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Phase Equilibrium in Polymer + Polymer + Solvent Ternary Systems. 2. Phase Diagram of Polystyrene + Polyisoprene + Cyclohexane

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ABSTRACT: Polystyrene (PS) and polyisoprene (PIP) are incompatible, and cyclohexane (CH) is a poor solvent for the former and a good one for the latter. Cloud point curves and binodals of the ternary system consisting of these components were determined as functions of the mixing ratio of the two polymers. It was found that the addition of PIP drastically changed the cloud points of PS + CH solutions. The χ function previously determined for this ternary system by light scattering was used to calculate cloud point curves and binodals, and the results were found to predict the experimental data almost quantitatively.

Phase diagrams on the composition triangle for ternary systems consisting of two chemically different polymers and a pure solvent may vary with the compatibility of the polymer components as well as the affinity of the solvent to them. An incompatible polymer pair in an ordinary solvent good for both polymer components gives binodals with the tie lines parallel to the polymer–polymer edge of the triangle, as has been shown by Narasimhan et al.[1,2] for polystyrene (PS) + polybutadiene in toluene or tetrahydrofuran. The main thermodynamic factor leading to this type of phase separation is the repulsive interaction of the polymer components. Closed binodals were observed by Patterson an co-workers[3,4] when they allowed a miscible polymer blend PS + poly(vinyl methyl ether) to be phase-separated in trichloroethene or chloroform. This type of phase separation is essentially caused by what they referred to as the "$\Delta\chi$ effect", which is concerned with the difference in affinity of the solvent to the polymer components. Quantitative description of these phase equilibria requires evaluation of the χ parameter as a function of the composition and the temperature, but no such work is as yet done.

In part 1[5] of this series, we made a light-scattering evaluation of χ for a ternary system containing PS and polyisoprene (PIP) in cyclohexane (CH). The present paper compares the predictions of the χ function so obtained with measured phase diagrams. PS and PIP are incompatible, and CH is a good solvent for PIP but a poor one for PS. Hence, we expected that this ternary system would exhibit phase equilibria which differ much from those of the systems mentioned in the preceding paragraph.

Experimental Section

The narrow-distribution PS and PIP samples, designated F4 and P-5 in part 1,[5] were used for the present experiment aiming at the measurement of phase separation behavior. The weight-average molecular weights determined by light scattering were 43 900 for F4 and 53 300 for P-5. The relative chain length P_i of component i calculated by

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

was 377 for F4 and 537 for P-5. Here, M_i and v_i are the molecular weight and specific volume of component i, respectively, with i = 0, 1, 2 corresponding to CH, PS, and PIP, respectively. The values used for v_i were 1.2923,[6] 0.9343,[7] and 1.0951[8] cm^3 g^{-1} for i = 0, 1, and 2, which were referred to 25 °C.

Solutions for cloud point measurements were prepared in the following way. First, proper amounts of dry PS and PIP were mixed at a desired ratio and dissolved in CH. The solution was divided into several parts by pouring it into cylindrical cells. This operation was performed in a heated box to prevent segregation of the polymer components. Then, the solution in each cell was freeze-dried to remove the solvent. Finally, a desired amount of carefully purified CH was added to the cell, which was then sealed.

The total volume fraction ϕ of the polymer mixture (PS + PIP) in the test solution so prepared was calculated from the relation

$$\phi = [1 + v_0(\omega_1 v_1 + \omega_2 v_2)^{-1}(w^{-1} - 1)]^{-1} \tag{2}$$

where w is the total weight fraction of the polymer mixture and ω_i the weight fraction of component i in this mixture. The volume fraction ξ_1 of PS in the polymer mixture was computed by

$$\xi_1 = [1 + (v_2/v_1)(\omega_1^{-1} - 1)]^{-1} \tag{3}$$

Cloud points were determined by the same method as described elsewhere.[9] The cell containing a test solution was mounted on a metal rack suspended in a thermostatically controlled water bath. The solution was warmed until it became homogeneous and then allowed to cool naturally under continuous stirring. The intensity of He–Ne laser transmitted through the solution was monitored as a function of temperature, and the cloud point was determined as the temperature at which the light intensity decreased sharply.

