Phase Equilibrium in Polymer + Polymer + Solvent Ternary Systems. 1. Light Scattering on Polystyrene + Polyisoprene + Cyclohexane

Zhen Tong, Yoshiyuki Einaga,* Hiraku Miyashita, and Hiroshi Fujita

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan.

Received December 8, 1986

ABSTRACT: Light-scattering measurements were made on polyisoprene (PIP, $M_w = 5.33 \times 10^4$) + cyclohexane (CH) binary solutions and polystyrene (PS, $M_w = 5.36 \times 10^4$ or 4.39×10^4) + PIP + CH ternary solutions in the range from 30 °C down to 10 °C for the former and from 30 °C down close to the cloud point for the latter. The data, along with those from our previous work on PS + CH binary solutions, were used to estimate $\chi_{12}^{t}(\phi_1,\phi_2)$ which appears in our recent formulation leading to $\chi = \xi_1^2\chi_{11}^{b}(\phi_1) + \xi_2^2\chi_{22}^{b}(\phi_2) + 2\xi_1\xi_2\chi_{12}^{t}(\phi_1,\phi_2)$. Here, χ represents the difference of a ternary system consisting of solvent 0 and chemically different polymers 1 and 2 from the Flory–Huggins athermal solution chosen as a reference system and $\chi_{ii}^{b}(\phi_i)$ the χ function for solvent 0 + polymer i, with ϕ_i being the volume fraction of polymer i and $\xi_i = \phi_i/(\phi_1 + \phi_2)$. Though estimated only approximately, χ_{12}^{t} was comparable in magnitude with χ_{11}^{b} and χ_{22}^{b}.

Motivated by either academic or practical interest, many studies have been made on phase equilibria in ternary systems consisting of two chemically different polymers (components 1 and 2) and a common solvent (component 0). One of the central subjects in these efforts has been the use of phase separation data for determination of the χ function of a given system. There, χ characterizes the deviation of the system from a Flory–Huggins athermal solution chosen as the reference system. In typical attempts reported so far, as exemplified by the work of Narasimhan et al.,[1] it was customary to represent χ as a quadratic form of the concentrations of polymers 1 and 2. This maneuver is equivalent to assuming that interaction parameters for pairs of different components are independent of the composition of the system and allows simple relations useful for data analysis to be derived. However, it was shown[1] that such a simplifying assumption failed to hold. This is not surprising in view of the well-known fact that the χ function for binary systems of a polymer and a solvent usually exhibits a significant dependence on concentration.[2] Thus, it is of interest to determine χ for ternary systems of the type considered, making no assumption for its composition dependence.

In a series of papers,[3] Vrij and co-workers applied the light-scattering method to estimate χ for a ternary system consisting of polystyrene (PS), poly(isobutylene), and toluene, but they used the equation for the excess Rayleigh ratio which incorporated the above-mentioned simplifying assumption for χ.

In this paper, we first derive the corresponding equation, leaving χ as a completely general function of the composition of the system; as far as we are aware, no such equation is yet presented in existing literature. We then apply it to light-scattering data on binary mixtures of PS and poly(isoprene) (PIP) in cyclohexane (CH). This ternary system was chosen for the following reasons: (i) narrow-distribution samples are commercially available for both PS and PIP, (ii) CH is a good solvent for PIP but a poor one for PS, and (iii) detailed information on the χ function of the binary system PS + CH is abundant in polymer literature.[2,4–6] Reason i is essential for preparing a well-defined ternary system. Reason ii is associated with our expectation that because of its stronger affinity with CH, PIP should abstract CH molecules from the surroundings of PS coils and thus should significantly affect phase separation of CH solutions of PS. Reason iii is related to the advantage that will be seen below in analyzing our light-scattering data.

Expression for the Excess Rayleigh Ratio

We consider a ternary solution consisting of pure solvent 0 and two monodisperse polymers 1 and 2 (either different or not chemically). For simplicity, we assume that the partial molar volumes of the three components may be treated as independent of system's composition and hence equal to their molar volumes V_i (i = 0, 1, 2). The volume fraction of component i, ϕ_i, is then expressed by

$$\phi_i = P_i n_i/(n_0 + P_1 n_1 + P_2 n_2) \qquad (1)$$

with n_i the amount of component i in moles and P_i the relative chain length of the same component defined as $P_i = V_i/V_0$. The composition of the system can be characterized either by the variables (ϕ_1,ϕ_2) or by the variables (ϕ,ξ_1). Here, ϕ is the overall polymer volume fraction, i.e.,

$$\phi = \phi_1 + \phi_2 \qquad (2)$$

and ξ_1 $(=1 - \xi_2)$ the volume fraction of polymer 1 in the mixture of polymers 1 and 2, i.e.,

$$\xi_1 = \phi_1/(\phi_1 + \phi_2) \qquad (3)$$

If the Flory–Huggins athermal solution composed of the three components considered is chosen as a reference system, the free energy of mixing, ΔG, of our ternary solution can be represented by

