Polymer−Polymer Interaction Parameters Obtained from Diffusion Coefficients of Ternary Polymer Solutions

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ABSTRACT: Dynamic light scattering and pulsed field gradient nuclear magnetic resonance were used to study ternary polymer solutions formed with poly(methyl methacrylate) and polystyrene dissolved in deuterated bromobenzene and also in deuterated toluene. The self-diffusion coeffient of each polymer and the slow mode diffusion coefficient were determined for each solution. These diffusion coefficients were then used to calculate the polymer−polymer interaction parameter χ for each solution assuming that the Borsali−Benmouna theory adequately described the dynamic light scattering observations. This procedure is complementary to that introduced by Sun and Wang. Both procedures recognize that additional experimental information is required if the variation of χ with solution composition is to be determined. Sun and Wang measured the dynamic light scattering mode amplitudes; this work measures the polymer self-diffusion coefficients. The values of χ obtained from the bromobenzene solutions compare favorably with those obtained by Fukuda et al. using classical light scattering under optical Θ conditions. Also the variation of χ with minority polymer molar mass was similar to the predicted variation of the critical value of χ. However, the values of χ obtained from the deuterated toluene solutions were larger and did not behave in a similar manner. This anomalous behavior is explained in terms of the phase stability of the deuterated toluene solutions. However, the possibility that the Borsali−Benmouna theory is inadequate for solutions formed with a solvent of unequal affinities for the two polymers when the solutions are close to phase separation is not discounted.

Introduction and Theory

The polymer−polymer interaction parameter χ is introduced in the Flory−Huggins theory of polymer mixtures. The theory has been developed by assuming χ to be constant for any given pair of polymers and that the compatibility of the two polymers is governed solely by χ. However, the theory is known to be incomplete, for χ is introduced as a constant independent of polymer composition, solvent, or temperature which is contrary to experiment.[1−3] Indeed, Saeki et al.[4] and Robard et al.[5] have separately shown that the compatibility of two polymers in a ternary solution depends on the solvent, even polymers with a negative χ value can separate into two-phased solutions if the solvent has sufficiently dissimilar affinities for the two polymers, thereby implying that the effective polymer−polymer interaction parameter for two polymers is solvent dependent. Nevertheless, χ has proven to be a valuable yardstick for describing the thermodynamic behavior of polymers in combination. A thorough discussion of polymer−polymer interaction parameters is presented by Kamide,[6] who also briefly describes the various methods employed in its determination.

Classical light scattering is one of the most useful techniques available even though precise measurements of χ are difficult to obtain using this method because the larger polymer−solvent interactions tend to dominate the smaller polymer−polymer interactions. However, reliable measurements can be made if care is taken to ensure that the polymer refractive indices satisfy one of two sets of stringent conditions. Either one of the polymers must be isorefractive with the solvent or the polymers must have equal contrast. The classical light scattering studies of Ould Kaddour and Strazielle[7] on solutions of polystyrene and poly(dimethylsiloxane) (PDMS), dissolved in four different solvents, and those of Fukuda et al.[8,9] on solutions of polystyrene and poly(methyl methacrylate) (PMMA), dissolved in bromobenzene, have provided valuable information on polymer−polymer interaction parameters and their variation with polymer molar mass, polymer relative abundances, polymer concentration, and solution temperature. Su and Fried[10] have also used classical light scattering to measure χ for dilute solutions of polystyrene and PMMA dissolved in bromobenzene; these authors also presented a detailed discussion pointing out the need for the theory to be extended to dilute solutions of asymmetric systems. Miyashita et al.[11] have used classical light scattering to investigate polymer blend solutions formed with deuterated benzene and very nearly equal molar mass polystyrene and PMMA, 355 000 and 327 000 Da, respectively. They presented an LCST-type phase diagram for the system from which they drew two conclusions: first, that χ had a positive temperature dependence and, secondly, that deuterated benzene was not an equally good solvent for these polymers. These authors did not attempt to measure χ, for they were primarily interested in the behavior of the solutions as phase separation was approached. They measured the critical exponents for osmotic susceptibility and correlation length and showed that, as expected, these values were consistent with the 3-D Ising values, though a weak polymer composition dependence was observed. Seils et al.[12] have also used classical light scattering to obtain the critical exponents of polymer blend solutions formed with nearly equal molar mass polystyrene and PMMA dissolved in bromobenzene. These authors used larger molar mass polymers (910 000 and 980 000 Da, respectively) and found the critical exponents to assume values intermediate between the mean field and the 3-D Ising values. These authors applied the theory developed by Benmouna et al.[13] for the critical behavior of symmetric solutions, that is solutions formed with equal molar mass polymers at equal abundances satisfying the equal contrast condition. They measured χ as a function of temperature and reported χ to increase as the solution approached phase separation. They were