Phase separation experiments were carried out at 15 and 30 °C. The composition of the separated phases was determined in the following way. A uniform solution of known ϕ and ξ_1 was allowed to cool slowly under continuous stirring to either of the above temperatures for phase separation. The attainment of the phase equilibrium was checked by observing the height of the phase boundary which became stationary. Samples of the solutions in two equilibrated phases were carefully drawn with dry syringes. The total polymer concentrations of the separated phases were determined from the weights of the phases and of the polymer mixtures recovered from them by freeze-drying. The composition of each polymer mixture was estimated by using the relation[10,11]

$$[\eta] = \omega_1[\eta]_1 + (1 - \omega_1)[\eta]_2 \tag{4}$$

where $[\eta]$, $[\eta]_1$, and $[\eta]_2$ are the intrinsic viscosities of PS + PIP, PS, and PIP in CH at 25 °C. Values of $[\eta]_1$ and $[\eta]_2$ were 15.8 and 55.3 cm^3 g^{-1}, respectively.

Results

Cloud Point Curves. Figure 1 depicts cloud point curves for PS + PIP + CH ternary solutions in which ξ_1 is fixed at different values from 0.019 to 1.00 (in the figure, the symbol ξ_{PS} is used instead of ξ_1 to help read the graph). It can be seen that the cloud point curves for different ξ_{PS} are nearly parallel with the T (temperature) axis at T above 15 °C. The marked difference between these curves for ξ_{PS} = 1.00 and 0.989 is worth noting, indicating that the addition of a very small amount of PIP drastically changes the phase separation behavior of the PS + CH binary system in the region above the critical concentration. This effect may be attributed to the incompatibility of PS with PIP which is hardly mitigated by raising temperature, but we must ask ourselves why it becomes so profound only above the critical concentration.

At T above 15 °C, the cloud points first move toward lower concentration and then turn toward higher concen-

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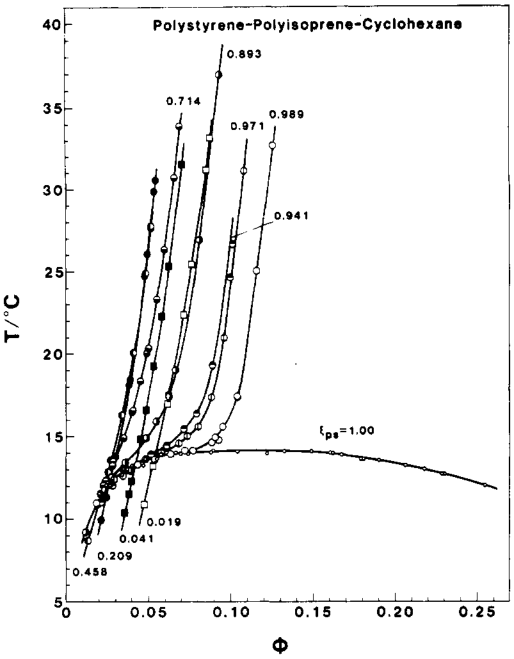

Figure 1. Observed cloud point curves for PS + PIP mixtures of indicated compositions in CH.

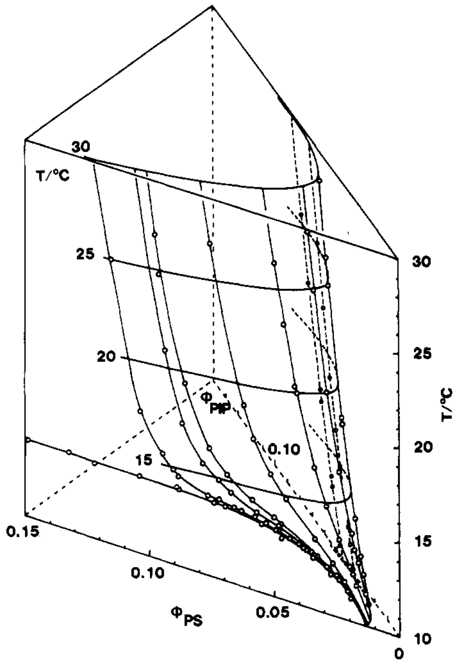

Figure 2. Three-dimensional representation of the binodal surface for the PS + PIP + CH ternary system. Circles, experimental data.