$$\Delta G = RT(n_0 + P_1 n_1 + P_2 n_2)[(1 - \phi) \ln (1 - \phi) + \phi_1/P_1 \ln \phi_1 + \phi_2/P_2 \ln \phi_2 + h(\phi_1,\phi_2,T,p)] \qquad (4)$$

where R is the gas constant, T the absolute temperature, p the pressure, and h a function which absorbs all the differences of our solution from the chosen reference one. It follows from eq 4 that the chemical potentials μ_0, μ_1, and μ_2 of solvent 0, polymer 1, and polymer 2 are given by

$$(\mu_0 - \mu_0^{\circ})/RT = \ln (1 - \phi) + (1 - P_n^{-1})\Phi + \chi\phi^2 \qquad (5)$$

$$(\mu_1 - \mu_1^{\circ})/RT = \ln (\phi\xi_1) + 1 - P_1(1 - \phi) - P_1 P_n^{-1}\phi + P_1[h + (1 - \phi)(\partial h/\partial\phi) + \phi^{-1}(1 - \xi_1)(\partial h/\partial\xi_1)] \qquad (6)$$

$$(\mu_2 - \mu_2^{\circ})/RT = \ln [\phi(1 - \xi_1)] + 1 - P_2(1 - \phi) - P_2 P_n^{-1}\phi + P_2[h + (1 - \phi)(\partial h/\partial\phi) - \phi^{-1}\xi_1(\partial h/\partial\xi_1)] \qquad (7)$$

where the superscript ° refers to the pure state of each component and P_n is defined by

$$P_n^{-1} = \xi_1 P_1^{-1} + (1 - \xi_1)P_2^{-1} \qquad (8)$$

The new quantity χ, which is a function of composition, T, and p, is related to h by

0024-9297/87/2220-1883$01.50/0

$$\chi = [h - \phi(\partial h/\partial \phi)_{\xi_1,T,p}]\phi^{-2} \qquad (9)$$

This is the definition of the χ function basic to the interpretation of thermodynamic behavior of our ternary system. Solving eq 9 for $h(\phi,\xi_1)$ and determining an unknown integration function of ξ_1 from the condition that $\mu_i^\infty(T) \equiv \lim_{\phi\to 0}(\mu_i - RT\ln\phi_i)$ $(i = 1, 2)$, we obtain

$$h = -\phi\int_0^\phi \chi(u,\xi_1)\,\mathrm{d}u + \phi[1 - \xi_1/P_1 - (1 - \xi_1)/P_2 + \xi_1(\mu_1^\infty - \mu_1^\circ)/RTP_1 + (1 - \xi_1)(\mu_2^\infty - \mu_2^\circ)/RTP_2] \qquad (10)$$

This equation allows the terms containing h in eq 6 and 7 to be expressed in terms of χ. The second term on the right-hand side disappears in deriving the light-scattering equation, so that the temperature dependence of μ_i° and μ_i^∞ is not a concern.

Now, at fixed T and p, the excess Rayleigh ratio at zero scattering angle, ΔR_0, for the ternary system considered is given by[7] (see the Appendix)

$$\Delta R_0 = KRTM_0V_0(1 - \phi)\sum_{i=1}^{2}\sum_{j=1}^{2}\tilde{\gamma}_i\tilde{\gamma}_jP_iP_j\Delta_{ij}/|\Delta| \qquad (11)$$

Here, K is a constant, M_0 the molar mass of the solvent,

$$\tilde{\gamma}_i = \gamma_i - \sum_{k=1}^{2}\gamma_k\phi_k \qquad (12)$$

with γ_i being the volume-fraction-basis refractive index increment of the system and Δ_{ij} the cofactor of the element μ_{ij} in the determinant

$$|\Delta| = \begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \qquad (13)$$

where

$$\mu_{ij} = (\partial\mu_i/\partial m_j)_{m_k} \qquad (14)$$

with m_i being the molality of component i. We note that eq 11 contains an important assumption that γ_i is independent of composition. Usually, this is a good approximation as far as we are concerned with relatively dilute solutions as treated in the present experimental work.

With eq 6 and 7 substituted into eq 11 and complicated algebra carried through (see the Appendix for some details), it is possible to derive the following expression for the experimentally measurable quantity $KV_0\phi/\Delta R_0$:

$$KV_0{}^\phi/\Delta R_0 = [1 + \phi(1 - \phi)^{-1}P_w - \phi(P_wL + Y)]/WX \qquad (15)$$

where

$$W = (\tilde{\gamma}_1{}^2P_1\xi_1 + \tilde{\gamma}_2{}^2P_2\xi_2)/(1 - \phi)^2 \qquad (16)$$

