

Figure 4. Three-dimensional representation of the binodal surface for the PS + PIB + benzene system. Circles: experimental data.

By cutting the binodal surface of a ternary system with a constant-temperature plane, we can construct a binodal

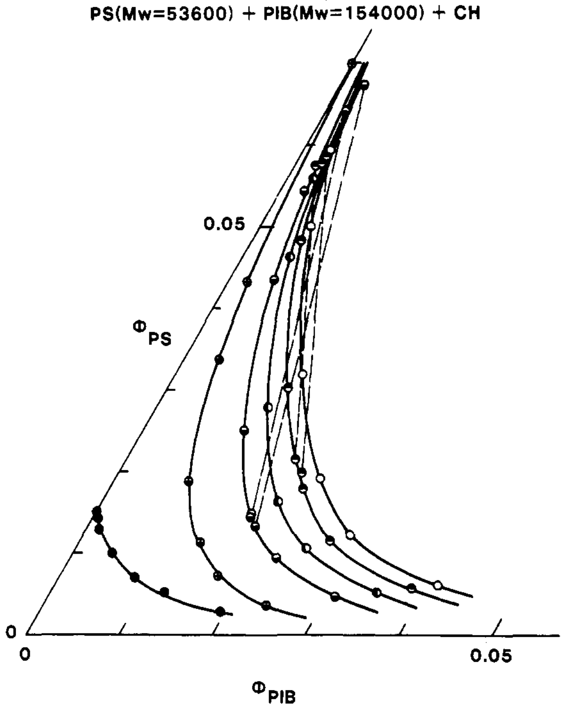

Figure 5. Experimental binodal curves (solid lines) and tie lines (dashed lines) for the PS + PIB + CH system: ○, 34.5; ◓, 30; ◐, 25; ◒, 20; ⊕, 15; ●, 12 °C.

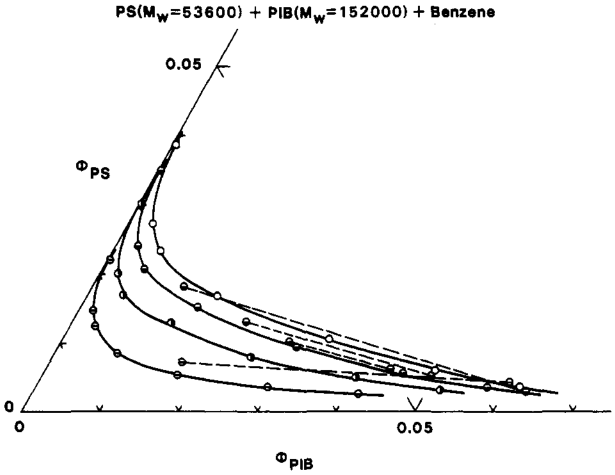

Figure 6. Experimental binodal curves (solid lines) and tie lines (dashed lines) for the PS + PIB + benzene system: ○, 35; ◒, 30; ◑, 25; ⊖, 20 °C.

curve for the system at a given temperature. The binodal curves so obtained for the PS + PIB + CH and PS + PIB + benzene systems are illustrated in Figures 5 and 6, together with the tie lines determined independently from phase-separation experiments at indicated temperatures. The binodal curve at a fixed temperature spreads from a point near the solvent apex toward the polymer–polymer edge, asymptotically approaching the ϕ_{PS} and ϕ_{PIB} axes with increasing concentration, except those at 12 and 15 °C for the PS + PIB + CH system. This observation qualitatively agrees with the experimental findings[2-8] reported for an incompatible polymer pair in a common good solvent as mentioned in the introduction. Roughly speaking, the shape of the binodal curve is primarily determined by polymer–polymer incompatibility.

However, our binodal curves are somewhat distorted toward the edge representing the binary system of the good solvent + polymer. This can be ascribed to a difference in solvent affinity to the polymer components. In the PS + PIB + CH system, the binodal curves reach the axis for the poor solvent + polymer binary system at 12 and 15 °C. The tie lines connect two distinctly different phases and are significantly tilted to the PS–CH edge in the PS + PIB + CH system and to the PIB–benzene edge in the PS + PIB + benzene system. These results along with those for the PS + PIP + CH system[1] indicate that the tie line for a ternary system is always tilted to the edge for the poor solvent + polymer binary system. The inclination of the tie lines becomes more pronounced with decreasing temperature.

