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CONCENTRATION DEPENDENCE OF INTERACTION FUNCTION χ FOR BINARY SYSTEMS OF POLYMER IN A GOOD SOLVENT DETERMINED BY LIGHT SCATTERING

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Abstract—Light scattering measurements were performed on binary systems of polystyrene ($\bar{M}_w = 53{,}600$) in benzene, polyisoprene ($\bar{M}_w = 53{,}300$) in cyclohexane, and polyisobutylene ($\bar{M}_w = 154{,}000$) in cyclohexane at concentrations up to 15% in volume. The interaction function χ was established from the data as a function of polymer concentration and temperature. The value of χ estimated for each system at each temperature first decreases and then increases with increasing polymer concentration, exhibiting a minimum in the curve of concentration dependence.

INTRODUCTION

The so-called Flory–Huggins interaction function χ, defined through the solvent chemical potential, remains a central subject for research on polymer solution thermodynamics. Description of the thermodynamic state and prediction of the phase relationships for polymer/polymer/solvent ternary systems require precise knowledge of the χ function. Experiments have unequivocally demonstrated that, even for a strictly binary system, the χ function generally depends on polymer concentration [1–3]. Most of the concentration dependent χ expressions reported so far are still too approximate for application in studies of ternary systems.

During recent investigation of phase equilibria in ternary systems containing two polymers and a solvent [4], we were able to make light scattering measurements to estimate χ for a binary solution consisting of a monodisperse (very narrow distribution) polymer and a solvent. Our thesis is essentially akin to that of Scholte [5], which led to some important contributions. When formulating the χ expressions from the experimental data, we formally adapted the hybrid approach by Koningsveld *et al.* [6], who composed χ of two functions characterizing dilute and concentrated solutions, respectively. We confined ourselves to a phenomenological approach and did not adhere to any molecular theory. In this way, the χ function was established for polystyrene (PS)/cyclohexane (CH) [7] and polyisoprene (PIP)/dioxane [8] binary systems, i.e. a polymer in a poor solvent, and the binodals, spinodals and critical points for each of the systems were almost quantitatively predicted with the corresponding determined χ function.

We then undertook a similar study on another type of binary system, viz. a polymer in a good solvent. In this paper, we report the χ functions of PS/benzene, PIP/CH and polyisobutylene (PIB)/CH binary systems determined by light scattering measurements at concentrations up to 15% by volume.

EXPERIMENTAL PROCEDURES

Polymer samples

The standard PS sample F4′ was kindly supplied by Tosho Co. The weight-average molecular weight ($\bar{M}_w$) was 53,600, determined by light scattering in benzene at 25°. GPC measurement confirmed a sufficiently narrow molecular weight distribution.

A living anionically polymerized PIP sample P-5 ($\bar{M}_w = 53{,}300$) was also supplied by Tosho Co. Its polydispersity index $\bar{M}_w/\bar{M}_n$, estimated by GPC, was < 1.08. The other characteristics of this sample have been given [8].

A commercial PIB sample was split into several fractions using benzene/methanol and a fraction (U-1) was used. $\bar{M}_w$, determined by light scattering in CH at 25° was 154,000, and $\bar{M}_w/\bar{M}_n$ by GPC was < 1.06.

Since the molecular weight distributions of the samples were narrow enough, the experimental systems were treated as strictly binary.

Preparation of solutions

Thoroughly dried polymer was dissolved in the given solvent freshly distilled after refluxing over Na for *ca* 6 hr. Binary solutions of various concentrations were made dust-free by filtration through a Millipore membrane of 0.22 μm pore size or by centrifugation at 14,000 rpm. The polymer volume fraction ϕ was evaluated from the polymer weight fraction w by the equation [9]

$$\phi = [1 + (v_0/v_p)(w^{-1} - 1)]^{-1} \tag{1}$$

where v_0 and v_p are the specific volumes of the solvent and the polymer respectively. The value used in units of $cm^3\,g^{-1}$ for v_p was 0.9343 for PS, 1.0951 for PIP and 1.0906 for PIB, and that for v_0 was 1.2923 for CH, 1.1446 for benzene, all

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referring to 25°. For the three binary systems studied, ϕ ranged from very dilute to *ca* 0.15.