$$X = 1 + (\tilde{\gamma}_1{}^2P_1\xi_1 + \tilde{\gamma}_2{}^2P_2\xi_2)^{-1}\xi_1\xi_2[(\tilde{\gamma}_1 - \tilde{\gamma}_2)^2P_1P_2[1 + (P_n{}^{-1} - 1)\phi]\phi - 2(\tilde{\gamma}_1 - \tilde{\gamma}_2)(\tilde{\gamma}_1P_1 - \tilde{\gamma}_2P_2)\phi - (\tilde{\gamma}_1 - \tilde{\gamma}_2)^2P_1P_2(1 - \phi)^2\phi L + 2(\tilde{\gamma}_1 - \tilde{\gamma}_2) \times (\tilde{\gamma}_1\xi_1 + \tilde{\gamma}_2\xi_2)P_1P_2(1 - \phi)\phi M + (\tilde{\gamma}_1\xi_1 + \tilde{\gamma}_2\xi_2)^2P_1P_2N] \qquad (17)$$

$$Y = \xi_1\xi_2[2(P_1 - P_2)M - P_1P_2[(1 - \phi)^{-1} + (P_n\phi)^{-1} - L]N + P_1P_2\phi M^2] \qquad (18)$$

with

$$P_w = P_1\xi_1 + P_2(1 - \xi_1) \qquad (19)$$

$$L = 2\chi + \phi(\partial\chi/\partial\phi)_{\xi_1} \qquad (20)$$

$$M = (\partial\chi/\partial\xi_1)_\phi \qquad (21)$$

$$N = -(\partial^2/\partial\xi_1{}^2)\int_0^\phi \chi(u,\xi_1)\,\mathrm{d}u \qquad (22)$$

In the special case where polymer 1 and 2 are the same chemical species so that $\gamma_1 = \gamma_2 = \gamma$, the denominator WX on the right hand of eq 15 reduces to $(P_w + \xi_1\xi_2P_1P_2N)\gamma^2$.

Expansion in powers of ϕ leads eq 15 to

$$KV_0\phi/\Delta R_0 = \bar{P}^{-1} + \bar{P}^{-2}\phi[(\gamma_1P_1\xi_1 + \gamma_2P_2\xi_2)^2(1 - 2\chi_0) - 2\xi_1\xi_2(\gamma_1P_1\xi_1 + \gamma_2P_2\xi_2)(\gamma_1P_1 - \gamma_2P_2)(\partial\chi_0/\partial\xi_1) - (\xi_1\xi_2)^2(\gamma_1P_1 - \gamma_2P_2)^2(\partial^2\chi_0/\partial\xi_1{}^2)] + \ldots \qquad (23)$$

where

$$\bar{P} = \gamma_1{}^2P_1\xi_1 + \gamma_2{}^2P_2\xi_2 \qquad (24)$$

and χ_0, which is a function of ξ_1, denotes the leading term in the expansion

$$\chi(\phi,\xi_1) = \chi_0(\xi_1) + \chi_1(\xi_1)\phi + \ldots \qquad (25)$$

Under the so-called "optical Θ" condition[8] which satisfies $\gamma_1P_1\xi_1 + \gamma_2P_2\xi_2 = 0$, eq 23 reduces to

$$KV_0\phi/\Delta R_0 = \bar{P}^{-1} - \bar{P}^{-2}\phi(\xi_1\xi_2)^2(\gamma_1P_1 - \gamma_2P_2)^2(\partial^2\chi_0/\partial\xi_1{}^2) + \ldots \qquad (26)$$

This enables us to evaluate $\partial^2\chi_0/\partial\xi_1{}^2$, i.e., the second derivative of χ at infinite dilution with respect to ξ_1, from the initial slope of $KV_0\phi/\Delta R_0$ plotted against ϕ, but it should be noted that the result refers to a special value of ξ_1 corresponding to the optical Θ condition. This is the maneuver used by Fukuda et al.[8] to estimate the polymer–polymer interaction parameter in their definition.

Finally, for the binary system of solvent 0 and polymer 1 we obtain from eq 15

$$KV_0\gamma_1{}^2/\Delta R_0 = 1/(1 - \phi) + 1/(P_1\phi) - L \qquad (27)$$

which allows L to be determined from measurement of $\Delta R_0(\phi)$.

Evaluation of χ

Obviously it is impossible to solve eq 15 for $\chi(\phi,\xi_1)$ when ΔR_0 is given experimentally as a function of ϕ and ξ_1. In practice all that can be done is to find by trial and error an analytic expression of $\chi(\phi,\xi_1)$ which allows this equation to fit the given data of ΔR_0 to the accuracy desired. In so doing, the following maneuver is useful.