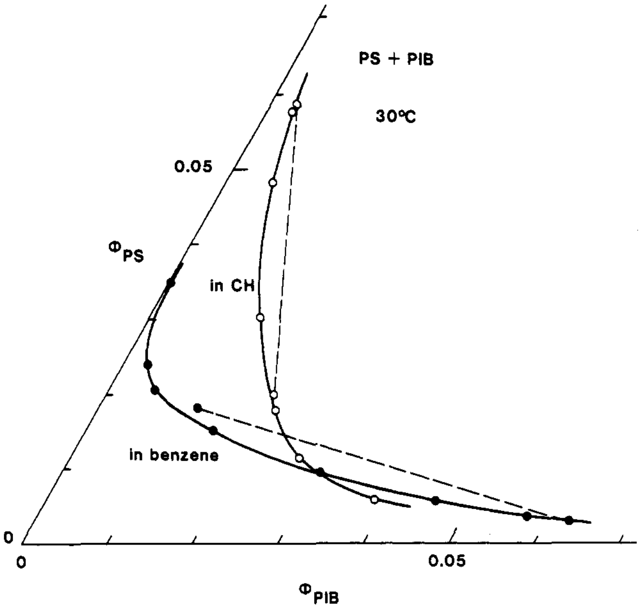

Figure 7. Binodal curves (solid lines) and tie lines (dashed lines) for the PS(F4′) + PIB(U-1) + CH (○) and PS(F4′) + PIB(U-2) + benzene (●) systems.

The solvent effect is more distinctly observed when the binodal curve and tie line for the PS(F4′) + PIB(U-1) + CH system are compared with those for PS(F4′) + PIB(U-2) + benzene system, as shown by Figure 7. Here, the same PS sample and the PIB samples of approximately equal molecular weight are used in both systems, and only the solvent is changed from CH to benzene. It can be seen that the change of the solvent leads to significant changes in the shape of the binodal curves and the inclination of the tie lines. It follows that the solvent property governs the phase relationships, especially the compositions of the two equilibrated phases. The solvent effect becomes especially noticeable in the temperature region where the binary solution of the poor solvent + polymer pair included in the ternary system undergoes phase separation.

Interaction Functions χ_{ii}^{b} for Binary Systems. According to the maneuver developed in our previous paper,[10] we require the interaction functions $\chi_{ii}^{b}(\phi_i)$ for the binary systems PS + CH, PIB + CH, PS + benzene, and PIB + benzene to determine the interaction function $\chi_{12}^{t}(\phi,\xi_1)$ for the ternary systems PS + PIB + CH and PS + PIB + benzene. Here, we determine the χ_{ii}^{b} functions for the PIB + CH and PS + benzene systems from light-scattering data and for the PIB + benzene from osmotic pressure data. The equation for χ_{11}^{b} of the PS + CH system has already been established by Einaga et al.[14]

Figures 8 and 9 illustrate the ϕ dependence of $L_{ii}/2$ for the binary systems PIB + CH and PS + benzene, respectively. The graphs for those polymer + good solvent systems have the following features in common: (i) The $L_{ii}/2$ value at infinite dilution is much smaller than 0.5, in contrast to the poor solvent + polymer system in which

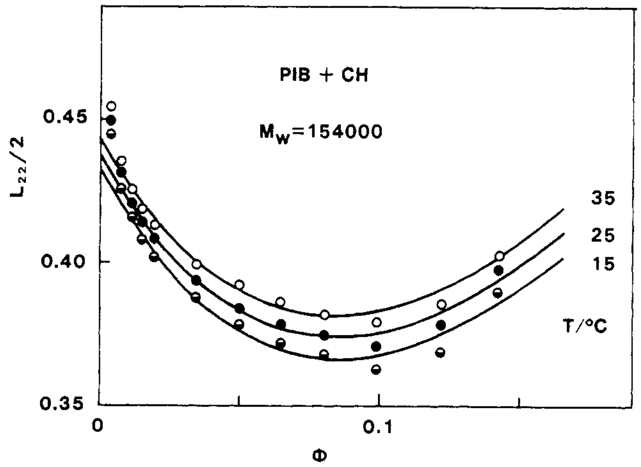

Figure 8. Plots of $L_{22}/2$ vs ϕ for PIB sample U-1 in CH at the indicated temperatures. Solid lines are calculated with eq 14.

