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Light Scattering from Polymer Blends in Solution. 2. Nondilute Solutions of Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: Light scattering from polystyrene/poly(methyl methacrylate) blends in bromobenzene solution was studied over a wide range of molecular weight and concentration, extending to the spinodal of each blend while keeping the blend composition constant at about 50 vol %. All the solutions studied met the optical as well as thermodynamical symmetry conditions to such a high degree that the Flory–Huggins interaction parameter χ_{12} between the two polymers could be determined with very little experimental and theoretical ambiguities. The following facts have been disclosed: (1) For each pair of the polymers, there exists a characteristic concentration ϕ^* below which χ_{12} is approximately constant but above which it increases rather sharply. (2) ϕ^* is molecular weight dependent and has a strong correlation with the calculated "overlap" concentration that is supposed to characterize the crossover between the dilute and semidilute regimes. (3) In the dilute regime ($\phi < \phi^*$), χ_{12} exhibits a molecular weight dependence, which was quantitatively interpreted according to the two-parameter excluded volume theories, whereas in the semidilute or nondilute regime ($\phi > \phi^*$), χ_{12} is a function of concentration ϕ only. (4) The extrapolation of the log χ_{12} vs. log ϕ curve to $\phi = 1$ gives a value of about 0.030 as an estimate for χ_{12} in the bulk. This value is comparable to the dilute solution value obtained after being corrected for the excluded volume effects.

Introduction

Interactions between different polymers are, in many cases, difficult to characterize by using dry blends, especially when they are immiscible under usual conditions. Introduction of a suitable solvent brings about miscibility between otherwise immiscible polymers, thus rendering experimental approaches feasible. However, it also brings about complexities arising from polymer–solvent interactions.

In the early days, the role of the solvent in a ternary solution was considered merely to dilute polymers so as to reduce the number of polymer–polymer contacts, the solvent thermodynamic nature being unimportant. This optimistic view, which appeared to be consistent with early theoretical[1,2] and experimental[3,4] results, is no longer held in these days, for later studies[5–11] unequivocally showed that the phase-separation behavior of ternary solutions strongly depends on the solvent nature. For example, two polymers miscible in bulk can be made immiscible in solution when the solution affinities for the two polymers differ sufficiently.[9,10] Such strong solvent effects are liable to mask desired information on polymer–polymer interactions. In addition, possible dependences of the interaction parameters on solution compositions make rigorous analysis difficult in many cases.[6,7] For these reasons, our understanding of ternary solutions as yet remains very poor, and the rather pessimistic view seems to be prevailing that ternary solution data may not provide any quantitative or even qualitative information on polymer–polymer interactions.

In a previous paper,[12] we studied light scattering from polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends in dilute solution of bromobenzene (BB). This solvent was chosen because it gives refractive index increments for the two polymers opposite in sign so that the interaction between the polymers can be selectively observed without interference by the polymer–solvent interactions. By this "optical Θ-state" method, we could determine the Flory–Huggins parameter[13] χ_{12} between PS and PMMA precisely enough to establish its molecular weight dependence in dilute solution.

Another merit of using this solvent is that its thermodynamic affinities for PS and PMMA are, as will be shown later, almost the same; viz., the system is thermodynamically as well as optically symmetrical. This not only eliminates theoretical difficulties to treat finite-concentration data but also enhances accuracy to evaluate χ_{12}, since light scattering from a perfectly symmetrical system is independent of polymer–solvent interactions. In this context, the solvent in our system is almost "inert".

On the basis of these principles, we herein examine the light scattering from PS/PMMA/BB solutions of differing polymer molecular weights over a wide range of concentration. In particular, we attempt to evaluate χ_{12} as a function of polymer concentration continuously from the dilute limit up to the region of phase separation. We hope, by doing so, to elucidate how polymer–polymer interactions manifest themselves in ternary solutions and to give one answer to the important question as to whether and how it is possible to derive from solution data quantitative information on polymer–polymer interactions. According to the previous results,[12] the PS/PMMA pair is characterized by a relatively weak interaction χ_{12}. Thus the system studied here will model the interesting case of symmetrical good solvent systems for which the scaling theoretical prediction on the concentration dependence of χ_{12} has been given.[14] This work will virtually be a first experimental approach to this problem also.

Theoretical Section

To make clear the basic assumptions involved and the physical significance obtained in this work, we consider the theoretical aspects is some detail. Partial reproduction of the previous results is inevitable for this purpose.