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also able to confirm that as phase separation was approached, an additional slow decay mode was engendered whose amplitude increased as the scattering vector was decreased and as phase separation was approached. Their method for determining χ requires much data manipulation and the uncertainties on the χ values are of the same order as χ itself. They reported χ to increase from 6.4×10^{-4} to 1.2×10^{-3} as the temperature was reduced from 30 to 2 °C, these values would seem to be approximately one-quarter of those reported by Fukuda et al.[9] for similar solutions. Nevertheless, these are valuable studies, for they examine the increase of χ as phase separation is approached.

A general theory of the behavior of χ with solution temperature, polymer molar masses, polymer concentration, and relative abundance is not available. But two expressions exist for the dependence of χ_c, the value of χ at phase separation. Tompa[14] quotes the Flory−Huggins formula as

$$\chi_c = 0.5[\sqrt{(V_s/V_1)} + \sqrt{(V_s/V_2)}]^2 \tag{1a}$$

where V_s, V_1, and V_2 are the molar volumes of the solvent and polymers. Eisele[15] rewrites this as

$$\chi_c = 0.5[\sqrt{(1/N_1)} + \sqrt{(1/N_2)}]^2 \tag{1b}$$

where N_1 and N_2 are the degrees of polymerization of polymers 1 and 2, respectively.

Also, Benmouna et al.[13] have obtained

$$1/\chi_c = 2\phi N x(1 - x) \tag{2}$$

for a solution formed of polymers with equal degrees of polymerization N, at total polymer volume fraction ϕ and relative abundance x. The x dependence of χ_c has been verified by the classical light scattering studies of Ould Kaddour and Strazielle[7] and the $N\phi$ dependence has been verified by Fukuda et al.[9] The general dependence of χ, as distinct from χ_c, on x is unknown; however, Broseta et al.[16] have used the 3D Ising model describing the critical behavior of ternary polymer solutions to show that χ varies with temperature as

$$\chi \propto [T/T_s]\chi_c \tag{3}$$

where T and T_s are the temperature and the spinodal temperature, respectively. Miyashita et al.[11] have shown that T_s varies slowly with x for solutions formed with PMMA and polystyrene dissolved in deuterated benzene, so $1/\chi$ can be expected to exhibit a parabolic dependence on x for concentrated solutions that are “equally far” from phase separation.

Giebel et al[17,18] have used dynamic light scattering to obtain a measure of the effective polymer−polymer interaction parameter of two polymers by applying the Borsali−Benmouna[19−23] theory of dynamic light scattering from semidilute ternary polymer solutions. This theory assumes that the solutions are far from phase separation and obtains general expressions for the dynamic scattering matrix and the diffusivity matrix. The following approximations are made to allow comparison between theory and experiment. The monomer friction coefficients of each polymer are assumed to be equal, and the solvent is assumed to have equal affinities for the polymers. No restriction is placed on the refractive indices of the solvent or polymers. The theory predicts that the field autocorrelation function of the scattered light comprises two decay processes, a fast decay due to a diffusion coefficient D_+ and a slow decay due to the diffusion coefficient, D_-. It should be noted that Akcasu et al.[24] have shown that in general these diffusion coefficients cannot be identified with the cooperative diffusion and interdiffusion coefficients, respectively, so these names will not be applied to the fast and slow diffusion coefficients. The theory developed by Borsali and Benmouna obtains expressions for the fast and slow diffusion coefficients so no such identification is necessary.