tration as ξ_{PS} increases from 0.019 to 0.989, with the lowest concentration appearing at $\xi_{PS} \sim 0.5$. The cloud point curves below 15 °C show different behavior, depending on whether ξ_{PS} is above or below this critical value. Those for $\xi_{PS} < 0.5$ penetrate into the demixing region for the PS + CH system, while those for $\xi_{PS} > 0.5$ tend to merge with the cloud point curve for this system as the concentration is lowered.

Binodals. Figure 2 illustrates a three-dimensional representation of the binodal surface constructed from the data of Figure 1. Here we have used ϕ_{PS} and ϕ_{PIP} for ϕ_1 and ϕ_2 to help read the graph. The following features should be observed. First, the demixing region, i.e., the space below the binodal surface, spreads from a point near the CH apex toward the PS–PIP edge. Single-phase solutions can appear only in the dilute region and the narrow wedgelike regions very close to the ϕ_{PS}–T and ϕ_{PIP}–T planes. Second, the binodal surface below 15 °C has a shelf near the ϕ_{PS}–T plane. This feature is related to the fact that the F4 + CH binary system has its upper critical temperature at 14.4 °C.

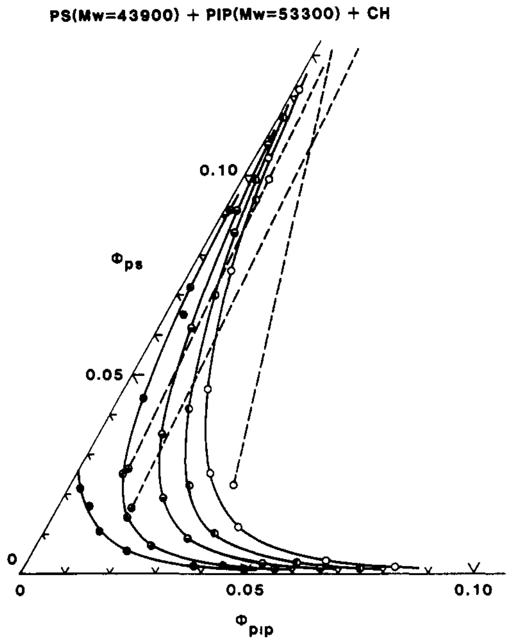

Figure 3. Binodals for the PS + PIP + CH ternary system: (- - -) tie line; (—) experimental binodal curve; (○) 30, (◐) 25, (⊖) 20, (⊕) 15, and (●) 12 °C.

Binodal curves for a ternary system can be found by cutting the binodal surface with constant temperature planes. The solid lines in Figure 3 show the binodal curves so obtained at 12, 15, 20, 25, and 30 °C from Figure 2, along with the tie lines (dashed lines) determined from phase separation data at 15 and 30 °C. As can be expected, the demixing region shrinks more gradually with increasing temperature. The tie lines connect distinctly different phases, one relatively dilute and the other highly concentrated. Their inclination relative to the ϕ_{PS} edge tends to zero with decreasing temperature. This behavior is in marked contrast with that observed by Narasimhan et al.[1,2] for PS + polybutadiene (PB) in tetrahydrofuran or toluene, in which the tie lines were nearly parallel with the PS–PB edge, though the binodals were very similar to those in Figure 3.