Free Energy Function. We give the free energy of mixing ΔG of two polymers 1 and 2 and one solvent 0 by the following form (cf. Koningsveld et al.[6]):

$$Z = \Delta G/NRT = \phi_0 \ln \phi_0 + (\phi_1/m_1) \ln \phi_1 + (\phi_2/m_2) \ln \phi_2 + \phi_0\phi_1 g_{01}(\phi) + \phi_0\phi_2 g_{02}(\phi) + \phi_1\phi_2 g_{12}(\phi_1,\phi_2) \tag{1}$$

where N is the total number of lattice sites (in moles), m_i is the degree of chain length, and ϕ_i is the volume fraction *before mixing*

$$m_i = M_i v_i / M_0 v_0 \tag{2}$$

$$\phi_i = w_i v_i / (w_0 v_0 + w_1 v_1 + w_2 v_2) \tag{3}$$

with w_i being the weight fraction of component i having a molecular weight M_i and specific volume v_i in the pure state (i = 0, 1, or 2). In eq 1, the polymers are assumed to be strictly monodisperse. Consequences of relaxing this restriction will be described later.

In eq 1, g_{0i}'s characterize the solvent–polymer interactions and are assumed to be a function of the total polymer fraction ϕ only

$$\phi = \phi_1 + \phi_2 \tag{4}$$

whereas g_{12} characterizes the polymer–polymer interaction and is assumed to be a function of both ϕ_1 and ϕ_2, viz., ϕ and x_i

$$x_1 = 1 - x_2 = \phi_1/\phi \tag{5}$$

In other words, g_{0i}'s are defined for the respective polymer/solvent binary solutions of concentration ϕ, and therefore g_{12} includes all the free energy change, except for the combinatorial entropy, due to mixing the two binary solutions. With g_{12} defined in this way, eq 1 is a perfectly general expression.

The solvent chemical potential $\Delta\mu_0$ derived from eq 1 takes the form (cf. Fujita and Teramoto[15])

$$\Delta\mu_0/RT = \ln \phi_0 + (1 - m_1^{-1})\phi_1 + (1 - m_2^{-1})\phi_2 + \phi^2(x_1\chi_{01}^* + x_2\chi_{02}^* - x_1x_2\chi_{12}^*) \tag{6}$$

$$\chi_{0i}^* = g_{0i} - \phi_0(\partial g_{0i}/\partial\phi), \quad i = 1 \text{ or } 2 \tag{7a}$$

$$\chi_{12}^* = g_{12} + \phi(\partial g_{12}/\partial\phi) \tag{7b}$$

We have attached an asterisk to these "chemical potential χ parameters" to distinguish them from the "light scattering χ parameters" that will most often appear in this paper.

Light Scattering Formulas. Combination of eq 1 with the general theory of light scattering from multicomponent solutions[16–18] gives the following expression for the excess forward intensity R_0 (cf. Stockmayer[18] and Scholte[20]):

$$R_0 = K^* V_0 (v/v_{\mathrm{id}}) \frac{\psi_2^2 a_{11} + \psi_1^2 a_{22} - 2\psi_1\psi_2 a_{12}}{a_{11}a_{22} - a_{12}^2} \tag{8}$$

$$K^* = (4\pi n^2)/(\mathrm{N_A}\lambda_0^4) \tag{9}$$

$$\psi_i = \partial n/\partial\phi_i \tag{10}$$

where $V_0 = M_0 v_0$ is the solvent molar volume, v is the specific volume of the solution, v_{id} ($=\sum w_i v_i$) is its value when no volume change on mixing is assumed, n is the refractive index of the solution, λ_0 is the wavelength under vacuum, and N_A is the Avogadro number. In eq 8, a_{ij} is written for

$$a_{ij} = \partial^2 Z/\partial\phi_i\partial\phi_j, \qquad i, j = 1 \text{ or } 2 \tag{11}$$

and can be given in the form (cf. Tompa[4])

$$a_{ii} = (1 - \phi)^{-1} + (m_i x_i \phi)^{-1} - 2\chi_{0i} \tag{12a}$$

$$a_{12} = (1 - \phi)^{-1} - \chi_{01} - \chi_{02} + \chi_{12} \tag{12b}$$

where the light scattering χ's are related to g's and χ^*'s by

$$\chi_{01} = \chi_{01}^* + (x_1\phi/2)(\partial\chi_{01}^*/\partial\phi) + (x_2\phi/2)(\partial\chi_{02}^*/\partial\phi) - x_2^3[(\partial g_{12}/\partial x_1) + (x_1/2)(\partial^2 g_{12}/\partial x_1^2)] - x_2\phi[(\partial g_{12}/\partial\phi) + x_1x_2(\partial^2 g_{12}/\partial\phi\partial x_1) + (x_1\phi/2)(\partial^2 g_{12}/\partial\phi^2)] \tag{13a}$$