As we have shown recently,[9] χ for our ternary system can be represented by

$$\chi = \xi_1{}^2\chi_{11}{}^{\mathrm{b}}(\phi_1) + \xi_2{}^2\chi_{22}{}^{\mathrm{b}}(\phi_2) + 2\xi_1\xi_2\chi_{12}{}^{\mathrm{t}}(\phi_1,\phi_2) \qquad (28)$$

where $\chi_{ii}{}^{\mathrm{b}}(\phi_i)$ denotes the χ function for the binary system of solvent 0 and polymer i at a polymer volume fraction of ϕ_i and $\chi_{12}{}^{\mathrm{t}}(\phi_1,\phi_2)$ is the contribution due to the thermodynamic interaction of polymers 1 and 2 in the ternary system at a composition specified by ϕ_1 and ϕ_2. Since $\chi_{ii}{}^{\mathrm{b}}$ can be obtained from separate experiments, the trial-and-error finding of χ is reduced to that of $\chi_{12}{}^{\mathrm{t}}$. In attempting to apply this maneuver, it is advantageous to choose a system for which information about $\chi_{ii}{}^{\mathrm{b}}$ is already available. For our PS + PIP + CH system this condition was met only with the pair PS and CH.

Experimental Section

Polymer Samples. Two standard PS samples F4 and F4′ were supplied by Toyo Soda Co. They were confirmed by GPC to be narrow enough in dispersion. The weight-average molecular weight M_w was 43 900 and 53 600 for F4 and F4′, respectively, when determined by light scattering in benzene at 25 °C. The relative chain length P_1 (PS is chosen as polymer 1) calculated by

$$P_1 = M_wv_1/(M_0v_0) \qquad (29)$$

was 377 and 460 for F4 and F4′, respectively. Here, M_0 is the molecular weight of cyclohexane (solvent 0), and v_0 and v_1 are the specific volumes of CH and PS, respectively, chosen to be

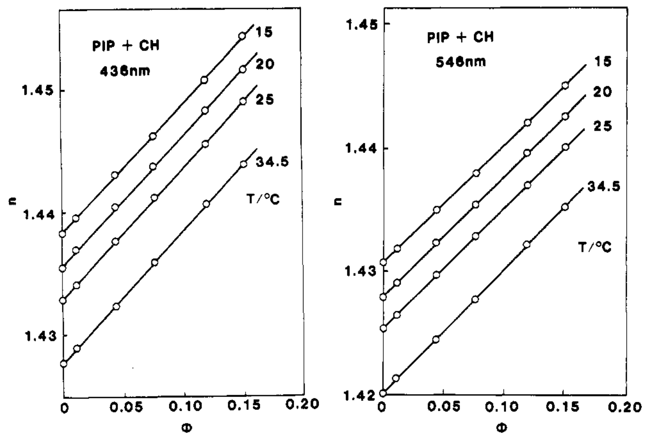

Figure 1. Concentration dependence of refractive index n for PIP sample P-5 in cyclohexane at the temperatures and wavelengths indicated.

1.2923 cm^3 g^{-1} for the former and 0.9343 cm^3 g^{-1} for the latter, both referred to 25 °C.

A living, anionically polymerized PIP sample P-5 (polymer 2) whose M_w was 53 300 was also supplied by Toyo Soda Co. Its relative chain length P_2 was 537 when calculated from eq 29 with v_2 of 1.0951 cm^3 g^{-1} in place of v_1. Some characteristics of this sample can be found in Takano et al.'s paper.[10]

Preparation of Solutions. Thoroughly dried PIP sample P-5 was dissolved in CH freshly distilled over sodium to make binary PIP + CH solutions of different concentrations. These solutions were made dust free by filtration through a Millipore membrane of 0.22-μm pore size or by centrifugation at 14 000 rpm and then used to determine $\chi_{22}{}^b$ by light scattering.

To prepare PS + PIP + CH ternary solutions the following procedure was used. First, dry PS and PIP samples were mixed at a desired composition and dissolved in CH. The solution was filtered throuth a Millipore membrane of 0.3-μm pore fize and then freeze-dried. The entire volume of the dry polymer mixture obtained was dissolved in freshly distilled CH; if only a fraction of the polymer mixture were used, the solution might have a polymer composition somewhat different from the desired one because of polymer segregation which would take place during the freeze-drying. The ternary solution so prepared was divided into several parts, and each was poured into a light-scattering cell through a Millipore membrane with a finer pore size. The solution in the cell was then diluted with CH to desired total polymer volume fractions ϕ.

The value of ϕ was estimated from the total polymer weight fraction w by

$$\phi = [1 + v_0/(\omega_1 v_1 + \omega_2 v_2)(w^{-1} - 1)]^{-1} \tag{30}$$

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

$$\xi_1 = [1 + v_2/v_1(\omega_1^{-1} - 1)]^{-1} \tag{31}$$

Light-Scattering Measurements. A Fica 50 light-scattering photometer was used with vertically polarized incident light, whose wavelength was 436 nm for PIP + CH binary solutions and 546 nm for PS + PIP + CH ternary solutions. The intensity of scattered light was measured at angles from 30° to 150°, and the data were graphically extrapolated to zero angle to estimate ΔR_0. For the binary system, ϕ was varied from 0.006 to 0.127, and T from 30 to 10 °C. For the ternary system, the measurement had to be limited to ϕ below 0.053 because of the occurrence of phase separation, and T was varied from 30 °C down to about 1 °C above the cloud point.

