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Light Scattering from Polymer Blend Solutions. 5. Characterization of Systems of Relatively High Incompatibility

Minoru Nagata, Takeshi Fukuda,* and Hiroshi Inagaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.

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ABSTRACT: Solutions of polymer blends polystyrene/poly(ethylene oxide), polystyrene/polyisoprene, and polystyrene/polyisobutylene were studied by the "optical Θ" light-scattering method. The interaction parameter χ_{12} between unlike polymers in dilute solution was determined for each system, with which the segment–segment interaction parameter $\chi_{12}{}^{\circ}$ was estimated by the aid of dilute solution excluded volume theories. These $\chi_{12}{}^{\circ}$ values are closely related with those estimated by the solubility parameter method and, moreover, seem compatible with the available experimental data on the solvent-free systems composed of much shorter chains or relevant copolymers. Several ternary solutions were studied up to concentrations near the spinodal points, indicating that at least in limited cases with highly incompatible (i.e., large $\chi_{12}{}^{\circ}$) systems, demixing can occur even in the "dilute" solution which is characterized by a concentration-independent and blend-ratio-independent value of χ_{12}. The molecular weight exponent of the spinodal concentration is roughly similar in all examined systems (about −0.6).

Introduction

Light scattering from a dilute ternary solution of the type polymer (1)/polymer (2)/solvent (0) is represented by eq 1, if the condition in eq 2 is met.[1] In eq 1 and 2,

$$K\phi/R_0 = (m_1x_1)^{-1} + (m_2x_2)^{-1} - 2\chi_{12}\phi + \ldots \qquad (1)$$

$$\psi_1 m_1 x_1 + \psi_2 m_2 x_2 = 0 \qquad (2)$$

R_0 is the scattering intensity at zero angle, ϕ is the sum of the volume fractions ϕ_1 and ϕ_2 of the polymers, $x_i = \phi_i/\phi$ is the blend composition, m_i is the *weight-average* degree of chain length, $\psi_i = \partial n/\partial\phi_i$ is the refractive index increment, and K is the optical constant proportional to $(\psi_1 - \psi_2)^2$. This "optical Θ" method permits determination of the polymer–polymer interaction parameter χ_{12} without knowing the solvent–polymer interactions χ_{01} and χ_{02}, hence with the highest possible precision[2,3] (see ref 4 for the definition of the χ parameters). The method has been successfully applied to some blend systems.[1,3,5,6]

The formal similarity of eq 1 to the scattering equation for dry blends[7] may be clear, the latter being obtained by setting $\phi = 1$ in eq 1 and neglecting higher terms in ϕ. Owing to this dilution factor ϕ, experimental approaches are feasible even to those systems which are difficult to characterize in the dry state due to large χ_{12}, viz., immiscibility. However, introduction of a solvent brings about complexities, too, arising from solvent–polymer interactions, rendering the solution χ_{12} usually very different in value from the bulk χ_{12}.[1] The main cause for the difference is considered to be the excluded volume effect between unlike polymers. This problem was the subject of a previous paper,[8] wherein we have proposed a simple method for analyzing dilute solution data for the "net" or "segment–segment" interaction parameter, $\chi_{12}{}^{\circ}$.[4] This parameter should be independent of chain length and, at least to a first approximation, of solvent, too. It is an important but still unanswered problem to examine to which extent parameter $\chi_{12}{}^{\circ}$ is related with the relevant parameter for the solvent-free system. This is the main subject of this paper. We will study by the mentioned light-scattering method some polymer blends which are rather highly incompatible in bulk, showing virtually for the first time that dilute ternary solution data are, in many cases, closely related with those for the bulk blends.

Experimental Section

The molecular characteristics of the polymer samples are listed in Table I. The samples of polystyrene (PS), poly(ethylene oxide) (PEO), and polyisoprene (PIP) have a narrow distribution in molecular weight and were used as received from the manufacturers, while those of polyisobutylene (PIB) are fractions of a commercial polymer, the fractionation being made with a cyclohexane/methanol system at 30 °C (for the sample sources, see Table I). The volume fraction ϕ_i and the degree of chain length were calculated with

$$\phi_i = w_i v_i/(w_0v_0 + w_1v_1 + w_2v_2) \qquad (3)$$

$$m_i = M_{i,\mathrm{w}} v_i/V_0 \qquad (4)$$

where w_i is the weight fraction, v_i is the specific volume in the pure state, $M_{i,\mathrm{w}}$ is the weight-average molecular weight, and V_0 is the molar volume of the solvent (i = 0, 1, or 2; thus $m_0 = 1$). The v_i values of the polymers were assumed to be given by the following relations determined for the liquid polymers:

$$v_1 = 0.9199 + (5.08 + 2.354 \times 10^{-3}t)10^{-4}t \quad (\mathrm{PS})^{9}$$

$$v_2 = 0.8726 + 6.9 \times 10^{-4}t \quad (\mathrm{PEO})^{10}$$

$$v_2 = 1.080 + 6.89 \times 10^{-4}t \quad (\mathrm{PIP})^{11}$$

$$v_2 = 1.077 + 6.45 \times 10^{-4}t \quad (\mathrm{PIB})^{12}$$

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Table I
Molecular Characteristics of Polymer Samples

sample		$10^{-4}M_w$[a]	M_w/M_n[b]	$[\eta]$,[c] dL/g	$\langle S^2\rangle_w^{1/2}$,[c,d] Å	χ_{0i}[c,e]
PS	F80[f]	77.5	1.01	2.24	366 (368)	0.466 (0.466)
	P30[g]	35.0	1.07	1.23	232	
	F20[f]	18.6	1.07	0.76	162	
	F10[f]	10.2	1.01	0.48	114	
	P3[g]	3.5	1.05	0.22	62	
PEO	SE70[f]	68.0	1.10	4.51	446 (443)	0.416 (0.439)
	SE30[f]	27.8	1.05	2.46	273	
	SE8[f]	7.3	1.02	0.98	130	
PIP	I10[g,h]	9.7	1.04	0.83	133	0.428 (0.418)
	I3[g,h]	3.1	1.05	0.36	70	
PIB	B80[g,i]	75.7	1.41	1.39	318 (331)	0.490 (0.494)
	B30[g,i]	32.5	1.30	0.80	198	0.490 (0.491)
	B20[g,i]	22.5	1.35	0.66	164	0.488 (0.489)

[a] Light scattering. [b] GPC. [c] Bromobenzene, 30 °C. [d] Calculated with eq 5–8 (cf. ref 8). Values in parentheses were determined by light scattering and corrected for polydispersity. [e] Calculated with eq 5, 6, 8, and 11 (cf. ref 8). Values in parentheses were determined by light scattering. [f] Supplied by Toyo Soda Co., Ltd. [g] Supplied by Polymer Laboratories Co., Ltd. [h] 95% + cis-1,4 structure. [i] Fraction of a commercial polymer.

where t is the temperature in °C.

The refractive index increments of the polymers in bromobenzene were determined on a Union Giken differential refractometer, Model RM102, Japan. Values of ψ_i at 30.0 °C were determined to be 0.0520 (PS), −0.685 (PEO), −0.0411 (PIP), and −0.0651 (PIB) for a wavelength of 436 nm.

Light-scattering measurements were made on a Fica light-scattering photometer, Model 50, France, by using a vertically polarized light of 436 nm. Each ternary solution consisted of a PS and one of the other polymers of a similar molecular weight, blended in such a ratio as to meet the condition in eq 2.

The intrinsic viscosity $[\eta]$ of each polymer in bromobenzene was determined on a Ubbelohde dilution viscometer. The hydrodynamic expansion factor α_η was evaluated by

$$\alpha_\eta^3 = [\eta]/K_0 M_w^{1/2} \qquad (5)$$

with values of K_0 (in mL g^{-1}) of 0.079 (PS), 0.200 (PEO), 0.097 (PIP), and 0.112 (PIB).[13] The mean-square radius of gyration $\langle S^2\rangle$ was then evaluated according to the following relations:[8]

$$\alpha_\eta^4 = 1 + (7/5)Z \qquad (6)^{14}$$

$$\alpha^2 = 0.541 + 0.459(1 + 6.04Z)^{0.46} \qquad (7)^{15}$$

$$[\eta]_0 = K_0 M_w^{1/2} = 6^{3/2}\Phi_0 \langle S^2\rangle_0^{3/2}/M_w \qquad (8)^{16}$$

where Φ_0 is assumed to be 2.5×10^{23} in all cases (the symbols in the above relations have the usual significances[8]). Table I lists the values of $[\eta]$ and $\langle S^2\rangle^{1/2}$ estimated in this way. To check these $\langle S^2\rangle$ values, a few high molecular weight samples were subjected to light-scattering measurements. The results indicate that the estimated values are sufficiently accurate for the present purpose, as Table I shows.