$$\chi_{12} = -(1/2)(\partial^2\omega/\partial x_1^2) = g_{12} - (x_2 - x_1)(\partial g_{12}/\partial x_1) - (x_1x_2/2)(\partial^2 g_{12}/\partial x_1^2) \tag{13b}$$

where $\omega = x_1x_2g_{12}$. To obtain χ_{02}, interchange x_1 and x_2 in eq 13a. We note that if g_{12} is independent of x_1, then $\chi_{12} = g_{12}$, and if all g_{ij}'s are independent of both ϕ and x_1, then $\chi_{0i} = \chi_{0i}^* = g_{0i}$.

For small values of ϕ, eq 8 with eq 12 can be expanded in powers of ϕ to give the following expression (cf. Stockmayer and Stanley[19]):

$$(R_0/K^*V_0\phi)(v_{\mathrm{id}}/v) = \psi_1^2 m_1 x_1 + \psi_2^2 m_2 x_2 - [\psi_1^2 m_1^2 x_1^2(1 - 2\chi_{01}) + \psi_2^2 m_2^2 x_2^2(1 - 2\chi_{02}) + 2\psi_1\psi_2 m_1 m_2 x_1 x_2(1 - \chi_{01} - \chi_{02} + \chi_{12})]\phi + \dots \tag{14}$$

In the dilute solution where only bimolecular clusters are to be considered, g_{12} should naturally be independent of x_1, and thus the χ's appearing in eq 14 satisfy the following equalities (cf. eq 13):

$$\chi_{0i} = \chi_{0i}^*, \qquad i = 1 \text{ or } 2 \tag{15}$$

$$\chi_{12} = \chi_{12}^* = g_{12} \tag{16}$$

When the optical Θ condition[12]

$$\psi_1 m_1 x_1 + \psi_2 m_2 x_2 = 0 \tag{17}$$

is met, eq 14 is transformed to

$$K\phi/R_0 = (m_1x_1)^{-1} + (m_2x_2)^{-1} - 2\chi_{12}\phi + \ldots \tag{18}$$

$$K = K^* V_0 (v/v_{\mathrm{id}})(\psi_1 - \psi_2)^2 \tag{19}$$

Equation 18 is equivalent to but somewhat simpler in form than the previous one.[12]

Up to now, we have assumed that the polymers are strictly monodisperse. With reference to Koningsveld et al.,[6] it is clear that the above light scattering formulas are still valid for polydisperse polymers if m_i's are regarded as weight-average values. Of course, this treatment is valid only when the distributions are not too broad, since the interaction parameters are generally dependent on molecular weight.

Experimental Approaches. As eq 13 indicates, light scattering from a ternary solution depends on subtle details of the composition dependence of the interaction parameters, and thus it is generally difficult to undertake a rigorous analysis for determining χ_{12}. Moreover, one cannot expect high precision if the required information is a small difference between large quantities, as is usually the case (cf. ref 12).

At the present time, we can think of two approaches in which the difficulties may be avoided. One is to study, as already suggested, dilute solutions under an optical Θ condition, where one can evaluate χ_{12} without any knowledge of χ_{0i}'s (cf. eq 18) and thus with the highest possible precision.[12]

The other is to study the spinodal of symmetrical or nearly symmetrical systems in which $m_1x_1 \sim m_2x_2$, and $\chi_{01} \sim \chi_{02}$. Also in this case, one need not know details of χ_{0i}'s for the following reason: The spinodal equation

$$a_{11}a_{22} - a_{12}^2 = 0 \tag{20}$$

can be solved for χ_{12} to obtain

$$2\chi_{12} = (m_1x_1\phi_{\mathrm{sp}})^{-1} + (m_2x_2\phi_{\mathrm{sp}})^{-1} - (a_{11}^{1/2} - a_{22}^{1/2})^2 \tag{21}$$

where ϕ_{sp} is the polymer concentration at the spinodal. If we write $a_{22} = a_{11} + \Delta a$ with

$$\Delta a = (m_2x_2\phi_{\mathrm{sp}})^{-1} - (m_1x_1\phi_{\mathrm{sp}})^{-1} + (\chi_{02} - \chi_{01})$$