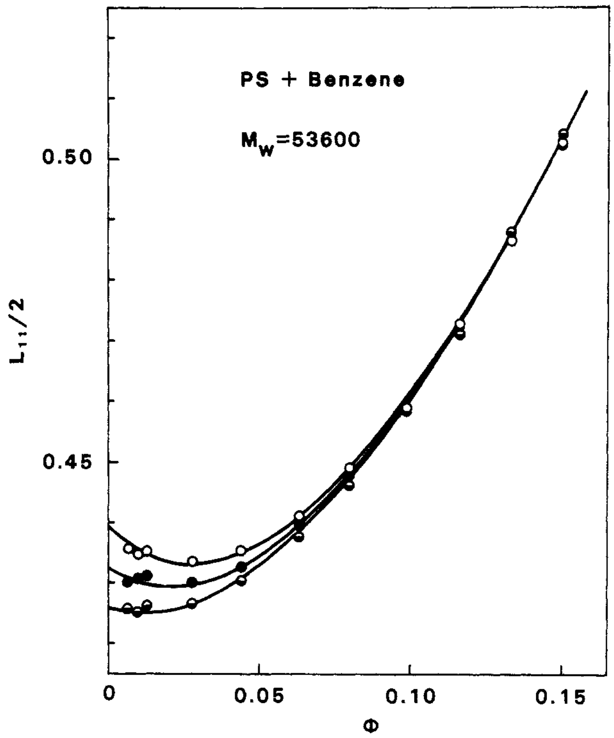

Figure 9. Plots of $L_{11}/2$ vs ϕ for PS sample F4′ in benzene: ○, 35; ●, 25; ◒, 15 °C. Solid lines are calculated with eq 15.

it is larger than 0.5 at temperatures below the θ temperature.[14,16] (ii) There appears a distinct minimum in the $L_{ii}/2$ vs ϕ curve at any temperature as reported for PS in toluene,[15] while $L_{ii}/2$ for the poor solvent + polymer systems, such as PS + CH[14] and PIP + dioxane,[16] increases monotonically with ϕ. These features are similar to those found in the PS + PIP + CH system.[10]

The above observations for the $L_{ii}/2$ vs ϕ curves suggest that L_{ii} can be formulated by using two functions $L_{\rm conc}$ and Q, the former increasing monotonically and the latter asymptotically decreasing to zero with increasing ϕ:

$$L_{ii} = L_{\rm conc} + (L^0_{\rm dil} - L^0_{\rm conc})Q \tag{13}$$

where $L^0_{\rm dil}$ and $L^0_{\rm conc}$ are the values of L_{ii} and $L_{\rm conc}$ at $\phi = 0$, respectively. The second term in this equation is considered to result from both the dilute-solution and excited-volume effects as pointed out by Koningsveld et al.[17]

Assuming a quadratic function of $L_{\rm conc}$ as to ϕ, we determined it to fit the data at sufficiently high concentrations. The $L_{\rm conc}$ function automatically gave the $L^0_{\rm conc}$ value. Then, we subtracted $L_{\rm conc}$ from the observed value of L_{ii} at fixed ϕ and calculated Q from the ratio of the difference to $(L^0_{\rm dil} - L^0_{\rm conc})$, where $L^0_{\rm dil}$ was evaluated by smooth extrapolation of the L_{ii} data to infinite dilution. The equation for Q, which should approach unity as $\phi \rightarrow 0$ and decrease monotonically to zero with increasing ϕ, was determined. The parameters in the empirical equation of L_{ii} were obtained as functions of T from the L_{ii} data taken at different temperatures. A possible P_i dependence of L_{ii} was beyond the present analysis, since only one polymer sample was experimentally treated in each binary system.

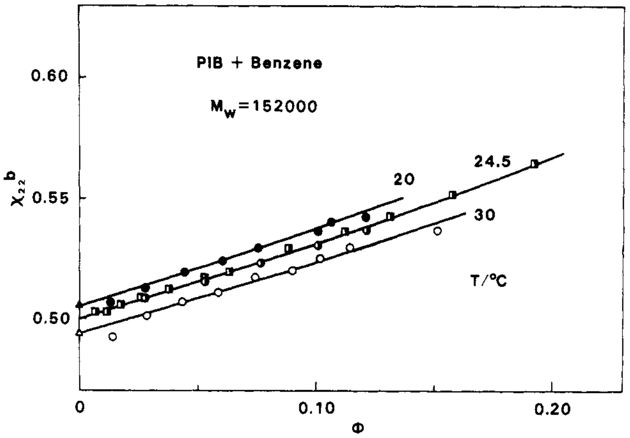

Figure 10. Experimental values of χ_{22}^b plotted against ϕ for PIB in benzene. Circles, this work; ◨, Flory and Daoust[19] (24.5 °C, M_n = 84 200); ▲ and △, Krigbaum and Flory[18] (20 and 30 °C, M_n = 101 000). Solid lines are calculated with eq 17.