Light scattering measurements

A Fica 50 photometer was used with vertically polarized incident light of 436 nm to measure the intensity of scattered light from the solution. The light scattering data were analyzed by using the relation [5] for the excess Rayleigh ratio ΔR_0 at zero scattering angle

$$K_\phi/\Delta R_0 = -(1/\mathrm{R}T\phi)(\partial\Delta\mu_0/\partial\phi) \qquad (2)$$

with

$$K_\phi = (4\pi^2 n^2/N_A\lambda_0^4)(\partial n/\partial\phi)^2 V_0. \qquad (3)$$

Here, $\Delta\mu_0$ is the excess chemical potential of the solvent, R the gas constant, T the absolute temperature, n the refractive index of the solution, N_A the Avogadro constant, λ_0 the wavelength of the incident light *in vacuo*, V_0 the molar volume of the solvent, and $\partial n/\partial\phi$ the refractive index increment. $\partial n/\partial\phi$ was measured on very dilute solutions ($\phi < 0.01$) with light of 436 nm, as a function of T. The $(\partial n/\partial\phi)$ equations derived are the following:

For PS in benzene

$$(\partial n/\partial\phi) = 0.0495 + 2.20 \times 10^{-4}T. \qquad (4a)$$

For PIP in CH

$$(\partial n/\partial\phi) = 0.0610 + 1.50 \times 10^{-4}T. \qquad (4b)$$

For PIB in CH

$$(\partial n/\partial\phi) = 0.0285 + 2.08 \times 10^{-4}T. \qquad (4c)$$

RESULTS AND DISCUSSION

Light scattering data

Figure 1 depicts the angular dependence of $K_\phi/\Delta R_\theta$ for PIB/CH solutions for three concentrations at 15 and 35° as examples. $K_\phi/\Delta R_\theta$ data at each temperature and concentration can be fitted by a straight line and extrapolated unambiguously to zero scattering angle to evaluate $K_\phi/\Delta R_0$ accurately. The results for PIB/CH solutions at other concentrations and for PS/benzene and PIP/CH solutions were similar. $K_\phi/\Delta R_0$ values for these bindary solutions were determined with sufficient accuracy irrespective of the temperatures and concentrations studied.

Substitution of the Flory–Huggins equation for $\Delta\mu_0$ into equation (2) shows that the function L defined by

$$L \equiv 2\chi + \phi(\partial\chi/\partial\phi) \qquad (5)$$

is represented as

$$L = 1/(1-\phi) + 1/(P\phi) - K_\phi/\Delta R_0 \qquad (6)$$

where P is the relative chain length of polymer to the solvent calculated from

$$P = \bar{M}_w v_p/M_0 v_0 \qquad (7)$$

where M_0 is the molecular weight of the solvent. With the corresponding v_p and v_0 values given in the preceding section, the value of P is 560 for PS sample F4′ in benzene, 537 for PIP sample P-5 in CH, and 1540 for PIB sample U-1 in CH. Since all the quantities appearing in the right-hand-side of equation (6) are experimentally measurable, light scattering measurements enable one to evaluate the function L but not χ itself.

Figures 2–4 illustrate the ϕ dependence of $L/2$ for the binary systems PS/benzene, PIP/CH and PIB/CH, respectively. Since all of them are composed of a polymer in a good solvent, the graphs for different systems possess the following common features:

(i) The $L/2$ value at infinite dilution is much <0.5, in contrast to the polymer/poor solvent system, such as PS/CH [7] and PIP/dioxane [8], in which it is >0.5 at temperatures below the θ point;

(ii) there appears a distinct minimum in each $L/2$ vs ϕ curve at each temperature studied, as was observed for PS in toluene by Scholte [5], while $L/2$ for the polymer/poor solvent system increases monotonically with ϕ following a curve bent upward [7, 8].