Δa is, for $m_1x_1 \sim m_2x_2$ and $\chi_{01} \sim \chi_{02}$, small as compared with a_{ii}, thus

$$a_{11}^{1/2} - a_{22}^{1/2} = \Delta a/(2a_{ii}^{1/2})$$

Neglecting trivial terms, we thus find

$$2\chi_{12} \sim (m_1x_1\phi_{\mathrm{sp}})^{-1} + (m_2x_2\phi_{\mathrm{sp}})^{-1} - \frac{(\chi_{02} - \chi_{01})^2(1 - \phi_{\mathrm{sp}})}{1 - (\chi_{01} + \chi_{02})\phi_{\mathrm{sp}}} \tag{22}$$

By referring to eq 13a, we can write

$$\chi_{01} - \chi_{02} = \chi_{01}^* - \chi_{02}^* + \Delta\chi \tag{23}$$

where $\Delta\chi$ is a function of the derivatives of g_{12} only and may legitimately be considered to be the same order in magnitude as g_{12} or χ_{12}. Therefore, the last term in the right-hand side of eq 22 is unimportant compared with the first two, insofar as $\chi_{01}^* - \chi_{02}^* \sim \chi_{12}$, and $\chi_{12} \ll 1$, which indeed is the case with our systems studied here.

It is clear that if *both* the optical and thermodynamic symmetry conditions are met, a rigorous and perhaps most accurate light scattering analysis is possible for any intermediate values of ϕ between the dilute limit and the spinodal. Such a study is reported in the following.

Table I
Characteristics of Polymer Samples

sample	$10^{-4}M_{\mathrm{w}}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$	$\chi_{0i,\mathrm{d}}$[a]
PS PC200	242	1.30	0.4743
F80	77.5	1.01	0.4661
49H	28.3	1.10	0.455[b]
39H	2.45	1.27	0.417
PMMA 75M	219	1.35	0.4752
78M	62.7	1.45	0.4633
31M	21.1	1.27	0.4544
91M	2.45	1.04	0.414

[a] Value for an infinitely dilute bromobenzene solution at 30 °C. [b] Estimated value.

Table II
Parameter Values for the Specific Volume *v* and the Refractive Index *n* of PS(1)/PMMA(2)/Bromobenzene(0) Ternary Systems (30 °C)[a]

v_0	B_1	B_2	B_{11}	B_{22}	B_{12}
0.6750	0.9150	0.8082	0.0435	0.0495	0.0485
n_0	D_1	D_2	D_{11}	D_{22}	D_{12}
1.5803	0.0717	−0.0742	−0.041	−0.014	−0.028

[a] v_0 and B's are in mL g^{-1}.

Experimental Section

The molecular characteristics of the PS and PMMA samples are listed in Table I, which shows that all the samples have a narrow or reasonably narrow molecular weight distribution (see ref 12 for more details).

Experimental data on the specific volume v and the refractive index n of PS/BB and PMMA/BB binary solutions were collected over considerably wide ranges of polymer concentration, extending to $\phi \sim 0.2$ in many cases. A 10-mL Weld-type pycnometer and a Union Giken differential refractometer Model RM102, Osaka, Japan, were used to measure solution densities and refractive index increments, respectively. The results are well represented by the formulas

$$v = w_0v_0 + B_1w_1 + B_2w_2 + B_{11}w_1^2 + B_{22}w_2^2 + 2B_{12}w_1w_2 \tag{24}$$

$$n = n_0 + D_1w_1 + D_2w_2 + D_{11}w_1^2 + D_{22}w_2^2 + 2D_{12}w_1w_2 \tag{25}$$

with the coefficient values listed in Table II.

Light scattering experiments were made on a Fica light scattering photometer Moodel 50, France, by using vertically polarized light of 436-nm wavelength. Measurements were made on the four pairs of PS and PMMA of similar molecular weight, blended in such a ratio as to meet the condition in eq 17 *at the infinite dilution.* Measurements were also made on several binaries to evaluate χ_{0i}'s as a function of concentration and molecular weight. The refractive index increment ψ_i was calculated by assuming eq 25 to be valid for all relevant concentrations, with relations such as

$$\psi_1 = \partial n/\partial\phi_1 = (\partial n/\partial w_1)(\partial w_1/\partial\phi_1) \tag{26}$$

where ϕ_i is given by eq 3 with v_1(PS) = 0.935 and v_2(PMMA) = 0.825 mL/g. Whenever filtration was difficult due to a high polymer concentration, a clarified dilute solution placed in a light scattering cell was concentrated by carefully evaporating the solvent in a vacuum oven. For more detalis, see ref 12 and 21.