Discussion

Thermodynamic Relations. The separation factor σ_i for polymer i is defined by[12]

$$\sigma_i = P_i^{-1} \ln (\phi_i''/\phi_i') \tag{5}$$

where single and double primes indicate the dilute and concentrated phases in thermodynamic equilibrium. With the phase equilibrium relations for components 0, 1, and 2 in our ternary system, it can be shown that σ_1 and σ_2 are expressed as

$$\sigma_1 = \Delta\left\{\ln (1 - \phi) + \phi\chi + \int_0^{\phi} [\chi(u, \xi_1) + (1 - \xi_1) \times (\partial\chi(u, \xi_1)/\partial\xi_1)] \, du\right\} \tag{6}$$

$$\sigma_2 = \Delta\left\{\ln (1 - \phi) + \phi\chi + \int_0^{\phi} [\chi(u, \xi_1) - \xi_1(\partial\chi(u, \xi_1)/\partial\xi_1)] \, du\right\} \tag{7}$$

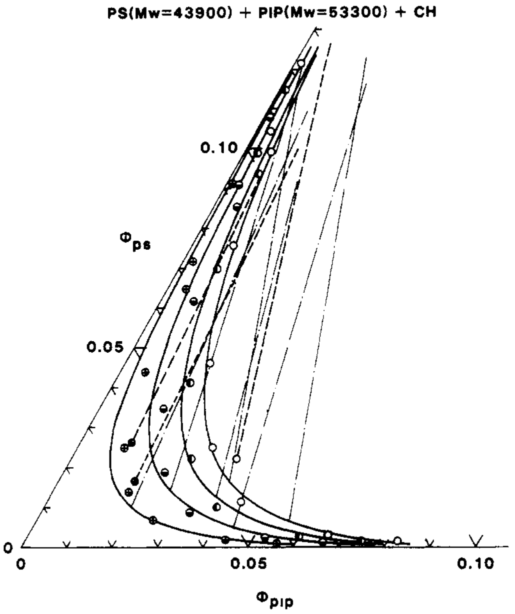

Figure 4. Comparison of calculated and observed binodals and tie lines: (—) calculated binodal curve; (-·-), calculated tie line; (- - -) observed tie line; circles, observed binodals; (○) 30, (◐) 25, (◒) 20, and (⊕) 15 °C.

where ΔX signifies the difference $X'' - X'$ and χ is a function of T and composition which is defined by

$$\Delta\mu_0/RT = \ln(1-\phi) + (1-P_n^{-1})\phi + \phi^2\chi \qquad (8)$$

with

$$P_n^{-1} = \xi_1 P_1^{-1} + (1-\xi_1)P_2^{-1} \qquad (9)$$

and $\Delta\mu_0$ being the chemical potential of the solvent in the system relative to that of the pure solvent.

Equation 8 substituted into the phase equilibrium relation $\Delta\mu_0' = \Delta\mu_0''$ and eq 5 combined with eq 6 and 7 give a set of three equations for five variables, ϕ_i', ϕ_i'' (i = 1, 2), and T. These equations along with one relation expressing the conservation of mass allow the compositions of the dilute and concentrated phases separated from a given "mother solution" at a given T to be calculated. Such calculations for a series of mother solutions and T make it possible to construct a binodal surface.

Calculated Phase Diagrams. We carried out this operation with the empirical expression of χ derived of our PS + PIP + CH ternary system in part 1[5] of the series. Here, the χ function was given by

$$\chi = \xi_1^2\chi_{11}^{b}(\phi_1) + (1-\xi_1)^2\chi_{22}^{b}(\phi_2) + 2\xi_1(1-\xi_1)\chi_{12}^{t}(\phi, \xi_1) \qquad (10)$$

where $\chi_{ii}^{b}(\phi_i)$ is the χ function for solvent 0 + polymer i binary solution and represents the interaction between polymer i molecules in solution. The χ_{12}^{t} function represents the contribution due to the interaction between polymers 1 and 2 in the ternary solution. Three interaction functions were determined from light-scattering experiments on the respective binary and ternary polymer solutions. In Figure 4, the solid curves illustrate the binodals so obtained at 15, 20, 25, and 30 °C and the dot-dash lines some associated tie lines. The points and the dashed lines here show the experimental results reproduced from Figure 3. It can be seen that the calculated binodals fit the data points fairly closely and the calculated tie lines change their direction with temperature as do the experimental ones.