Our final equations for L_{ii} obtained by a trial-and-error method are summarized as follows:

For PIB(U-1) + CH

$$L_{ii} = 0.13 + 0.0017T + 6\phi^2 + (1.05 - 0.0017T - 90/T)\exp(-15\phi) \tag{14}$$

For PS(F4′) + benzene

$$L_{ii} = 0.82 + 0.48\phi + 5\phi^2 + (-0.36 + 0.00136T)\exp(-26\phi) \tag{15}$$

These equations yield a close fit to the L_{ii} data as shown by the solid lines in Figures 8 and 9. The $L_{ii}(\phi)$ equations give $\chi_{ii}^b(\phi_i)$ by

$$\chi_{ii}^b(\phi_i) = (1/\phi_i^2)\int_0^{\phi_i} L_{ii}(u)u\,{\rm d}u \tag{16}$$

The values of χ_{22}^b for the PIB(U-2) + benzene system obtained from the osmotic pressure measurements are plotted against PIB volume fraction ϕ in Figure 10, together with the data of Flory and co-workers.[18,19] The present data are in good agreement with theirs. It is seen that the χ_{22}^b values at each temperature increase with ϕ following a curve slightly bent upward and those at fixed ϕ decrease with increasing temperature. These data can be approximated by a quadratic equation of ϕ_2 $(=\phi_{\rm PIB})$:

$$\chi_{22}^b = 0.5 + 0.34(\Theta/T - 1) + [0.29 + 0.72(\Theta/T - 1)]\phi_2 + 0.2\phi_2^2 \tag{17}$$

where Θ is the Θ temperature (297.65 K)[12] for this system. The solid lines in Figure 10 represent the χ_{22}^b values calculated by this equation, which fit the data points closely.

Light Scattering on the Ternary Systems. The $KV_0\phi/\Delta R_0$ data for the ternary systems PS(F4′) +

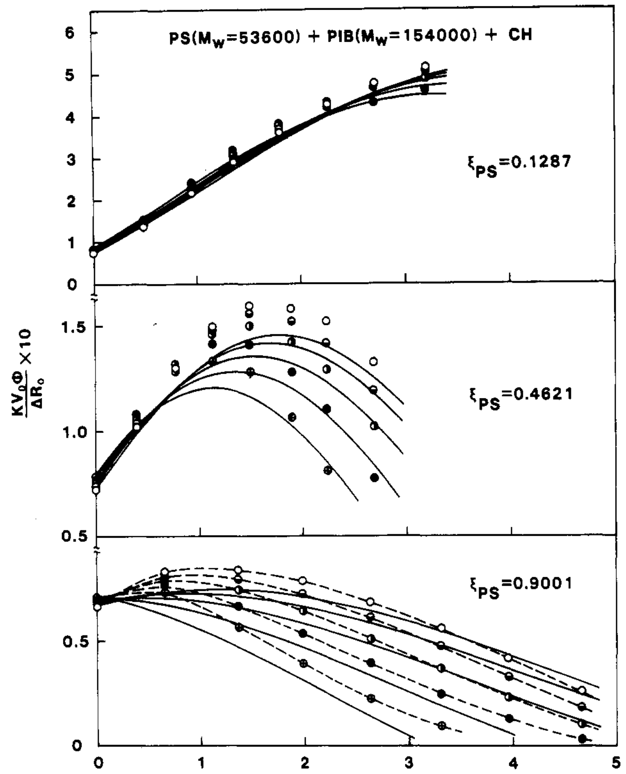

Figure 11. Concentration dependence of $KV_0\phi/\Delta R_0$ for the PS(F4′) + PIB(U-1) mixtures with indicated ξ_{PS} in CH: ○, 34.5; ⊖, 30; ◑, 25; ●, 20; ⊕, 15 °C. Solid lines are calculated values; dashed lines are fit to the experimental data.