Results and Discussion

As has been pointed out, optical and thermodynamic symmetry of the system is essential to obtain accurate and well-defined information. In this respect, our PS/PMMA/BB systems are nearly ideal. This is indicated by Figure 1. In each part of the figure, the values of χ_{0i} for the PS and PMMA samples composing the ternary solution studied here are plotted as a function of ϕ for the sake of comparison. Even though the individual values of χ_{0i} show significant dependences on both concentration and molecular weight, the difference between the paired

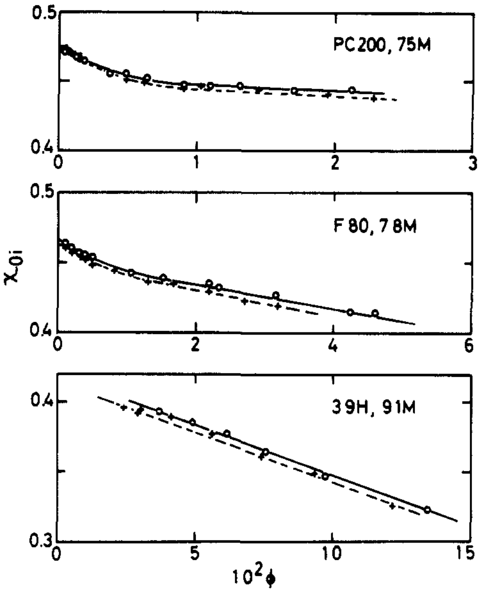

Figure 1. Comparison of the values of χ_{0i} for the PS (circles and solid curve) and PMMA (crosses and broken curve) samples composing each blend solution.

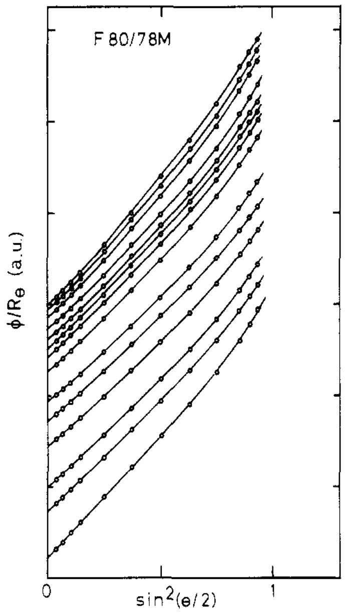

Figure 2. Angular dependence of ϕ/R_θ for PS(F80)/PMMA(78M)/bromobenzene ternary solution: the ordinate scale is in arbitrary units. Values of 10^2 ϕ are, from top downward, 0.243, 0.484, 0.840, 1.298, 1.891, 2.17, 2.41, 2.74, 3.47, 3.92, 4.45, 5.28, 5.66, and 6.39.

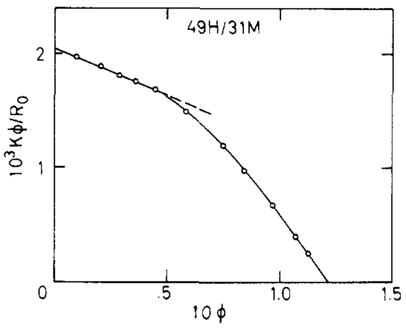

Figure 3. Plot of $K\phi/R_0$ vs. ϕ for PS(49H)/PMMA(31M)/bromobenzene ternary solution.

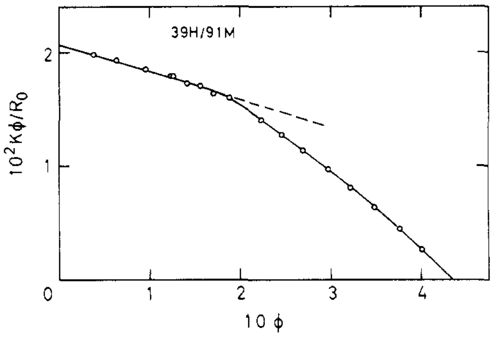

Figure 4. Plot of $K\phi/R_0$ vs. ϕ for PS(39H)/PMMA(91M)/bromobenzene ternary solution.