Results and Discussion

A typical example of the Zimm plot for the ternary solution meeting the optical Θ condition is given in Figure 1, which was obtained for a PS with $m_1 = 6850$ and a PIB with $m_2 = 7840$ blended in a volume ratio of 0.593/0.407. As is judged from the χ_{0i} values given in Table I, bromobenzene is a moderate solvent for PS and a near-Θ solvent for PIB. Both the angular and concentration envelopes of the plot are characterized by a set of curves almost parallel with each other. This was the case with all examined ternary systems. The ordinate intercept of the plot presents a value 5.4×10^{-4}, which is close to the theoretical value for $(m_1x_1)^{-1} + (m_2x_2)^{-1}$ of 5.6×10^{-4}. The apparent radius $\langle S^2\rangle_{app}^{1/2}$ from the figure is 380 Å, which agrees well with the theoretical value[17]

$$\langle S^2\rangle_{app} = [m_2x_2\langle S_1^2\rangle_z + m_1x_1\langle S_2^2\rangle_z]/(m_1x_1 + m_2x_2) \qquad (9)$$

of 373 Å (cf. Table I, which gives the weight-average radius estimated with the observed z-average value, according to $\langle S^2\rangle_z/\langle S^2\rangle_w = (1 + 2p)/(1 + p)$ with $p + 1 = M_w/M_n$). The concentration envelope for zero scattering angle has a fairly large negative slope and is nearly linear down to the spinodal defined as the intercept with the horizontal axis. The figure gives a χ_{12} value of 0.0225 and a spinodal concentration ϕ_{sp} of 0.0117.

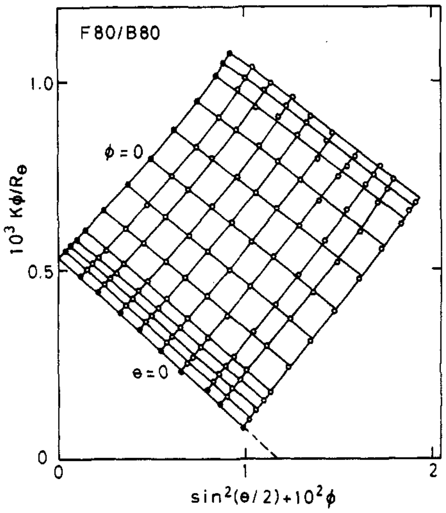

Figure 1. Zimm's plot for PS F80/PIB B80/bromobenzene ternary solution in optical Θ state (30 °C).

In Figures 2, 3, and 4 are shown only the concentration envelopes for blends of PS/PEO, PS/PIP, and PS/PIB, respectively. In all cases, this $K\phi/R_0$ vs. ϕ plot is linear up to a high enough concentration to provide a well-defined value of χ_{12}. Values of χ_{12} determined from the initial slopes of the curves are listed in Table II. Also given in the table are values of ϕ_{sp} for those systems which were studied up to high enough concentrations.

As has been previously discussed,[8] the parameter χ_{12} for infinitely dilute solution may be described with sufficient precision by

$$\chi_{12} = (1 - \chi_{01}^\circ - \chi_{02}^\circ + \chi_{12}^\circ)h_0(\bar{Z}_{12}) - (1/2)[(1 - 2\chi_{01}^\circ)h_0(\bar{Z}_1) + (1 - 2\chi_{02}^\circ)h_0(\bar{Z}_2)] \qquad (10)$$

with

$$h_0(X) = (2.193X)^{-1}[1 - (1 + 3.537X)^{-0.620}] \qquad (11)^{18}$$

$$\bar{Z}_{12} = 0.3723[\sigma^{5/2} + \sigma^{-5/2} - (\sigma + \sigma^{-1})^{5/2} + (5/2) \times (\sigma^{1/2} + \sigma^{-1/2})](\epsilon\sigma^{-3/2}\bar{Z}_1 + \epsilon^{-1}\sigma^{3/2}\bar{Z}_2)(1 + \kappa) \qquad (12)^8$$

Table II
Light-Scattering Results for PS/PEO, PS/PIP, and PS/PIB Blends in Bromobenzene at 30 °C

polymer 1		polymer 2		ξ_{PS}[a]	$10^3 I_0$[b]	$\chi_{12,d}$[c]	$10^2 \phi_{sp}$	$\chi_{12}{}^{\circ}$[d]
PS	F80	PEO	SE70	0.511	0.64 (0.66)	0.0133	2.41	0.263
	P30		SE30	0.493	1.45 (1.50)	0.0176	4.12	0.296
	F10		SE8	0.467	5.30 (5.44)	0.0246		0.276
								0.278 (0.058) av
PS	F10	PIP	I10	0.507	4.37 (4.31)	0.0218		0.168
	P3		I3	0.497	13.6 (12.9)	0.0259		0.130
								0.149 (0.135) av
PS	F80	PIB	B80	0.631	0.54 (0.56)	0.0225	1.17	0.436
	P30		B30	0.619	1.28 (1.27)	0.0310	1.86	0.401
	F20		B20	0.679	2.25 (2.15)	0.0386	2.57	0.448
								0.428 (0.411) av
PS		PMMA						0.031[e] (0.038) av