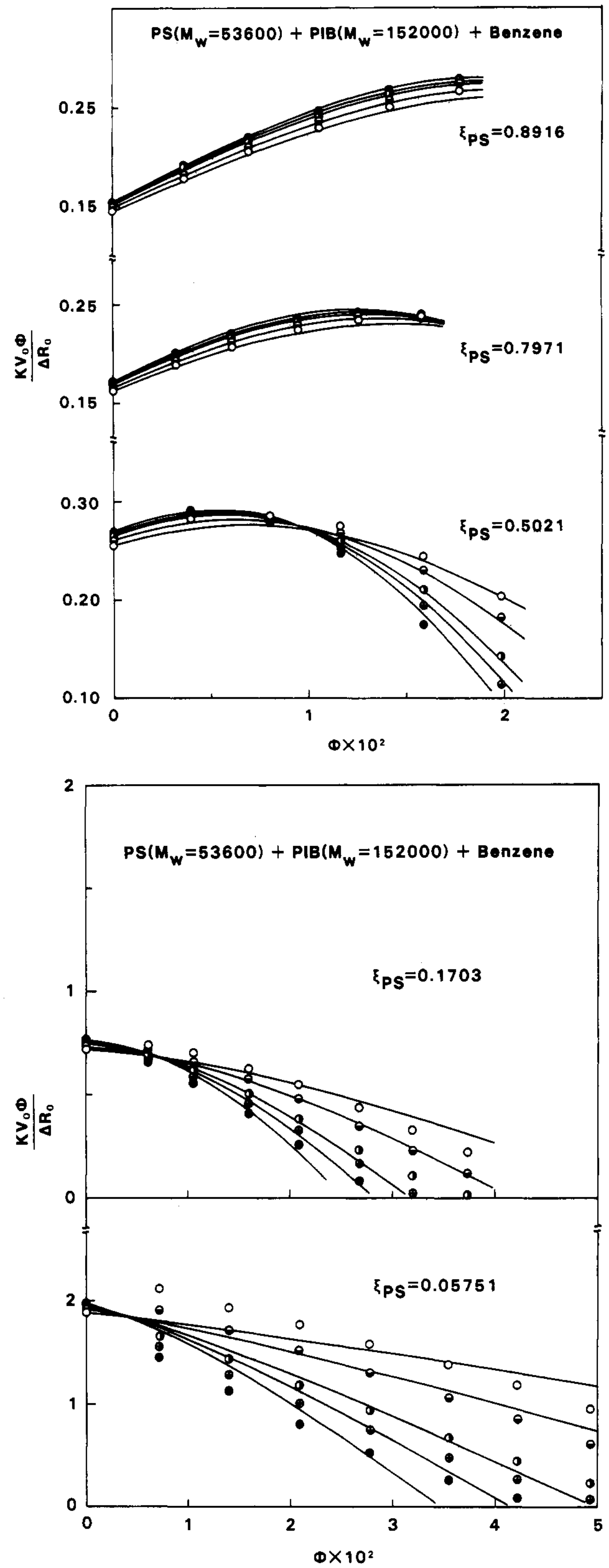

Figure 12. Concentration dependence of $KV_0\phi/\Delta R_0$ for the PS(F4′) + PIB(U-2) mixtures with indicated ξ_{PS} in benzene: ○, 35; ⊖, 30; ◑, 25; ⊕, 23; ●, 21 °C. Solid lines are calculated values.

PIB(U-1) + CH and PS(F4′) + PIB(U-2) + benzene are plotted against ϕ in Figures 11 and 12, respectively. The $\bar{P}^{-1}$ values on the ordinate axis were computed from

$$\bar{P} = \gamma_1^2 P_1 \xi_1 + \gamma_2^2 P_2 \xi_2 \qquad (18)$$

with the known values of P_i and γ_i. They vary with temperature through the temperature dependence of γ_i.

As was found for the PS + PIP + CH system,[10] the ϕ dependence of $KV_0\phi/\Delta R_0$ significantly varies with the composition of the polymer mixture. At $\xi_{PS} \approx 0.5$, $KV_0\phi/\Delta R_0$ first increases from the $\bar{P}^{-1}$ value, passes through a broad maximum, and then decreases with increasing ϕ at any T. The ϕ value at which $KV_0\phi/\Delta R_0$ becomes maximum decreases with increasing T. At small ξ_{PS} for the PS + PIB + CH system or at large ξ_{PS} for the PS + PIB + benzene system, $KV_0\phi/\Delta R_0$ at fixed T monotonically increases following a curve slightly bent downward up to the highest ϕ examined, which is very close to the cloud-point concentration. For ξ_{PS} close to unity, $KV_0\phi/\Delta R_0$ for the PS + PIB + CH system asymptotically approaches zero with increasing ϕ. The curve fitting the data set at a given T gradually changes from convexity to concavity upon lowering T or increasing ϕ, as shown by the dashed lines in Figure 11. Similar behavior is observed in Figure 12 for the PS + PIB + benzene system, when ξ_{PS} is close to zero. The shape of the $KV_0\phi/\Delta R_0$ vs ϕ curve at fixed T also varies with changing ξ_{PS}, as illustrated in Figure 13. A similar finding was reported on the PS + PIB + toluene system by van den Esker et al.[20]