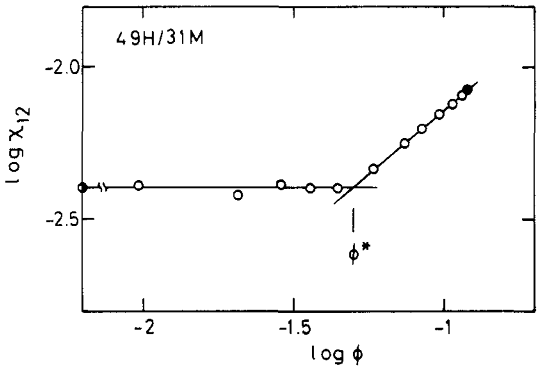

Figure 5. Plot of log χ_{12} vs. log ϕ for PS(49H)/PMMA(31M)/bromobenzene ternary solution: the filled and half-filled circles represent the values at the spinodal and dilute limit, respectively.

two exceeds in no case 0.01 in the examined ranges of concentration.

An example of light scattering results on ternary solutions is presented in Figure 2, in which ϕ/R_θ is plotted against $\sin^2(\theta/2)$ for various values of ϕ, where R_θ is the scattering intensity observed at an angle θ. In this and all other cases examined, the angular dependence was characterized by a set of curves that are nearly parallel to each other over the entire ϕ range. This qualitatively confirms the scattering function recently proposed by Benoit and Benmouna,[22] insofar as the present special cases are concerned.

Figures 3 and 4 show examples of the $K\phi/R_0$ vs. ϕ plot, where R_0 was obtained by extrapolating R_θ to zero θ. In both cases, the curve is linear up to a considerably high concentration, above which R_0 increases more rapidly with increasing concentration, approaching the spinodal defined as the intercept with the horizontal axis. The value of χ_{12} evaluated from the slope of the initial linear portion of the curve (cf. eq 18) was discussed previously.[12] In this paper, this value of χ_{12} is designated as $\chi_{12,\mathrm{d}}$, with the subscript d denoting dilute solutions.

In order to analyze the finite concentration data, we simply assume that χ_{0i}'s are independent of ϕ; i.e., $\chi_{0i} = \chi_{0i,\mathrm{d}}$ for all values of ϕ, even though this is not true, as we have seen. The adequacy of this approximation can be confirmed by means of numerical simulation based on eq 13 and 22 and the χ_{0i} data given in Figure 1. Equation 8 with eq 12 can now be solved for χ_{12} for arbitrary values of ϕ to obtain results such as presented in Figures 5 and 6. Interestingly, the figures indicate that each blend has a characteristic concentration ϕ^*, below which χ_{12} is approximately constant and equal to $\chi_{12,\mathrm{d}}$ but above which it increases rather sharply with increasing ϕ. Values of ϕ^* are collected in Table III together with values of $\chi_{12,\mathrm{d}}$, $\chi_{12,\mathrm{sp}}$, and ϕ_{sp}, where the subscript sp denotes spinodal.

In symmetrical ternary solutions with small χ_{12}, such as those studied here, the interaction χ_{12} will cause only a weak perturbation on the solution structure which is akin

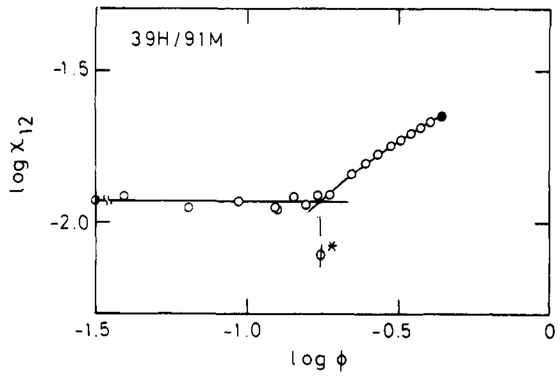

Figure 6. Plot of log χ_{12} vs. log ϕ for PS(39H)/PMMA(91M)/bromobenzene ternary solution: see the caption for Figure 5.