D_+ and D_- are given by

$$D_+/D_{s2} = A + 0.5\sqrt{F - E + Q} \tag{4}$$

$$D_-/D_{s2} = A - 0.5\sqrt{F - E + Q} \tag{5}$$

$$A = 0.5[N_2/N_1 + 1 + v\phi N_2] \tag{6}$$

$$E = -4xv\phi N_2(1 - N_2/N_1) \tag{7}$$

$$F = 8x(1 - x)(v\chi N_2)^2\chi/v \tag{8}$$

$$Q = 4(A - N_2/N_1)^2 \tag{9}$$

In the above x is the relative abundance of polymer 2, N_1 and N_2 are the degrees of polymerization of polymers 1 and 2, v is the polymer excluded volume parameter, and D_{s2} is the self diffusion coefficient of polymer 2. One should be aware that these equations are a little more complex than they appear to be, for χ, v, and D_{s2} are not constants but depend on ϕ, x, N_1, N_2, and temperature.

The slow mode diffusion coefficient is sensitive to the value of χ. Experiments are usually (though not exclusively) performed when the slow mode is overwhelmingly dominant. Whereas the diffusion coefficients do not depend on the refractive index increments of the polymers with the solvent, $(\partial n/\partial c)_1$ and $(\partial n/\partial c)_2$, the amplitudes of the decay modes and hence their visibilities do. The fast mode visibility is diminished when the majority polymer is isorefractive with the solvent (vanishing refractive index increment) or when the polymers have equal contrast. This condition is strictly specified as

$$(\partial n/\partial c)_1 N_1(1 - x) + (\partial n/\partial c)_2 N_2 x = 0 \tag{10}$$

These are precisely the conditions under which it is convenient to use classical light scattering to determine χ. However, whereas in classical light scattering it is imperative for one of these conditions be very closely satisfied, these conditions need not be satisfied in dynamical light scattering studies since the diffusion coefficients are independent of the polymer refractive index increments. Nevertheless, measurement of the slow mode decay rate is facilitated if the fast mode amplitude is much smaller than the slow mode amplitude, and this can be ensured by approximately meeting one of these conditions.

If D_{s2} is unknown, χ can be found by measuring either D_- or the ratio of the mode amplitudes as a function of the relative abundance parameter while keeping all other quantities constant. These procedures have been used by Giebel et al.,[18] but they are very sensitive to the molar masses of the polymers (more correctly the degree of polymerization of the polymers) and the polymer refractive indices.[25] This method also tacitly assumes that χ is independent of the relative abundance of the polymers. In fact Giebel et al. did not report values for χ but gave values for $N\phi\chi$ instead. They studied solutions formed by dissolving 730 000 Da PMMA and 717 000 Da PDMS in each of three solvents, tetrahydrofuran, toluene, and chloroform. All solutions were made to the same total polymer concentration, and the relative abundance of the PMMA was varied. The data were analyzed by fitting the field autocorrelation function to a sum of two exponential Kohlrausch–Williams–Watts functions. This procedure has been discussed by Patterson[26] who states that although there is no *a priori* reason for the fit, it does describe the data very well and it gives precise values for the mode amplitudes. The value of $N\phi\chi$ was calculated twice, once from the ratio of the mode amplitudes and once from the value of D_{-}; the reported values of $N\phi\chi$ differ by approximately 10%.

Sun and Wang[27] have published an alternative theory to describe dynamic light scattering from semidilute ternary polymer solutions. This theory is very similar to the Borsali–Benmouna theory, it takes the same expression for the diffusivity and dynamic scattering matrices but applies a different approximation to allow comparison with experiment, one of the polymers is assumed to be isorefractive with the solvent. Although this theory is restricted to isorefractive systems, no restrictions are placed on the monomer friction coefficients nor is the solvent required to have equal affinities for the two polymers. This theory requires the mode amplitudes and the mode decay rates to be used together to calculate the elements of the 2 × 2 diffusivity matrix. These elements are then used to calculate the polymer self-diffusion coefficients and the polymer–polymer interaction parameter. Sun and Wang have applied their theory to the data collected by Giebel et al.[18] on solutions of PDMS and PMMA dissolved in toluene. Sun and Wang calculated values for the self-diffusion coefficients (D_{s1} and D_{s2}) of the polymers and for χ from the mode amplitudes and diffusion coefficients (D_{-} and D_{+}) reported by Giebel et al. They calculated χ to decrease monotonically from 0.029 to 0.017 as the relative abundance, x, of the PMMA in the solutions was increased from 0.13 to 0.85. Thus not confirming that χ varies parabolically with x.