As pointed out in our previous paper,[10] the general theory of light scattering for ternary solutions only provides an integro-differential equation for $\chi_{12}{}^{t}$ after the empirical equations of $\chi_{ii}{}^{b}$ are substituted. Thus, values of $\chi_{12}{}^{t}$ at finite polymer concentrations cannot be directly obtained from experimental $KV_0\phi/\Delta R_0$ data. Further, no information is available in advance about the form of $\chi_{12}{}^{t}$ as a function of ϕ and ξ_1. Therefore, we assume a working equation

$$\chi_{12}{}^{t} = k_0 + [k_1\xi_1 + k_2(1 - \xi_1)]\phi \qquad (19)$$

which may be regarded as a truncated form of the general expansion of $\chi_{12}{}^{t}$ in powers of ϕ, and tried to evaluate k_0,

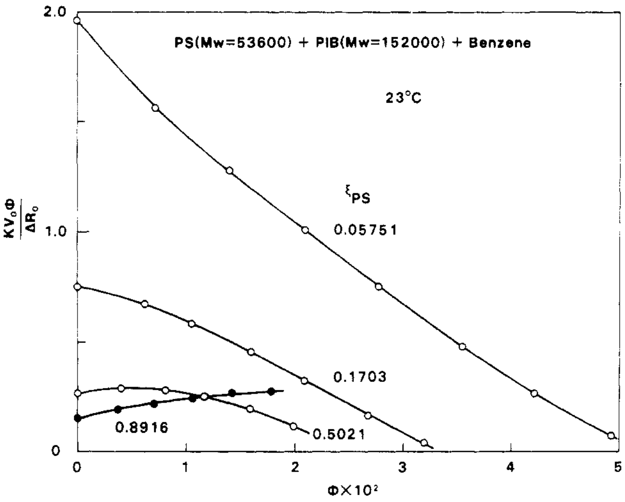

Figure 13. Concentration dependence of $KV_0\phi/\Delta R_0$ for the PS(F4′) + PIB(U-2) mixtures with indicated ξ_{PS} in benzene at 23 °C.

k_1, and k_2 so as to optimize the agreement between calculated and observed values of $KV_0\phi/\Delta R_0$ in a relatively concentrated region. The results so obtained are

$$k_0 = 0.348 + 30/T, \quad k_1 = -4.5 + 1507/T, \quad k_2 = -0.9 \tag{20}$$

for the PS + PIB + CH system and

$$k_0 = 0.454, \quad k_1 = -0.7, \quad k_2 = 0.1 \tag{21}$$

for the PS + PIB + benzene system.

In these two systems, k_0 takes values of about 0.45 at ambient temperature, and k_i (i = 1 or 2) is positive or negative depending on whether the solvent is poor or good for polymer i. The solid curves in Figures 11 and 12 represent the calculated $KV_0\phi/\Delta R_0$ values. As can be seen, they well describe the observed features, especially the variation of $KV_0\phi/\Delta R_0$ with T and ξ_{PS} and the concentration dependence of $KV_0\phi/\Delta R_0$ at fixed T and ξ_{PS}. Though the fit is yet not complete, the largest discrepancy remains within about 10% in both systems.

Calculated Binodals. Compositions of two separated phases in equilibrium can be calculated by simultaneously solving the phase equilibrium conditions, i.e., $\mu_0' = \mu_0''$ and $\mu_i' = \mu_i''$ (i = 1, 2), where μ_i represents the chemical potential of component i and single and double primes signify the conjugated dilute and concentrated phases. These equations contain two sets of unknown composition variables (ϕ', ξ_1') and (ϕ'', ξ_1'') for two equilibrated phases at a given temperature, after the $\chi_{11}{}^{b}$, $\chi_{22}{}^{b}$, and $\chi_{12}{}^{t}$ equations corresponding to a given ternary system have been substituted. In this work, we computed ϕ', ϕ'', and ξ_1'' for each given value of ξ_1' at fixed T to an accuracy of better than ±0.001% for each of three equilibrium conditions.