Because of the assumption made in deriving eq 15 it is legitimate to use γ_1 and γ_2 in this equation, the infinite-dilution values obtained for the binary systems PS + CH and PIP + CH, respectively. Thus, we computed γ_1 from Scholte's equation[11] $(\partial n/\partial w)_{w=0} = 0.069\,37 + (2 \times 10^{-4})T$ (T in K) along with the relation between w and ϕ (which is given by eq 30 with $\omega_1 = 1$ and $\omega_2 = 0$) as $\gamma_1 = 0.095\,95 + (2.77 \times 10^{-4})T$ for 546-nm light and γ_2 from our data shown in Figure 1, which gives $\gamma_2 = 0.061\,03 + (1.5 \times 10^{-4})T$ for 436-nm light and $\gamma_2 = 0.037\,10 + (2.05 \times 10^{-4})T$ for 546-nm light.

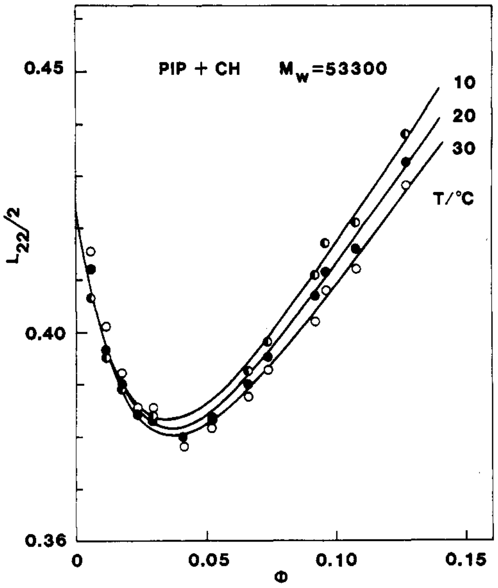

Figure 2. Plots of $L_{22}/2$ vs. ϕ for PIP sample P-5 in cyclohexane at the temperatures indicated. Solid line, calculated with eq 39, 40, and 41.

Results and Discussion

PS + CH Binary System. An extensive study on this system was carried out by Einaga et al.,[4] who determined L in eq 27 to calculate χ. Their results give the following:

$$\chi_{11}{}^b(\phi_1) = (1/\phi_1{}^2)\int_0^{\phi_1} L_{11}(u)u \, du \tag{32}$$

where

$$L_{11}(u) = 2[\chi^\circ{}_{\text{conc}} + u/2 + Au^4/(1 + Bu^2) + (\chi^\circ{}_{\text{dil}} - \chi^\circ{}_{\text{conc}})R(P_1{}^{1/2}u)] \tag{33}$$

with

$$\chi^\circ{}_{\text{conc}} = 0.4930 + 0.345(\Theta/T - 1) + (-0.075P_1{}^{-1/2} - 45P_1{}^{-2} + 0.007)\exp[-(40 - 520P_1{}^{-2/3})(\Theta/T - 1)] \quad (T \text{ and } \Theta \text{ in K}) \tag{34}$$

$$\chi^\circ{}_{\text{dil}} = 0.5 + 0.26(\Theta/T - 1) + 4.6(\Theta/T - 1)^2 \tag{35}$$

$$A = 1.4P_1{}^{1/3} \tag{36}$$

$$B = 7P_1{}^{1/3}\exp[-18(\Theta/T - 1)] \tag{37}$$

$$R(x) = \exp(-x - 0.3x^3) \tag{38}$$

and Θ denotes the the Θ temperature (34.5 °C) for PS in CH. We note that L was denoted by $2Z$ in Einaga et al.'s paper[4] and that L_{11} signifies L for the system for solvent 0 and polymer 1.

PIP + CH Binary System. Figure 2 depicts $L_{22}/2$ (L_{22} is L for the system of solvent 0 and polymer 2) vs. ϕ plots for this system at three temperatures, obtained by substituting our light-scattering data into eq 27 in which γ_1 and P_1 are replaced by γ_2 and P_2, respectively. It is seen that L_{22} exhibits a sharp minimum at any T, as was observed for PS in toluene by Scholte.[11] This behavior is distinctly different from that of L for a poor solvent system, such as PS + CH and PIP + dioxane,[10] in which L increases monotonically with ϕ.

As in our previous papers, we resolve L_{22} into two parts $(L_{22})_{\text{dil}}$ and $(L_{22})_{\text{conc}}$ as