Sun and Wang also reported that the self-diffusion coefficient of the PDMS approximately halved and that of the PMMA approximately doubled as the PMMA relative abundance was increased while keeping the total polymer concentration constant. These calculated variations of D_{s1} and D_{s2} are surprising as they imply a very significant difference in the behaviors of the monomer friction coefficients of the polymers. An increase of the relative abundance of the glassy polymer PMMA at the expense of the mobile polymer PDMS would be expected to increase the monomer friction coefficients of both polymers (the extent of the increase being determined by the total polymer concentration). Hence one would expect the self-diffusion coefficients of both polymers to decrease if the relative abundance of the glassy polymer were sufficiently increased. Daivis et al.[28] have used pulsed field gradient nuclear magnetic resonance (pfg nmr) to investigate the effect of increasing the relative abundance of the glassy polymer polystyrene at the expense of the mobile polymer poly(vinyl methyl ether), in ternary solutions formed with deuterated toluene. Nuclear magnetic resonance spectral resolution problems limited their study to measurement of the polystyrene self-diffusion coefficient only. They found no significant change in the polystyrene self-diffusion coefficient as the polystyrene relative abundance was increased from 0.001 to 0.246. Yet Sun and Wang calculate that the self-diffusion coefficient of the PMMA increased by more than 40% as the relative abundance of the PMMA increased up to 0.25. Although Daivis et al. did not study the same system as Sun and Wang, there are obvious similarities between the two systems and the marked disagreement between the observations of Daivis et al. and the calculations of Sun and Wang should not pass without comment. Indeed, Sun and Wang have discussed the calculation of the self-diffusion coefficients at some length but were unable to explain the remarkable difference in behavior of the polymers. Neither the fact that one of the polymers is more flexible than the other nor the fact that the flexible polymer has a greater degree of polymerization would seem to help account for the significantly different dependence of the polymer self-diffusion coefficients on relative polymer abundance.

Direct comparisons between the values of D_{s1}, D_{s2}, and χ calculated by Sun and Wang and the values of D_{s2} and χ calculated by Giebel et al. using the Benmouna theory is somewhat elusive since Giebel et al. calculated average values for D_{s2} and $N\phi\chi$, and also only an approximate value of $N\phi$ is known. However, the value of D_{s2} reported by Giebel et al. is consistent with the mean values of D_{s1} and D_{s2} reported by Sun and Wang. Moreover, taking $N\phi$ to be 90, the value of χ reported by Giebel et al. approximates the mean of the values calculated by Sun and Wang.

Sun and Wang[29] have recently published a new study of dynamic light scattering from ternary solutions formed with 185 000 Da polystyrene and 285 000 Da PMMA dissolved in benzene, which is approximately isorefractive with PMMA. The polydispersities of the polymers were 1.05 and 1.13, respectively. Sun and Wang also fitted the field autocorrelation function to a sum of two exponential Kohlrausch–Williams–Watts functions to improve the precision of the determination of the mode amplitudes. They quote the uncertainty on the fast mode amplitude to be 8% when the relative amplitude of the fast mode was 0.29. Two experiments were reported. In the first the relative abundance of the visible polymer, polystyrene, was maintained constant at 0.9 and the total polymer concentration was increased from 0.025 to 0.073 g mL^{-1}. The authors found the self-diffusion coefficient of each polymer to decrease as the total polymer concentration was increased, as one might expect. They also found that χ increased as the total polymer concentration was increased. This is in broad agreement with the observations of Fukuda et al., although those authors found χ to double in value, whereas Sun and Wang report χ to increase by only 25% as the polymer concentration increased from 0.025 to 0.073 g mL^{-1}. In the second experiment the total polymer concentration was maintained at 0.042 g mL^{-1} and the relative abundance of the polystyrene was increased from 0.5 to 0.95. No observations were reported with the relative abundance of the visible polymer less than 0.5. Presumably because the Sun and Wang theory requires the amplitude of both the fast and slow modes to be known accurately, and the relative amplitude of the fast mode is only 0.1 when x is 0.5, and if x were to be reduced to, e.g., 0.25, the relative amplitude of the fast mode would diminish to approximately 0.05, which is possibly too small for its magnitude to be determined with sufficient precision. The authors report that the self-diffusion