The calculated binodal curves and tie lines for the PS + PIB + CH and PS + PIB + benzene systems are depicted in Figures 14 and 15, respectively, together with the observed results. It can be seen that for both systems, the agreement between calculated and observed binodal curves is almost quantitative and the calculated tie lines change their direction with temperature as do the experimental ones. The calculations correctly describe the experimental finding that the shape of the binodal curves and the direction of the tie lines for the same PS + PIB pair vary with the solvent used. This implies that our χ expressions for these ternary systems correctly take into account the solvent affinity to the two polymer components.

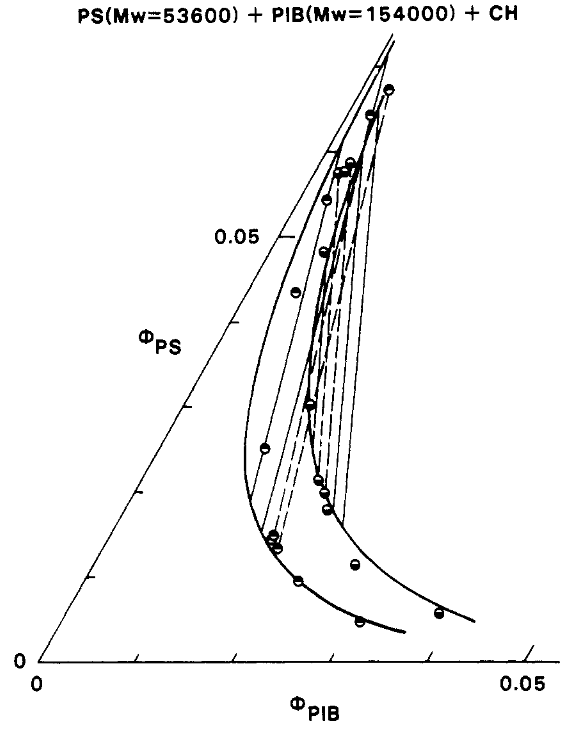

Figure 14. Comparison of calculated and observed binodals and tie lines for the PS(F4′) + PIB(U-1) + CH system. Circles are observed binodals: ◒, 30; ◓, 20 °C. Thick solid lines are calculated binodals; thin solid lines are calculated tie lines; dashed lines are observed tie lines.

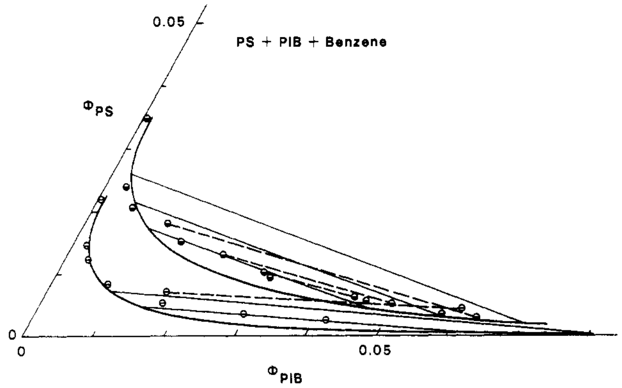

Figure 15. Comparison of calculated and observed binodals and tie lines for the PS(F4′) + PIB(U-2) + benzene system. Circles are observed binodals: ◒, 30; ⊖, 20 °C. Thick solid lines are calculated binodals; thin solid lines are calculated tie lines; dashed lines are observed tie lines.

However, we can see some quantitative deviations of the calculated results from the observations. At $\xi_{PS} > 0.5$ for the PS + PIB + CH system or at $\xi_{PS} < 0.5$ for the PS + PIB + benzene system, the predicted binodal curves are more round than the observed ones. Since the critical points roughly estimated by extrapolating the midpoints of the tie lines to the binodal curve are located in these ξ_{PS} regions, this difference may have something to do with critical phenomena that cannot be described by classic thermodynamic theory.