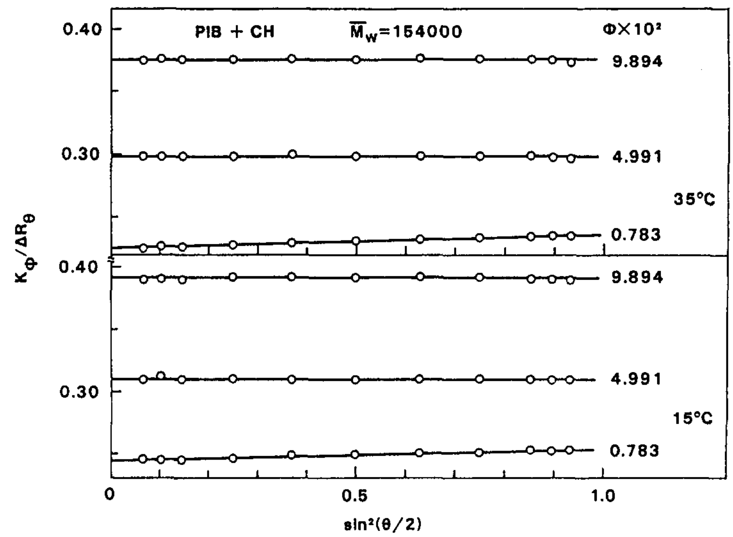

Fig. 1. Angular dependence of $K_\phi/\Delta R_\theta$ for PIB/CH solutions at the indicated concentrations and temperatures.

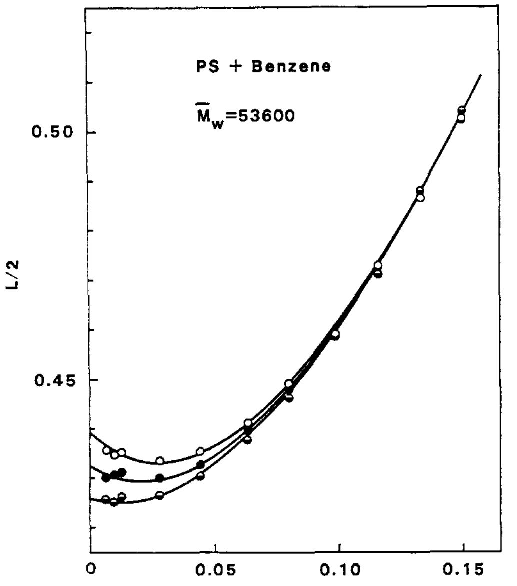

Fig. 2. Plots of $L/2$ vs ϕ for PS sample in benzene. ○, 35°; ●, 25°; ⊖, 15°. Solid lines, calculated with equation (10).

Formulation of L function

The above observations of the $L/2$ vs ϕ plots suggest that L contain two factors, one increasing monotonically and the other decreasing with increasing ϕ. According to the hybrid approach [6], L can be expressed as

$$L = L_{\text{dil}}Q + L_{\text{conc}}(1 - Q). \tag{8}$$

Here L_{dil} and L_{conc} denote the L functions characterizing dilute and concentrated solutions, respectively, and Q denotes the probability that a small volume element in the solution does not contain any polymer segments. Unlike Koningsveld *et al.* [6], we make no assumption about Q. It is worth noting that mathematically Q approaches unity as $\phi \rightarrow O$ and physically should decrease asymptotically to zero with increasing ϕ. We may suppose that the L_{dil} team arises from the facts that in a very dilute solution the spatial distribution of polymer segments is inherently non-uniform and that the polymer chain takes on a more expanded conformation. By analogy with the Koningsveld *et al.* treatment [6], equation (8) is approximated by

$$L = L_{\text{conc}} + (L^{\circ}_{\text{dil}} - L^{\circ}_{\text{conc}})Q \tag{9}$$

where L°_{dil} and L°_{conc} are the infinite-dilution values of L_{dil} and L_{conc}, respectively.

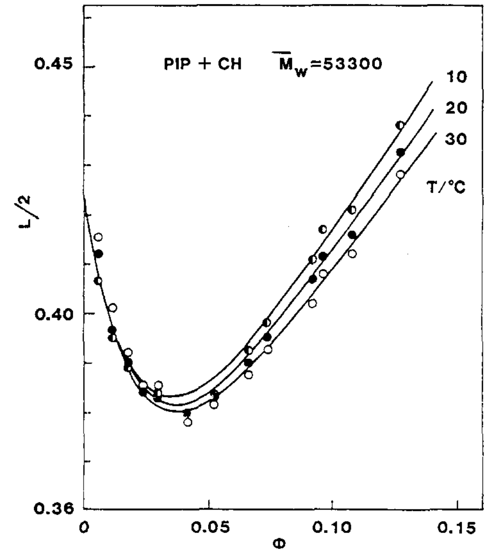

Fig. 3. Plots of $L/2$ vs ϕ for PIP sample in CH at the indicated temperatures. Solid lines, calculated with equation (11).