$$L_{22} = (L_{22})_{\text{dil}} + (L_{22})_{\text{conc}} \tag{39}$$

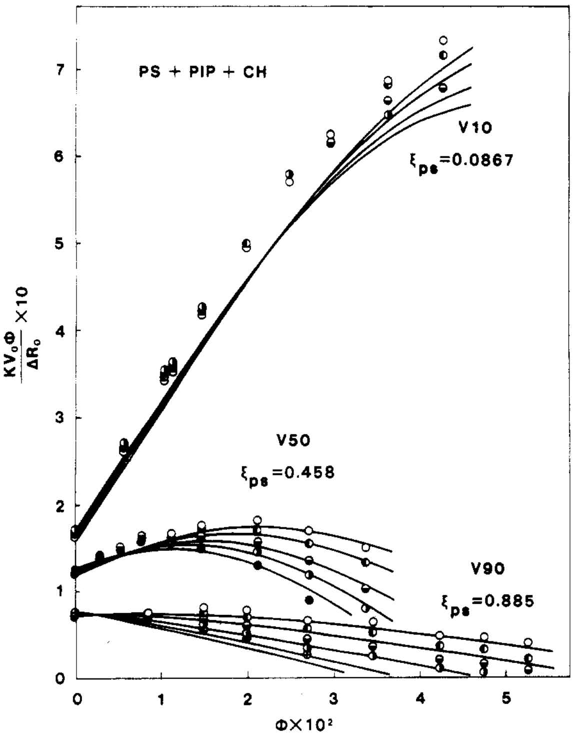

Figure 3. Concentration dependence of $KV_0\phi/\Delta R_0$ for PS + PIP mixtures with indicated ξ_{PS} in cyclohexane: (○) 30; (◐) 25; (⊖) 20; (◑) 17; (⊕) 15; (●) 14 °C. Solid line, calculated values.

Table I
Composition of Polymer Mixtures

code	ξ_{PS}	components
V10	0.0867	F4′ + P-5
V50	0.458	F4 + P-5
V90	0.885	F4′ + P-5

where $(L_{22})_{conc}$ represents the high-concentration branch of L_{22} and $(L_{22})_{dil}$ is the term added to $(L_{22})_{conc}$ to allow for a sharp drop of L_{22} at low concentrations. Following Koningsveld et al.,[12] we may consider that $(L_{22})_{dil}$ arises from both dilute-solution and excluded-volume effects. After several trials we found that the empirical expressions

$$(L_{22})_{dil} = 0.170 \exp(-47\phi) \tag{40}$$

and

$$(L_{22})_{conc} = 0.68 + (-0.88 + 680/T)\phi \qquad (T \text{ in K}) \tag{41}$$

yield a close fit of eq 39 to the experimental L_{22} data, as illustrated in Figure 2. When substituted into the relation

$$\chi_{22}{}^{b}(\phi_2) = (1/\phi_2{}^2)\int_0^{\phi_2} L_{22}(u)u \, du \tag{42}$$

these expressions yield

$$\chi_{22}{}^{b}(\phi_2) = 0.34 + (2/3)(-0.44 + 340/T)\phi_2 + 0.17[1 - (1 + 47\phi_2)\exp(-47\phi_2)]/(47\phi_2)^2 \tag{43}$$

Since we worked on a single PIP sample, the possible dependence of $\chi_{22}{}^{b}$ on the relative chain length P_2 was left for a future study.

PS + PIP + CH Ternary System. We made light-scattering measurements on three PS + PIP mixtures V10, V50, V90 which had ξ_{PS} (equal to ξ_1 in the above presentation) of 0.0867, 0.458, and 0.885, respectively (see Table I). Figure 3 shows the ϕ dependence of $KV_0\phi/\Delta R_0$ for these mixtures in CH at several fixed temperatures. The data points on the ordinate axis indicate the values of $\bar{P}^{-1}$ computed by substituting the experimental values of P_1, P_2, γ_1, and γ_2 into eq 24. Those at nonzero ϕ can be extrapolated to these points, as should be expected from eq 23.

Table II
Values of $\chi_{11}{}^{b}(0)$, $\chi_{22}{}^{b}(0)$, and $\chi_{12}{}^{t}(0,0)$

T/°C	$\chi_{11}{}^{b}(0)$	$\chi_{22}{}^{b}(0)$	$\chi_{12}{}^{t}(0,0)$ for ξ_{PS} = 0.458
30	0.5049	0.425	0.36
25	0.5130	0.425	0.37
20	0.5241	0.425	0.37
17	0.5324	0.425	0.37
14	0.5420	0.425	0.37

It is seen that the set of data points at fixed ξ_{PS} and T follows a curve convex upward and that these curves for mixture V50 and those for mixture V90 at higher temperatures exhibit maxima at certain concentrations which decrease with lowering temperature. The latter behavior suggests that phase separation of the solution occurs with increasing ϕ beyond the maxima. In fact, as will be shown in the following paper,[13] we observed that CH solutions of mixtures V50 and V90 began separating into two phases at concentrations a little higher than those studied here.

The data for mixture V90 in Figure 3 can be used to estimate spinodal concentration ϕ_{sp} as a function of T by extrapolating them to the abscissa axis. Though roughly, the same can be done with those for mixture V50. Thus we find that for either mixture, ϕ_{sp} decreases with lowering T and that when compared at the same T, ϕ_{sp} for mixture V50 is probably somewhat smaller than that for mixture V90.