Figure 5 shows the predicted cloud point curves and corresponding shadow curves for various compositions of the polymer mixture PS + PIP. When compared with Figure 1, the former display the overall features of the experimental results, i.e., the cloud point temperature increases very sharply with the polymer concentration ϕ in the region above 15 °C, and the cloud point curves for ξ_{PS} < ~0.6 penetrate into the demixing region for the PS + CH system, whereas those for ξ_{PS} > ~0.6 converge to the cloud point curve for this binary system as ϕ is decreased.

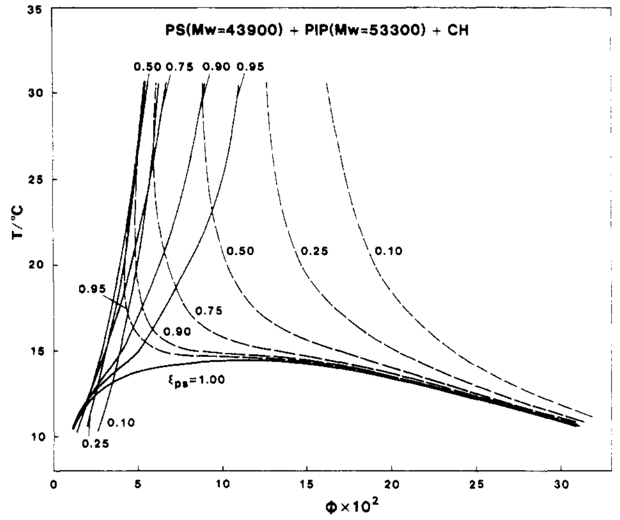

Figure 5. Calculated cloud point (—) and shadow curves (- - -) for the PS + PIP + CH ternary solutions of indicated ξ_{PS}.

Detailed comparison, however, reveals that the agreement between predicted and experimental results is not quantitatively satisfactory. For example, in the range from 15 to 22 °C, the calculated cloud points for ξ_{PS} > 0.90 appear at concentrations lower than the measured ones. Such discrepancy is not unexpected because our χ function is approximate in that its χ_{12}^{t} part associated with the interaction between PS and PIP was evaluated only roughly.

From the results obtained above, we see that even the approximate empirical χ function determined by light scattering in part 1[5] is capable of explaining the phase separation behavior of our PS + PIP + CH ternary system rather satisfactorily. To the best of our knowledge, this work is the first demonstraton of the (semiquantitative) predictability of the binodals and cloud point curves of a ternary system containing two chemically different polymers in a pure solvent, though model calculations impertinent to experimental observations were already reported.[13] We are being engaged in a similar study on the system consisting of PS, polyisobutylene (PIB), and benzene. Here, PS and PIB are incompatible, and benzene is a good solvent for the former and a poor one for the latter. The results will be reported in the following parts of this series.

Registry No. PS, 9003-53-6; PIP, 9003-31-0; CH, 110-82-7.

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Concentration Fluctuations in Polymer–Polymer–Solvent Systems

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ABSTRACT: We examine the dynamics of concentration fluctuations and spinodal decomposition in ternary systems composed of two polymers and a single solvent, assumed to be well-described by the Flory–Huggins model. The dynamic light-scattering spectrum in the one-phase region is calculated for systems in which one of the polymers is isorefractive with the solvent. It is shown that the spectrum in this case is well represented, in the limit $qR_G < 1$, by a sum of two exponentials. Only in the limit where the probe species is infinitely dilute does single-exponential behavior occur. Recent experimental results showing nonsingle-exponential behavior and in some cases the existence of two distinct modes of decay are discussed in light of these predictions. The theory of spinodal decomposition as formulated for binary systems is extended to the ternary case. It is shown that the light-scattering spectrum will evolve as the sum of three exponentials after quenches into the spinodal region. Recent experimental results are in qualitative agreement with this finding.