[a] Weight fraction of PS. [b] Value of $K\phi/R_0$ at zero ϕ. Values in parentheses are theoretical. [c] Value of χ_{12} at zero ϕ. [d] Value for V_0 = 106 mL mol^{-1}. Values in parentheses were calculated with eq 13. [e] Average value in bromobenzene, 30 °C, from ref 8.

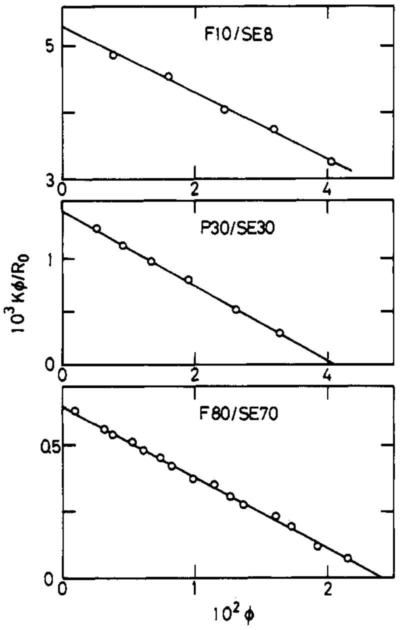

Figure 2. Plot of $K\phi/R_0$ vs. ϕ for PS/PEO/bromobenzene ternary solutions in optical Θ state (30 °C).

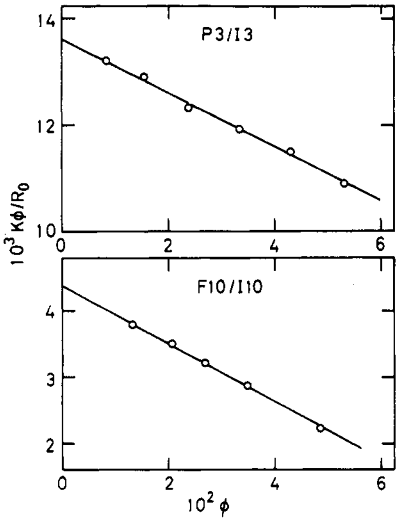

Figure 3. Plot of $K\phi/R_0$ vs. ϕ for PS/PIP/bromobenzene ternary solutions in optical Θ state (30 °C).

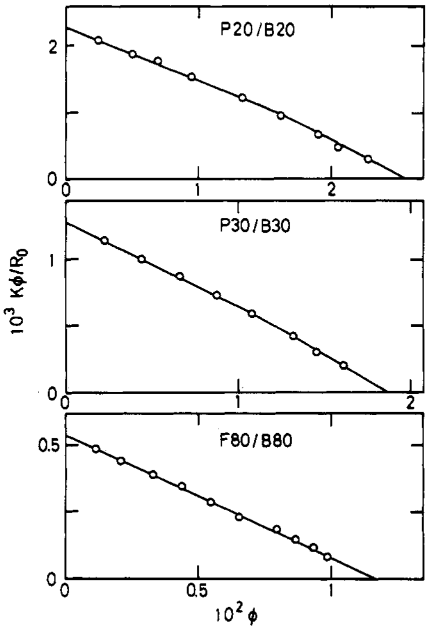

Figure 4. Plot of $K\phi/R_0$ vs. ϕ for PS/PIB/bromobenzene ternary solutions in optical Θ state (30 °C).

where $\epsilon = m_2/m_1$, $\sigma = \langle S_1{}^2\rangle^{1/2}/\langle S_2{}^2\rangle^{1/2}$, and $\kappa = \chi_{12}{}^{\circ}(1 - \chi_{01}{}^{\circ} - \chi_{02}{}^{\circ})$. Using the data in Tables I and II, we have numerically solved eq 10 for the parameter $\chi_{12}{}^{\circ}$ for each system. The analysis according to this scheme should be valid, since σ is close to unity in all cases ($0.8 < \sigma < 1.2$). See ref 8, for more details.