From eq 25 and 28 it follows that

$$\chi_0 = \xi_1{}^2\chi_{11}{}^{b}(0) + \xi_2{}^2\chi_{22}{}^{b}(0) + 2\xi_1\xi_2\chi_{12}{}^{t}(0,0) \tag{44}$$

The second and third columns of Table II give the values of $\chi_{11}{}^{b}(0)$ and $\chi_{22}{}^{b}(0)$ computed from eq 32 and 43, respectively. Substitution of eq 44 into eq 23 allows the initial slope of $KV_0\phi/\Delta R_0$ plotted against ϕ to be expressed in terms of $\chi_{11}{}^{b}(0)$, $\chi_{22}{}^{b}(0)$, and $\chi_{12}{}^{t}(0,0)$. The last column of Table II shows the values of $\chi_{12}{}^{t}(0,0)$ estimated from the data for mixture V50 in Figure 3 by using this expression and the tabulated values of $\chi_{11}{}^{b}(0)$ and $\chi_{22}{}^{b}(0)$. It is seen that $\chi_{12}{}^{t}(0,0)$ is comparable in magnitude with $\chi_{11}{}^{b}(0)$ and $\chi_{22}{}^{b}(0)$.

The concentration dependence of $\chi_{ii}{}^{b}(\phi_i)$ (i = 1, 2) at low concentrations is complex owing to the dilute-solution and excluded-volume effects. Probably, this should be the case with respect to $\chi_{12}{}^{t}(\phi_1,\phi_2)$. Therefore, we have tried to look for a simple expression of $\chi_{12}{}^{t}$ which optimizes the agreement between experimental and calculated values of $KV_0\phi/\Delta R_0$ at relative high concentrations. The solid curves in Figure 3 illustrate the results from the trial in which $\chi_{12}{}^{t}$ was expressed as

$$\chi_{12}{}^{t} = k_1 + (k_2\xi_1 + k_3\xi_2)\phi \tag{45}$$

and the parameters k_1, k_2, and k_3 were chosen as

$$k_1 = 0.44; \quad k_2 = -6.1 + 2000/T; \quad k_3 = -4.8 + 1300/T \qquad (T \text{ in K}) \tag{46}$$

As can be seen, the fit of the curves to the data points is only moderate. Especially for mixture V10, it leaves much to be desired. However, we have not attempted to improve the agreement by using a more complex expression for $\chi_{12}{}^{t}$. In Part 2 of this series,[13] observed phase-separation data will be compared with the predictions by the χ function determined in the present work.

Equation 45 predicts $\chi_{12}{}^{t}(0,0) = k_1 = 0.44$, which is significantly different from the $\chi_{12}{}^{t}(0,0)$ values shown in Table II. This difference should not be taken seriously, since the value k_1 is merely what is obtained when the expression for $\chi_{12}{}^{\mathrm{t}}$ fitting high-concentration data of $KV_0\phi/\Delta R_0$ is extrapolated to $\phi = 0$. Both dilute-solution and excluded-volume effects should be responsible for it.

Acknowledgment. We are much indebted to Dr. M. Fukuda of Toyo Soda Co. who kindly supplied us with the polymer samples used in this work.

Appendix

At constant T and p, the excess Rayleigh ratio ΔR_0 due to concentration fluctuation may be represented by[14]

$$\Delta R_0 = Kv_M RT\sum_i\sum_j \psi_i\psi_j\Delta_{ij}/|\Delta| \tag{A1}$$

where K is the optical constant $2\pi^2 n^2/N_A\lambda_0{}^4$, with n the refractive index, N_A the Avogadro constant, λ_0 the wavelength of incident light in vacuo, RT with the usual meaning, v_M the volume of the solution containing unit mass of the solvent, i.e.,

$$v_M = V_0(n_0 + \sum_{i=1}^{2} n_iP_i)/n_0M_0 \tag{A2}$$

$$= V_0/M_0(1-\phi) \tag{A3}$$

and ψ_i the molality-basis refractive index increment of component i

$$\psi_i \equiv (\partial n/\partial m_i)_{T,p,m_k} \tag{A4}$$

The volume fraction ϕ_i is related to molality m_i by

$$\phi_i = M_0m_iP_i/(1 + M_0\sum_{i=1}^{2} m_iP_i) \tag{A5}$$

from which it follows that

$$\partial\phi_i/\partial m_i = M_0P_i(1-\phi_i)(1-\phi) \tag{A6}$$

$$\partial\phi_j/\partial m_i = -M_0P_i\phi_j(1-\phi) \tag{A7}$$

and

$$(\partial/\partial m_i)_{m_k} = M_0(1-\phi)P_i[(\partial/\partial\phi_i)_{\phi_k} - \sum_{j=1}^{2}\phi_j(\partial/\partial\phi_j)_{\phi_k}] \tag{A8}$$