Table 1

polymer	supplier	molar mass (Da)	M_w/M_n
polystyrene	Pressure Chemical Co.	110 000	1.06
polystyrene	Pressure Chemical Co.	233 000	1.06
polystyrene	Pressure Chemical Co.	390 000	1.1
polystyrene	Pressure Chemical Co.	598 000	1.1
polystyrene	Polysciences	929 000	1.10
PMMA	Polymer Laboratories	107 000	1.1
PMMA	Polymer Laboratories	185 000	1.1
PMMA	Polymer Laboratories	265 000	1.1
PMMA	Polymer Laboratories	330 000	1.1
PMMA	Polymer Laboratories	400 000	1.1
PMMA	Polymer Laboratories	500 000	1.1
PMMA	Polymer Laboratories	690 000	1.1

solvent	supplier	lot no.
deuterated bromobenzene	Aldrich Chemical Co.	072267
deuterated toluene	Sigma Chemical Co.	61F-0461

coefficient of the polystyrene was sensibly constant and the self-diffusion coefficient of the PMMA reduced by 25%, as the polystyrene relative abundance was increased. More significantly, they report that χ increased from 0.008 to 0.024 as x was increased from 0.5 to 0.95. This variation of χ with x is in approximate agreement with eq 2, although these results cannot confirm a parabolic variation of χ with x since no observations were reported with x less than 0.5. The studies reported by Sun and Wang are important, for their theory relaxes some of the restrictions of the simple Benmouna theory for isorefractive ternary solutions. But the theory needs to be subjected to more rigorous testing: first, by comparing the calculated polymer self diffusion coefficients directly with observations, secondly, by extending the range of visible polymer relative abundances, and thirdly, by applying the theory to other systems.

The work to be presented here describes the calculation of polymer−polymer interaction parameters using dynamic light scattering to obtain the slow diffusion coefficient D_-, and also pfg nmr to obtain the self-diffusion coefficients of each polymer in the same ternary solution. The observations have been interpreted through the Borsali−Benmouna theory since equal contrast as well as isorefractive solutions are considered. This procedure is complementary to the one introduced by Sun and Wang. Each procedure recognizes that additional experimental parameters must be known if the variation of χ with solution composition is to be determined. Sun and Wang measured the mode amplitudes; the work to be presented here measures the polymer self-diffusion coefficients. This procedure enables a direct calculation of χ using eq 5 twice, once with one of the polymers designated as polymer 2, and again with the other polymer designated as polymer 2. Thus two simultaneous equations are obtained with v and χ as unknowns. This method does not assume χ, D_{s1}, or D_{s2} to be constants and enables χ to be calculated for each solution independently.

Methods and Materials

The suppliers and relevant properties of the polymers and solvents used in this study are given in Table 1. All the polymers were monodisperse with M_w/M_n less than 1.1, and both solvents had a better than 99% deuteration ratio. Deuterated solvents were used to facilitate the pfg nmr observations. The solutions were prepared using scrupulously clean glassware, the solvents being filtered through 0.2 μm Millipore filters and added directly to the previously weighed polymers in 5 mm nmr tubes. These tubes were flame sealed after solutions of the desired concentration and composition were formed.

Four categories of ternary solution were studied: solutions in the first two categories approximated the equal contrast condition, and solutions in the last two categories approximated the isorefractive condition. The relative polymer abundance was maintained at 3:1 to facilitate measurement of the self-diffusion coefficient of the minority polymer.

The first group of solutions were formed with 390 000 molar mass polystyrene dissolved in deuterated bromobenzene with PMMA of molar mass 107 000, 185 000, 265 000, 330 000, 400 000, 500 000, or 690 000 Da. The relative abundance of polystyrene to PMMA was 3:1 by weight; i.e. the relative abundance (x) of the PMMA was 0.25. All solutions were made to the same total polymer volume fraction of 0.065. The net ratio of M_w to M_n in the solutions varied from 1.19 to 1.08.