The results are listed in Table II. In each system, χ_{12} shows an increasing trend with decreasing molecular weight, a phenomenon which has been already noted for the PS/PMMA system,[3,5] whereas $\chi_{12}{}^{\circ}$ shows no such trend, as it should be. Probable values of $\chi_{12}{}^{\circ}$ are 0.28 ± 0.02 for PS/PEO, 0.15 ± 0.02 for PS/PIP, and 0.43 ± 0.02 for PS/PIB. These values are quite large as compared with the value 0.028 ± 0.006 for PS/PMMA.[8]

It may be interesting to compare these values of $\chi_{12}{}^{\circ}$ with those calculated by the solubility parameter method:

$$\chi_{12}{}^{\circ} = (V_0/RT)(\delta_1 - \delta_2)^2 \qquad (13)$$

Following Krause's recommendation,[19] we use calculated values of solubility parameter δ instead of experimental values which are seriously scattered in some cases.[20] We calculated δ's using Hoy's table of molar attraction constants.[19-21] For the sake of simplicity,[19] we henceforth assume V_0 to be 100 mL mol^{-1}. Accordingly, our experimental values of $\chi_{12}{}^{\circ}$ appearing in the following discussion will be standardized by multiplying the original values by $100/V_0$ (V_0 = 106 for bromobenzene). Figure 5 shows that the experimental and calculated values agree unexpectedly well for the PS/PMMA, PS/PIP, and PS/PIB systems

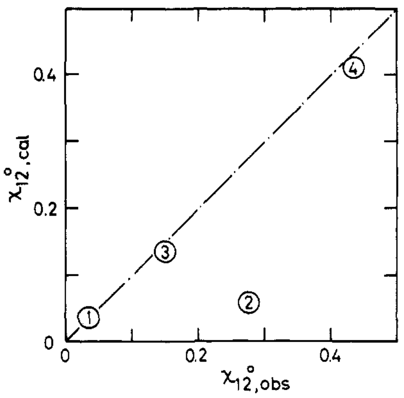

Figure 5. Comparison of the segment–segment interaction parameters observed, $\chi_{12}{}^{\circ}{}_{,\mathrm{obsd}}$, with those calculated, $\chi_{12}{}^{\circ}{}_{,\mathrm{cal}}$, for PS/PMMA (1), PS/PEO (2), PS/PIP (3), and PS/PIB (4) blends.

but very poorly for the PS/PEO system. The good agreement in the former three systems indicates that the polymer–polymer interactions in these systems are predominantly of enthalpic origin, whereas the poor agreement in the last system implies the presence of a specific interaction which cannot be taken into account in such a calculation scheme. Experimentally, PEO is known to show several different values of δ depending on the types of solvents employed for its determination.[22]

We now look at the experimental situation of the solvent-free systems. As to a bulk PS/PIP system, there has been reported the relation[23]

$$\chi_{12}/V_0 = -0.90 \times 10^{-3} + 0.75/T \quad (\mathrm{mol\ mL^{-1}}) \quad (14)$$

where T is the absolute temperature. This relation has been recently confirmed by an X-ray scattering study on a disordered PS/PIP block copolymer system.[24] For a temperature of 30 °C (and for $V_0 = 100$), eq 10 gives a χ_{12} value of 0.16. This is close to our $\chi_{12}{}^{\circ}$ of 0.14. Koningsveld and Kleintjens[25] report the cloud-point curves for some low-molecular weight binary mixtures of PS and PIB along with the location of the critical points for two of them. If the χ_{12} at the critical temperature, T_c, of each blend is evaluated according to

$$(m_1x_1)^{-1} + (m_2x_2)^{-1} = 2\chi_{12}(T_c) \qquad (15)$$

and fitted to a relation analogous to eq 14, there comes out a χ_{12} value of about 0.45 for 30 °C. This value, too, is comparable to our $\chi_{12}{}^{\circ}$ of 0.40. As far as we are aware, no such data have been reported for PS/PEO binaries. As to the PS/PMMA system, we previously analyzed the concentrate-solution light-scattering data for some PS/PMMA blends in bromobenzene and estimated, by extrapolation, the χ_{12} for the bulk to be about 0.028 at 30 °C for the mentioned reference volume of solvent. This value is close to the dilute ternary solution value of $\chi_{12}{}^{\circ} = 0.026$ and also to the value of 0.032 obtained by the intrinsic viscosity analysis on S-MMA copolymers in various types of solvents.[14] Interestingly, Benoit et al.[26] have carried out a neutron-scattering study on a dry block copolymer of PS/PMMA type to suggest a χ_{12} value near 0.005 at 160 °C. Because of the large temperature difference, this value cannot be directly compared with ours but seems to be compatible in magnitude with ours. We also note that the optical Θ light-scattering work by Klotz et al.[6] indicates a negative value of $\chi_{12}{}^{\circ}$ for a PS/poly(vinyl methyl ether) system. This system, in fact, is known to be a miscible blend in bulk. All these results show that there is a strong, nearly quantitative correlation between the parameter $\chi_{12}{}^{\circ}$ derived from dilute solutions and the χ_{12} for dry blends.