Table III
Values of $\chi_{12,\mathrm{d}}$, ϕ^*, ϕ_{sp}, and $\chi_{12,\mathrm{sp}}$ for PS/PMMA/Bromobenzene Ternary Systems (30 °C)

blend						
PS	PMMA	$\xi_{\mathrm{PS}}{}^a$	$\chi_{12,\mathrm{d}}{}^b$	ϕ^*	ϕ_{sp}	$\chi_{12,\mathrm{sp}}$
PC200	75M	0.455	0.0026	0.019	0.031	0.0034
F80	78M	0.427	0.0030	0.023	0.067	0.0052
49H	31M	0.407	0.0040	0.050	0.119	0.0084
39H	91M	0.479	0.0117	0.180	0.439	0.0225

[a] Weight fraction of PS. [b] From ref 12.

to that of a binary solution. In such a case, the observed value of χ_{12} will more or less directly reflect the solution structure or the probability of contacts of polymer segments. If the structure is "random" or the contact probability is given by $\phi_1\phi_2$, as is assumed in the Flory–Huggins theory, one will observe a constant χ_{12} independently of concentration and chain length. Insofar as dilute solutions with a good solvent are concerned, this, of course, is not true. In this case, polymer chains interpenetrate each other only to a limited extent, and thus the contact probability is generally smaller than $\phi_1\phi_2$. Then, if we write χ_{12} as

$$\chi_{12} = f\chi_{12}{}^\circ \tag{27}$$

where $\chi_{12}{}^\circ$ is supposed to be a constant, the factor f is generally a function of chain lengths, solvent affinities, and polymer concentrations. The factor f for the infinitely dilute solution can be evaluated on the basis of the two-parameter theory on the second virial coefficient[12]

$$f_{\mathrm{d}} = \partial\Psi(\bar{Z})/\partial\bar{Z} \tag{28}$$

where Ψ is the interpenetration function, a function only of $\bar{Z} = Z/\alpha^3$, with Z being the excluded-volume parameter and α^3 the cubic expansion factor.[23] We previously showed[12] that the dilute solution data for the PS/PMMA/BB systems of varying chain lengths can be adequately described by eq 27 and 28, giving an estimate for $\chi_{12}{}^\circ$ of about 0.025. In a forthcomming paper, we will propose a more general treatment of dilute solution data, reconfirming the adequacy of eq 28 for the present particular systems.[23b]

The ϕ dependence of χ_{12} as shown in Figures 5 and 6 could, therefore, be understood as a ϕ dependence of the contact probability. In the region $\phi < \phi^*$, the probability factor f remains nearly constant and equal to f_{d}, whereas in the region $\phi > \phi^*$, it increases with increasing ϕ. This characteristic behavior of χ_{12} brings to mind the notion of "dilute" and "semidilute" solutions,[14] and thus it may be interesting to compare ϕ^* with the "overlap" concentration ϕ^*_{c} defined by

$$\phi^*_{\mathrm{c}} = (\textstyle\sum n_i m_i v_i)/(N_{\mathrm{A}}\sum n_i \langle S_i^2\rangle^{3/2}) \tag{29}$$

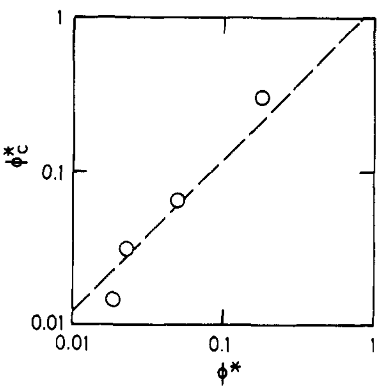

Figure 7. Comparison of ϕ^* and ϕ^*_{c}: the broken curve represents $\phi^* = 0.8\phi^*_{\mathrm{c}}$.

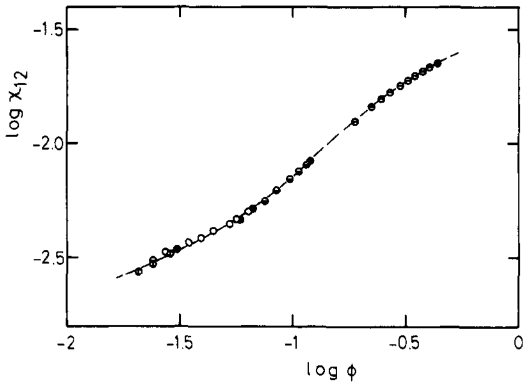

Figure 8. Plot of log χ_{12} vs. log ϕ for PS/PMMA/bromobenzene ternary solutions: the presented data are relevant to concentrations higher than the ϕ^*'s of the individual blends. Different symbols refer to different blends, and the filled circles represent the spinodal.