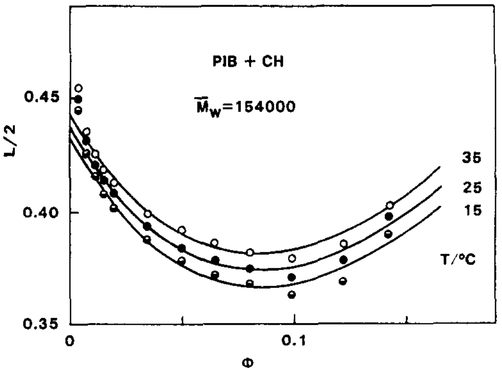

Fig. 4. Plots of $L/2$ vs ϕ for PIB sample in CH at the indicated temperatures. Solid lines, calculated with equation (12).

Figure 5 is intended to show the actual procedure for formulating L as a function of ϕ according to equation (9). The solid line stands for the measured $L/2$ data at various concentrations at a given temperature. Since there were $L/2$ data covering the very

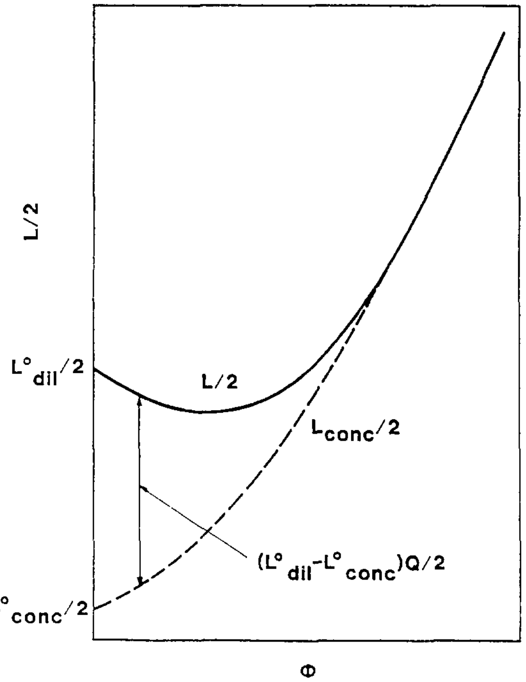

Fig. 5. Schematic representation of $L/2$ as a function of ϕ (see text for details).

dilute region, the solid line can be smoothly extrapolated to the infinite-dilution ($\phi \to 0$) giving L°_{dil}. We then determined an equation of ϕ which can fit as closely as possible the $L/2$ data in the relatively concentrated region. This equation is L_{conc} shown by the dashed curve in Fig. 5, which coincides with the solid line in the concentrated region. When $\phi = 0$ was substituted, the L_{conc} function gave the L°_{conc} value. Finally, we subtracted L_{conc} from the observed value of L at a fixed ϕ and took the ratio of the difference to $(L^{\circ}_{\text{dil}} - L^{\circ}_{\text{conc}})$ as the value of Q [i.e. $Q = (L - L_{\text{conc}})/(L^{\circ}_{\text{dil}} - L^{\circ}_{\text{conc}})$]. The equation for Q was determined to fit these Q values as a function of ϕ. The Q equation so obtained was found to meet the physical and mathematical demands mentioned in the above paragraph.

Some of the parameters contained in the empirical equation for L were obtained as a function of T from the L data determined at various temperatures. In most cases, several trial-and-error processes were required to arrive at satisfactory results. Our final equations for L are summarized as follows:
For PS (F4′) in benzene

$$L = 0.82 + 0.48\phi + 5\phi^2 + (-0.36 + 0.00136T)\exp(-26\phi). \quad (10)$$

For PIP (P-5) in CH

$$L = 0.68 + (-0.88 + 680/T)\phi + 0.17\exp(-47\phi). \quad (11)$$

For PIB (U-1) in CH

$$L = (0.13 + 0.0017T) + 6\phi^2 + (1.05 - 0.0017T - 90/T)\exp(-15\phi). \quad (12)$$

The solid lines in Figs 2–4 represent L values calculated by equations (10)–(12), respectively. They fit the experimental data reasonably well. For each binary system, only one polymer sample was examined; hence no explicit molecular weight dependence of L was obtained.