Up to this point, we have implicitly assumed χ_{12} to be independent of composition. However, observed cloud-point curves, e.g., are not always simple enough to be describable with a composition-independent interaction parameter. The PS/PIB blends studied by Koningsveld and Kleintjens[25] provide such an example. These blends are characterized by bimodal cloud-point and spinodal curves, the description of which demands at least a quadratic dependence of the interaction parameter on composition.[25] On the other hand, an infinitely dilute solution will be characterized by a composition-independent χ_{12}, since we therein observe bimolecular interactions only. For this reason, one should not put too much quantitative importance on the comparison between dilute-solution and dry-blend data.

Another limitation of the dilute solution approach may be that its precision depends severely on the precision of the theory employed. This is especially so, when the experiments are made in too high a $\bar{Z}_{12}$ region for the interpenetration function $\Psi(\bar{Z}_{12}) = \bar{Z}_{12}h_0(\bar{Z}_{12})$ to be sensitive enough to $\bar{Z}_{12}$ and hence $\chi_{12}{}^{\circ}$ (cf. eq 10–12).

Despite these limitations, the present study well establishes that the segment–segment interactions in solution and those in the bulk are similar in the main, although they may be different in the details. Particularly because of its composition-independent nature, the parameter $\chi_{12}{}^{\circ}$ derived from dilute solution may be useful as the simplest, semiquantitative measure for the compatibility of the relevant polymers.

Behavior at Finite Concentrations. Some words may be due regarding the concentration of demixing and the concentration dependence of χ_{12}. We previously studied nondilute bromobenzene solutions of PS/PMMA blends to determine the χ_{12} as a function of concentration.[1] Becuase of the small magnitude of the $\chi_{12}{}^{\circ}$ and the high degree of symmetry of this system, we could study up to fairly high concentrations without demixing but with little theoretical ambiguity. The observed χ_{12} vs. ϕ curves indicated that there exists a characteristic concentration ϕ^* below which χ_{12} is approximately constant, but above which it increases rather sharply. This concentration, ϕ^*, was found to be approximately represented by

$$\phi^* = 0.8\phi^*_c \qquad (16)$$

where ϕ^*_c is defined as the (average) ratio of the molecular volume, $mV_0/$(Avogadro's number), to the cubic radius, $\langle S^2\rangle^{3/2}$ (see Figure 7 in ref 1). We thus considered this ϕ^* to define the crossover between dilute and semidilute solutions.[27] We also observed that χ_{12} in semidilute solution is independent of chain length, being an increasing function of ϕ. These features of symmetrical solutions should be basically correct also for asymmetrical solutions.

It is generally difficult to derive well-defined information from nondilute asymmetrical solutions. However, we wish here to emphasize that a study of the spinodal composition may provide at least semiquantitative information, if the system is highly incompatible. We show this in the following.

The value of χ_{12} at the spinodal can be represented by[1]

$$\chi_{12,\mathrm{sp}} = \chi_{12,\mathrm{sym}} - (a_{11}{}^{1/2} - a_{22}{}^{1/2})^2/2 \qquad (17)$$

with the new parameter $\chi_{12,\mathrm{sym}}$ defined by

$$\chi_{12,\mathrm{sym}} = (2\phi_{\mathrm{sp}})^{-1}[(m_1x_1)^{-1} + (m_2x_2)^{-1}] \qquad (18)$$

where a_{ii}'s are the second derivatives of the free-energy function. Clearly, $\chi_{12,\mathrm{sp}}$ is never greater than $\chi_{12,\mathrm{sym}}$, the equality $\chi_{12,\mathrm{sp}} = \chi_{12,\mathrm{sym}}$ holding for a symmetrical case, i.e.,

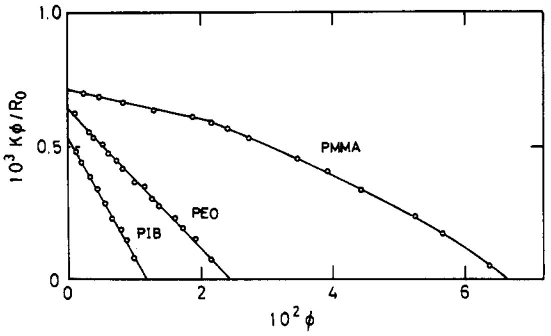

Figure 6. Comparison of the $K\phi/R_0$ vs. ϕ curves for PS/PMMA,[1] PS/PEO, and PS/PIB/bromobenzene solutions including a common PS (sample F80) and a second polymer of similar molecular weight (PMMA 78M,[1] PEO SE70, and PIB B80, respectively.