where n_i denotes the number of molecules. For a solution with a single polymer that has a molecular weight distribution of the Schulz–Zimm type and a radius vs. molecular weight relation of the type $\langle S^2\rangle \sim M^b$, ϕ^*_{c} can be given by

$$\phi^*_{\mathrm{c}} = (M_{\mathrm{n}}v/N_{\mathrm{A}}\langle S^2\rangle_z{}^{3/2})[\Gamma(h)/\Gamma(h+1.5b)] \times [\Gamma(h+b+2)/\Gamma(h+2)]^{3/2} \tag{30}$$

where $\langle S^2\rangle_z$ is the z-average mean-square radius, Γ is a gamma function, and $h^{-1} = (M_{\mathrm{w}}/M_{\mathrm{n}}) - 1$. For a solution of two such polymers, we have

$$1/\phi^*_{\mathrm{c}} = (x_1/\phi^*_{\mathrm{c},1}) + (x_2/\phi^*_{\mathrm{c},2}) \tag{31}$$

The necessary data to compute eq 30 for the present systems are found in ref 12. The ϕ^*_{c} thus obtained is compared with ϕ^* in Figure 7, which shows a close correlation between these quantities. This indicates that by observing the change in the trend of χ_{12}, we are indeed observing the crossover between the dilute and semidilute solutions.

In semidilute solutions, χ_{12} as well as other thermodynamic properties are expected to be independent of chain length. In Figure 8 are collected and plotted the χ_{12} data relevant to concentrations higher than the ϕ^* of the individual blends as a function of ϕ. All the data points seem to form a single composite curve, which means that χ_{12} or f in this region is a function of ϕ only.

In this connection, de Gennes[14] expects, on the basis of the scaling theory,[24] that f for semidilute solutions varies as

$$f_{\mathrm{sd}} \sim \phi^{1/4} \tag{32}$$

On the other hand, the slope of the experimental curve is not constant but varies with ϕ, exceeding $^1/_2$ in the entire range of ϕ studied. As we have already seen, the factor f is, for $\phi < \phi^*$, approximately given by the $f_d(\bar{Z})$ in eq 28, and it shifts to another function, $f_{sd}(\phi)$, of ϕ only, as ϕ increases passing through ϕ^*. Thus, postulating that $f_{sd} = f_d$ at $\phi = \phi^*$ and that ϕ^* is equal to the $\phi^*{}_c$ given by eq 29, we can compute f_{sd} on the basis of analytical theories on Ψ and α such as those due to Flory et al.[23]

$$\Psi = \ln(1 + 5.73\bar{Z})/5.73 \tag{33}$$

$$\alpha^5 - \alpha^3 = 1.276Z \tag{34}$$

The function $f_{sd}(\phi)$ evaluated in this way has a complicated structure and cannot be represented by a simple power law, but it can be shown to converge to the de Gennes equation 32 in the limit of large m, i.e., small ϕ. Use of different functions for Ψ and α leads to different limiting power laws, however. In any case, it may be necessary to go down to an extremely low ϕ region to check the limiting behavior, but this may not be easy in practice.

The absence of chain-length dependence in χ_{12} in nondilute solutions may be of special significance. It will greatly simplify thermodynamic descriptions of nondilute ternary solutions which may in many cases consist of an asymmetric pair of polydisperse polymers. Particularly, it justifies, at least to some extent, trials for estimating the χ_{12} in a dry blend on the basis of nondilute solution data. As already noted, no adequate theory is as yet available that explains the functional form of χ_{12} as displayed in Figure 8 and permits prediction of its behavior at concentrations closer to $\phi = 1$. However, a simple extrapolation of the curve to $\phi = 1$ suggests that $\chi_{12}{}^\circ$ is about 0.030 for the dry blend. At this time, there is only one reported value of χ_{12} for the PS/PMMA pair in a dry state,[25] but it is relevant to a much higher temperature and thus cannot be directly compared with our value.

On the other hand, it is interesting that the present value is comparable to the aforementioned dilute solution value[12] of $\chi_{12}{}^\circ = 0.025$. We also note that a current analysis of the intrinsic viscosity data for S-MMA statistical copolymers dissolved in various solvents has provided a solvent-independent value of 0.032 for the corresponding parameter,[26] which is close to either of the ternary solution values. These indicate that the PS/PMMA systems may possibly be characterized, at least to a first approximation, by a single interaction parameter value that is independent of chain length, solvent quality, and concentration. In this context, solution data do provide quantitative and useful information on polymer-polymer interactions, if they are analyzed in adequate manners. In this paper, the blend composition x has been fixed to a constant value near 0.5 in all cases, and the above discussion has implicitly assumed that the x dependence of χ_{12} is not very significant. Of course, more rigorous discussion requires this dependence to be disclosed.

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