χ expressions

The interaction function χ can be derived by integrating L according to equation (5).

$$\chi = (1/\phi^2)\int_0^{\phi} L(u)u\,\mathrm{d}u \quad (13)$$

With equations (10), (11), and (12), we obtained the χ functions for these binary systems.
For PS (F4′) in benzene

$$\chi = 0.41 + 0.16\phi + 1.25\phi^2 + (-0.36 + 0.00136T) \times [1 - (1 + 26\phi)\exp(-26\phi)]/(26\phi)^2. \quad (14)$$

For PIP (P-5) in CH

$$\chi = 0.34 + (-0.29 + 227/T)\phi + 0.17[1 - (1 + 47\phi)\exp(-47\phi)]/(47\phi)^2 \quad (15)$$

For PIB (U-1) in CH

$$\chi = (0.065 + 0.00085T) + 1.5\phi^2 + (1.05 - 0.0017T - 90/T) \times [1 - (1 + 15\phi)\exp(-15\phi)]/(15\phi)^2. \quad (16)$$

Figure 6 illustrates the χ values calculated for the PS/benzene, PIP/CH and PIB/CH systems at 25°. χ values for the PS/toluene system estimated from Scholte's light scattering data [5] are also shown in the same figure for comparison. Since all systems refer to a polymer in a good solvent, there are some common characteristics similar to those found in the L data: χ for each system at each temperature follows a curve convex downward exhibiting a minimum at

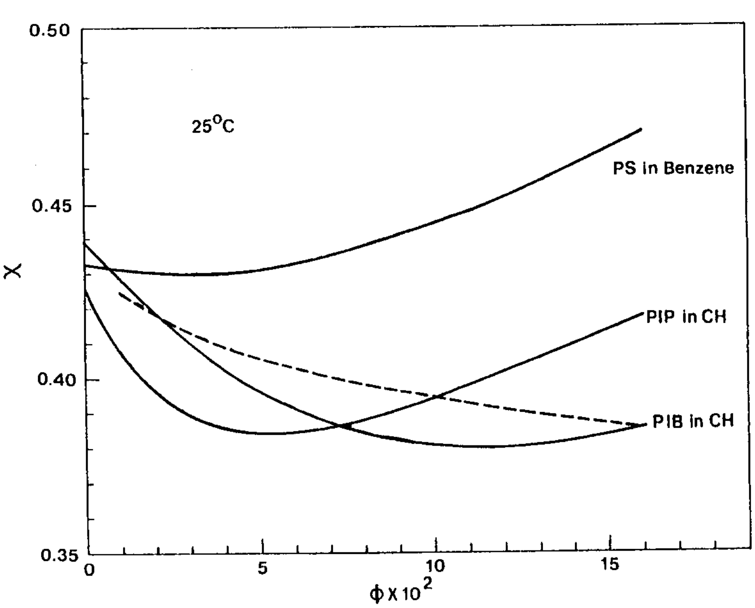

Fig. 6. Calculated values of χ (solid lines) for the systems PS/benzene [equation (14)], PIP/CH [equation (15)], and PIB/CH [equation (16)] with the χ values estimated from Scholte's light scattering data for PS/toluene system [5] (dashed line).

a certain concentration. Although it is a critical examination of the established χ expressions whether they can predict observed phase relations with satisfactory accuracy [7, 8], no phase equilibrium data are available for these binary systems. Therefore, further examination was not attempted for the determined χ expressions.

A question may be raised as to the concentration range in which these χ expressions hold. We find literature χ data determined from vapour pressure measurements on highly concentrated PS/benzene [10, 11] and PIB/CH [12, 13] binary solutions. They are much lower than the corresponding χ values computed from equations (14) and (16) when extrapolated smoothly to this concentration region, though the data are considerably scattered owing to experimental difficulty. Thus, it cannot be expected that our χ expressions are valid for such high concentrations. In this respect, it must be noted that the χ expressions holding over the entire concentration region (i.e. ϕ from zero to unity) is still far from completion because the concentration dependence of χ is very subtle and experimental methods available at present cannot provide precise data covering such a wide range of concentrations.

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