$a_{11} = a_{22}$. With the expressions for a_{ii}'s given by eq 12 in ref 1, eq 17 can be written

$$\chi_{12,\mathrm{sp}} = \chi_{12,\mathrm{sym}} - \frac{[(\chi_{01} - \chi_{02}) + \{(m_1x_1)^{-1} - (m_2x_2)^{-1}\}/(2\phi_{\mathrm{sp}})]^2}{2[(1-\phi_{\mathrm{sp}})^{-1} - \chi_{01} - \chi_{02} + (\chi_{12,\mathrm{sp}} + \chi_{12,\mathrm{sym}})/2]} \qquad (19)$$

Because the spinodal concentration, ϕ_{sp}, can usually be determined with high precision, the ambiguity in determination of $\chi_{12,\mathrm{sp}}$ arises mainly from that of χ_{0i}'s. Equation 19 shows that this ambiguity becomes relatively smaller and smaller, as $\chi_{12,\mathrm{sp}}$ or $\chi_{12,\mathrm{sym}}$ increases (or ϕ_{sp} decreases). Another point to be made is that when $\chi_{12,\mathrm{sp}}$ is sufficiently large, the spinodal can exist in the "dilute" region where χ_{12} may be considered to remain nearly constant, as suggested by the above-mentioned symmetrical solution study. In such a case, we may expect the approximate equalities $\chi_{12,\mathrm{sym}} \cong \chi_{12,\mathrm{sp}} \cong \chi_{12,\mathrm{d}}$ to hold, where the subscript "d" denotes the dilute limit.

Figure 6 shows the $K\phi/R_0$ vs. ϕ plots for the PS/PMMA, PS/PEO, and PS/PIB bromobenzene solutions. Each system has a PS in common and a second polymer of similar size, blended in a roughly similar ratio. The plots for PS/PIP and PS/PIB are nearly linear up to the spinodal, whereas that for PS/PMMA has a significant curvature at high concentrations. The spinodal concentration decreases in the order PS/PMMA > PS/PEO > PS/PIB, essentially reflecting the increasing order of $\chi_{12}{}^0$. As has been noted, the spinodal of PS/PMMA exists in the "semidilute" region. The crossover concentration, ϕ^*, for this system was found to be about 0.023, and this value should approximately apply to the other systems. Thus, the spinodal of the PS/PEO solution may exist in the crossover region, whereas that of the PS/PIB solution may exist in the dilute region. The values of $\chi_{12,\mathrm{d}}$ and $\chi_{12,\mathrm{sym}}$ for the three systems are

	PS/PMMA	PS/PEO	PE/PIB
$\chi_{12,\mathrm{d}}$	0.0030	0.0133	0.0225
$\chi_{12,\mathrm{sym}}$	0.0053	0.0133	0.0239

In PS/PMMA, $\chi_{12,\mathrm{sym}}$ is considerably larger than $\chi_{12,\mathrm{d}}$. This is essentially due to an increase of χ_{12} itself in the semidilute region, possibly reflecting an increased number of contacts between unlike as well as like segments in this region.[1] In the other systems, the two parameters are nearly the same. According to the argument given above, we consider that these systems, especially PS/PIB, are typical examples of those highly incompatible systems in which bad balance of the solvent affinities for the two polymers (cf. Table I) makes no serious contribution to the location of the spinodal and in which ϕ_{sp} is so small that the ϕ dependence of χ_{12} is trivial.