The last relation gives

$$\psi_i = M_0(1-\phi)P_i[(\partial n/\partial\phi_i)_{\phi_k} - \sum_{j=1}^{2}\phi_j(\partial n/\partial\phi_j)_{\phi k}] \tag{A9}$$

$$= M_0(1-\phi)P_i\tilde{\gamma}_i \tag{A10}$$

with

$$\tilde{\gamma}_i = \gamma_i - \sum_{j=1}^{2}\gamma_j\phi_j \tag{12}$$

$$\gamma_i = (\partial n/\partial\phi_i)_{\phi_k} \tag{A11}$$

Substituting eq A3 and A10 into eq A1, we arrive at eq 11 in the text:

$$\Delta R_0 = KRTM_0V_0(1-\phi)\sum_{i=1}^{2}\sum_{j=1}^{2}\tilde{\gamma}_i\tilde{\gamma}_jP_iP_j\Delta_{ij}/|\Delta| \tag{11}$$

In terms of the composition variables (ϕ, ξ_1), eq A8 can be rewritten

$$(\partial/\partial m_1)_{m_2} = M_0(1-\phi)P_1[(1-\phi)(\partial/\partial\phi)_{\xi_1} + \phi^{-1}(1-\xi_1)(\partial/\partial\xi_1)_\phi] \tag{A12}$$

$$(\partial/\partial m_2)_{m_1} = M_0(1-\phi)P_2[(1-\phi)(\partial/\partial\phi)_{\xi_1} - \phi^{-1}\xi_1(\partial/\partial\xi_1)_\phi] \tag{A13}$$

With the aid of these relations, eq 14 with eq 6 and 7 gives

$$\mu_{11}/RT = M_0P_1{}^2(1-\phi)[(1-\phi_1)/P_1\phi_1 + (1-P_1{}^{-1}) - (1-P_n{}^{-1})\phi - (1-\phi)^2L - 2(1-\phi)(1-\xi_1)M + (1-\xi_1)^2N/\phi] \tag{A14}$$

$$\mu_{22}/RT = M_0P_2{}^2(1-\phi)[(1-\phi_2)/P_2\phi_2 + (1-P_2{}^{-1}) - (1-P_n{}^{-1})\phi - (1-\phi)^2L + 2(1-\phi)\xi_1M + \xi_1{}^2N/\phi] \tag{A15}$$

$$\mu_{12}/RT = \mu_{21}/RT = M_0P_1P_2(1-\phi)[(1-P_1{}^{-1}-P_2{}^{-1}) - (1-\phi)^2L - (1-\phi)(1-2\xi_1)M - \xi_1(1-\xi_1)N/\phi] \tag{A16}$$

where

$$L \equiv -(\partial^2h/\partial\phi^2)_{\xi_1} = 2\chi + \phi(2\chi/\partial\phi)_{\xi_1} \tag{A17}$$

$$M \equiv \phi^{-2}[(\partial h/\partial\xi_1)_\phi - \phi(\partial^2h/\partial\phi\partial\xi_1)] = (\partial\chi/\partial\xi_1)_\phi \tag{A18}$$

$$N \equiv \phi^{-1}(\partial^2h/\partial\xi_1{}^2)_\phi = -\int_0^\phi(\partial^2\chi/\partial\xi_1{}^2)_u\,\mathrm{d}u \tag{A19}$$

If these expressions are substituted, eq 11 gives the desired equation for ΔR_0 (eq 15 in the text) after a lengthy but straightforward manipulation.

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

References and Notes

(1) Narasimhan, V.; Huang, R. Y. M.; Burns, C. M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1993; *J. Polym. Sci., Polym. Symp.* **1986**, *74*, 265.
(2) For example: Kurata, M. *Thermodynamics of Polymer Solutions*; translated from the Japanese by H. Fujita; Harwood Academic: Switzerland, Chur, 1982; Chapter 2.
(3) van den Esker, M. W. J.; Vrij, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1943. van den Esker, M. W. J.; Laven, J.; Broeckman, A.; Vrij, A. *Ibid.* **1976**, *14*, 1953. van den Esker, M. W. J.; Vrij, A. *Ibid.* **1976**, *14*, 1967.
(4) Einaga, Y.; Ohashi, S.; Tong, Z.; Fujita, H. *Macromolecules* **1984**, *17*, 527.
(5) Einaga, Y.; Tong, Z.; Fujita, H. *Macromolecules* **1985**, *18*, 2258.
(6) Scholte, Th. G. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 1553.
(7) Reference 2, Chapter 3.
(8) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548.
(9) Einaga, Y.; Tong, Z.; Fujita, H. *Macromolecules*, in press.
(10) Takano, N.; Einaga, Y.; Fujita, H. *Polym. J.* **1985**, *17*, 1123.
(11) Scholte, Th. G. *Eur. Polym. J.* **1970**, *6*, 1063.
(12) Koningsveld, R.; Stockmayer, W. H.; Kennedy, J. W.; Kleintjens, L. A. *Macromolecules* **1974**, *7*, 73.
(13) Tong, Z.; Einaga, Y.; Miyashita, H.; Fujita, H. *Macromolecules*, following paper in this issue.
(14) Reference 2, eq 3.3.7 in Chapter 3.