Introduction

Concentration fluctuations in polymer–solvent systems have been studied extensively in recent years. Both dynamic and static light scattering techniques have been used to provide much new information on the behavior of dilute and semidilute solutions. These developments, along with numerous theoretical advances, notably the scaling laws,[1] have greatly increased our understanding of polymer–solvent systems in the one-phase region. Much less work has been done on polymer–polymer systems, both as a consequence of the comparative rarity of compatible polymer systems and as a result of the experimental difficulties that arise when studying such systems. Dynamic light scattering has been applied to low molecular weight polymer mixtures as studied recently by Murschall et al.[2] For higher molecular weights, Rutherford back-scattering spectrometry[3] have been found to be extremely useful. While considerable effort is being made to understand polymer–solvent and polymer–polymer systems in the one-phase region, there is also increased interest in the dynamics of phase separation in such systems. In particular, recent developments in the theory of spinodal decomposition in polymer–polymer mixtures have led to several experimental studies.[4–6] de Gennes[7] has shown that for quenches into the spinodal region, the structure factor associated with the total intensity at time t, $\langle|\delta\phi_A(q,t)|^2\rangle$, can be described in the early stages of spinodal decomposition by

$$\langle|\delta\phi_A(q,t)|^2\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-2\tau^{-1}(q)t} \qquad (1)$$

where ϕ_A is the volume fraction of polymer A and the relaxation time, $\tau(q)$, is given by

$$\tau^{-1}(q) = q^2\Lambda(q)\left(\frac{1}{N\phi_A\phi_B} - 2\chi_{AB} + \frac{a^2q^2}{18\phi_A\phi_B}\right) \qquad (2)$$

where q is the scattering wave vector, $\Lambda(q)$ the q-dependent Onsager coefficient of the binary system, N the degree of polymerization of both species, χ_{AB} the Flory interaction parameter, and a the statistical segment length of each polymer. Binder[8] has modified the above approach to take account of random thermal fluctuations and obtains

$$\langle|\delta\phi_A(q,t)|^2\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-2\tau^{-1}(q)t} + \langle|\delta\phi_A(q,\infty)|^2\rangle(1 - e^{-2\tau^{-1}(q)t}) \qquad (3)$$

where $\langle|\delta\phi_A(q,\infty)|^2\rangle$ is the structure factor as $t \rightarrow \infty$. In the early stages of spinodal decomposition and for q-values such that $q < q_c$, q_c being the wave vector at which $\tau(q)$ changes sign, both equations predict that the structure factor will grow exponentially with time for quenches into the spinodal region, but for quenches in the one-phase region, Binder's approach predicts that the structure factor will decay to a finite value $\langle|\delta\phi_A(q,\infty)|^2\rangle$ rather than zero, in agreement with experiment. It should be stressed, however, that both theories are linear in nature and will not be able to describe the later stages of spinodal decomposition where nonlinear effects will be dominant.

The above predictions have largely been confirmed in recent experiments on polymer–polymer phase separation. For example, Snyder et al.[6] have used light scattering to monitor the time evolution of the structure factor after quenches into the spinodal region of a polystyrene–poly(vinyl methyl ether) mixture. In the early stages of spinodal decomposition, a plot of the logarithm of the total intensity vs. time yields a straight line in agreement with the predictions of theory. In the later stages of phase separation considerable deviation occurs due to the increased importance of nonlinear processes.

Less well understood are the dynamics in ternary systems composed of two polymers and a solvent. Recent experiments on both rigid[9] and flexible[10] polymers indicate that the dynamic light scattering spectrum in the one-phase region is well approximated (in the limit $qR_G < 1$ where R_G is the radius of gyration) by a sum of two exponentials. In addition, many authors[11–16] have investigated dynamics in "isorefractive" systems, i.e., systems in which one of the polymer species is refractive-index matched to the solvent and hence presumably contributes very little to the excess scattering from the solution. At very low concentrations of the "optically labeled" or probe species, initial experiments[14] found single-exponential behavior of the correlation function, i.e.,

$$\langle\delta\phi_A(q,t)\delta\phi_A(-q,0)\rangle = \langle|\delta\phi_A(q,0)|^2\rangle e^{-q^2\lambda_1 t} \qquad (4)$$

where λ_1 has been taken to be identical with the tracer

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