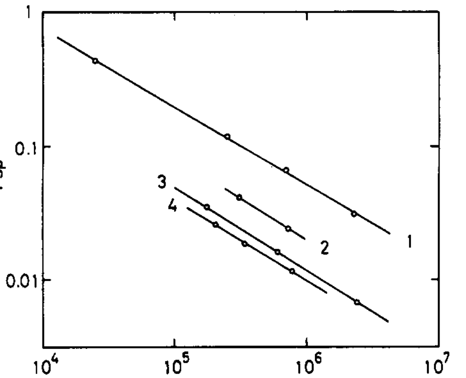

Figure 7. Spinodal concentration ϕ_{sp} as a function of the average molecular weight $\bar{M} = (M_{1,\mathrm{w}}M_{2,\mathrm{w}})^{1/2}$ for PS/PMMA/bromobenzene[1] (curve 1), PS/PEO/bromobenzene (curve 2), PS/PIB/toluene[27] at critical point (curve 3), and PS/PIB/bromobenzene (curve 4). In all cases, $M_{1,\mathrm{w}} \cong M_{2,\mathrm{w}}$, and the blend composition is nearly invariant with molecular weight.

Thus, demixing seems to take place even in dilute solution at least in limited cases.[29] A "dilute" ternary solution has the simple feature that it is characterized by a single χ_{12} ($\cong\chi_{12,\mathrm{d}}$) which is approximately independent of both ϕ and x (but, of course, dependent on m_i's due to the excluded volume effect). The work of van den Esker and Vrij[28] on PS/PIB/toluene solutions is interesting in this connection. Their systems resemble ours except for the fact that toluene is a somewhat better solvent than bromobenzene for both PS and PIB. By light scattering, they determined ϕ_{sp} for varying values of m_1 ($\cong m_2$) and x. When compared on a common level of m_i and x, their values of ϕ_{sp} are generally close to ours, indicating that their systems also are essentially "dilute". In Figure 7, their values of ϕ_{sp} at the critical point ($x_{\mathrm{PS}} \cong 0.36$) are plotted as a function of $\bar{M} = (M_{1,\mathrm{w}}M_{2,\mathrm{w}})^{1/2}$ and compared with our results for the bromobenzene solutions ($x_{\mathrm{PS}} \cong 0.6$). The small difference (~20%) between the two sets of data should be ascribed more to the difference in the solvent power rather than to the difference in x: As the solvent power toward the polymers increases, $\chi_{12,\mathrm{d}}$ and hence $\chi_{12,\mathrm{sp}}$ would become smaller due to an increased excluded volume effect, and thus ϕ_{sp} would increase. This is in line with the observations. On the basis of an equation equivalent to eq 17 with simplifying assumptions for a_{ii}'s, the same authors[28] estimated the values of $\chi_{12,\mathrm{sp}}$. Those values are nearly constant in a middle range of x and similar in magnitude to our $\chi_{12,\mathrm{d}}$ values, when compared on a common level of molecular weight. However, they evidently show an increasing trend as x_1 or x_2 approaches zero. A main reason for this may be the following: As x_1, e.g., approaches zero with χ_{12} and other parameter values assumed to be constant, polymer concentration has to be increased more and more to get to spinodal. This will be clear, if one examines eq 17–19. Thus, the solution eventually enters the semidilute region, in which the chains interpenetrate more significantly than in the dilute region, thus a larger χ_{12} being observed.[1] These authors[28] also discuss the nature of the small magnitude of their $\chi_{12,\mathrm{sp}}$ values. It may be said that they are small essentially because of the dilute solution excluded volume effect (since $\chi_{12,\mathrm{sp}} \cong \chi_{12,\mathrm{d}}$).

Figure 7 shows that the exponent ν in the relation

$$\phi_{\mathrm{sp}} = A\bar{M}^{-\nu} \qquad (20)$$

takes a value close to 0.6 for all the systems discussed in this paper. More specifically, ν is about 0.58 for PS/PMMA/bromobenzene,[1] about 0.60 for PS/PIB/bromobenzene, about 0.62 for PS/PIB/toluene (at the critical compositions),[28] and about 0.62 for PS/PEO/bromobenzene (this last value is less reliable because of the lack of the sufficient data points). So far as these data are concerned, there seems to be no large difference in this exponent between dilute and semidilute solutions. Clearly, more extended and systematic experimental work is required to establish this exponent and check theoretical predictions.[30,31]

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(4) Equation 12 in ref 1 defines the χ parameters appearing in our light-scattering work. In short, they are phenomenological correction functions akin to the g functions introduced by Koningsveld and others (e.g.: Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, Ser. A* **1970**, *319*, 331), the relations between the χ's and g's being given in ref 1. On the other hand, the parameter χ° can be brought into correspondence with the binary cluster integral β's between polymer segments through, e.g.,[8] $\chi_{12}^{\circ} = (N_A/V_0)[\beta_{12} - (\beta_{11} + \beta_{22})/2]$.

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