$\chi_{ii}{}^{b}$ and $\chi_{12}{}^{t}$ Functions. Our empirical expressions for the $\chi_{ii}{}^{b}$ and $\chi_{12}{}^{t}$ functions are found to give an almost quantitative prediction of the phase relationships observed for the ternary polymer systems. Here, we investigate effects of solvent quality and composition of a given solution on these functions. The interaction function $\chi_{ii}{}^{b}$ and $\chi_{12}{}^{t}$ are exactly related to the binary cluster integral at infinite dilution and to the higher order cluster integrals

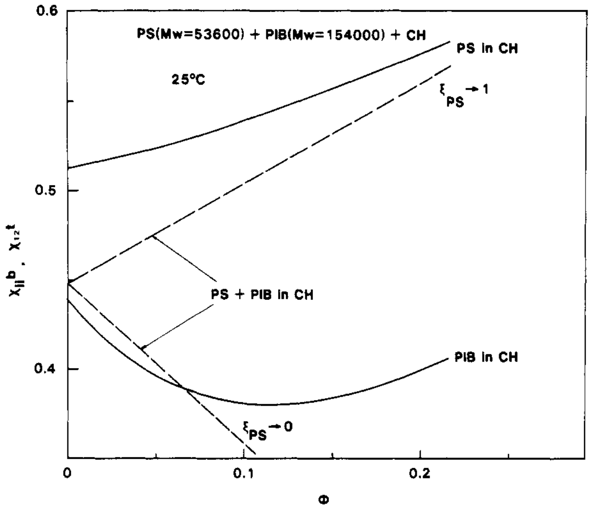

Figure 16. Calculated values of χ_{ii}^b (solid lines) are χ_{12}^t (dashed lines) plotted against ϕ for the systems PS + CH,[14] PIB + CH (eq 14 and 16), and PS + PIB + CH (eq 20).

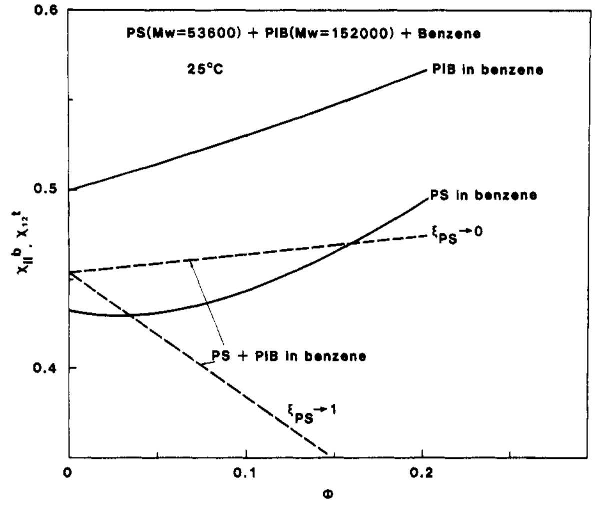

Figure 17. Calculated values of χ_{ii}^b (solid lines) and χ_{12}^t (dashed lines) plotted against ϕ for the systems PS + benzene (eq 15 and 16), PIB + benzene (eq 17), and PS + PIB + benzene (eq 21).

at higher concentrations for the same and different polymer species, respectively.[9,21]

Figures 16 and 17 depict χ_{ii}^b and χ_{12}^t calculated for the binary and ternary systems at 25 °C as functions of ϕ. The χ_{ii}^b value is larger for the poor solvent + polymer binary system than for the good solvent + polymer one when compared at a fixed ϕ. It is seen that χ_{ii}^b for each binary system follows a curve convex downward, with more significant curvature for the latter than for the former. The curve for the latter system exhibits a minimum at a certain concentration.

The two dashed lines in each figure show the upper and lower bounds of χ_{12}^t as ξ_{PS} approaches unity or zero. Hence χ_{12}^t at fixed ϕ should vary with ξ_{PS} between these lines. At low concentrations, χ_{12}^t assumes a value between χ_{11}^b and χ_{22}^b depending on ξ_{PS}. For the same PS + PIB mixture, χ_{12}^t at a given ϕ increases in CH but decreases in benzene with increasing ξ_{PS}. This different ξ_{PS} dependence of χ_{12}^t for the two ternary systems indicates that this interaction function depends not only on incompatibility between two polymer components but also on the difference in solvent affinity to them. χ_{12}^t at a finite concentration increases with the composition of the polymer component for which the solvent is poor.

Generally speaking, it is a difficult task to determine a polymer–polymer interaction parameter as a function of the composition of a given ternary polymer solution. The present paper along with the previous one[1] demonstrates that our experimental method allows us to determine the interaction function for two chemically different polymers in solution with sufficient accuracy, thereby predicting the phase relationships correctly.

Registry No. PS, 9003-53-6; PIB, 9003-27-4; CH, 110-82-7; benzene, 71-43-2.

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