The second group of solutions were formed with 400 000 molar mass PMMA dissolved in deuterated bromobenzene with polystyrene of molar mass 110 000, 233 000, 293 000, 390,000, or 598 000 Da. The relative abundance of PMMA to polystyrene was 3:1 by weight (x of the PMMA was 0.75). All solutions were made to the same total polymer volume fraction of 0.055. The net ratio of M_w to M_n in the solutions varied from 1.04 to 1.19.

The third group of solutions were formed with 265 000 molar mass PMMA dissolved in deuterated toluene with polystyrene of molar mass 110 000, 233 000, 390 000, or 598 000 Da. The relative abundance of PMMA to polystyrene was 3:1 by weight (x of the visible polymer was 0.25), and all solutions were made to the same total polymer volume fraction of 0.051. The net ratio of M_w to M_n in the solutions varied from 1.00 to 1.17.

The fourth group of solutions were formed with 107 000 molar mass PMMA dissolved in deuterated toluene with polystyrene of molar mass 110 000, 233 000, 390 000, 590 000, or 929 000 Da. The relative abundance of PMMA to polystyrene was 3:1 by weight (x of the visible polymer was 0.25), and all solutions were made to the same total polymer volume fraction of 0.051. The net ratio of M_w to M_n in the solutions varied from 1.00 to 2.30.

The solutions were stored at 30 °C for several months before any measurements were attempted.

The pulsed field gradient nmr measurements were nontrivial since the pfg nmr spectra of the polymers were not entirely resolved, and measurements were made using the protocol described previously.[30] All pfg nmr measurements were made at 30 °C and subsequently normalized to 25 °C using the temperature dependence of the solvent viscosity.

The dynamic light scattering measurements were made at 25 °C using the methods and apparatus previously described.[28] The observed intensity autocorrelation functions of the scattered light were normalized and converted to estimates of the field autocorrelation function using the Siegert relation;[31] the theoretical baseline was used in these calculations. The data were then analyzed by two methods, a single exponential was fitted to the field autocorrelation function, and the method of cumulants was used. The first datum point was routinely excluded from the fitting procedures in case it included contributions from a fast decay mode. The methods yielded essentially the same decay rates.

Results and Discussion

Deuterated Bromobenzene Solutions. Deuterated bromobenzene was chosen as a solvent because its refractive index is approximately the mean of those of PMMA and polystyrene, so ternary solutions of PMMA and polystyrene dissolved in deuterated bromobenzene approximately satisfy the equal contrast condition. The self-diffusion coefficient of each polymer in each solution was determined by pfg nmr. The intensity autocorrelation function of the light scattered from each solution was very nearly a single exponential slow decay mode. The data and the fitted autocorrelation function for the solution formed with 400 000 molar mass PMMA and 233 000 molar mass polystyrene dissolved in deuterated bromobenzene are plotted to logarithmic ordinate scales and compared in Figure 1. If a single decay process

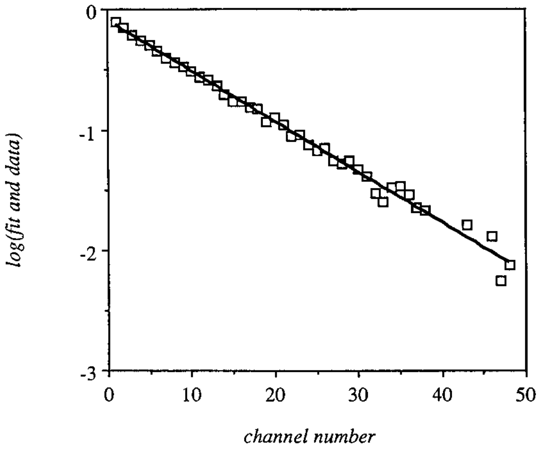

Figure 1. Comparison between dynamic light scattering data (□) and the theoretical single exponential fit (line) for the solution formed with 400 000 molar mass PMMA and 233 000 molar mass polystyrene dissolved in deuterated bromobenzene. The time scale for the correlator channels was 140 μs, the scattering angle was 30°, and the temperature was 25 °C. The single exponential fit gave D_- to be 1.01(±0.01) × 10^{-12} m^2 s^{-1}, as did the cumulants fit.

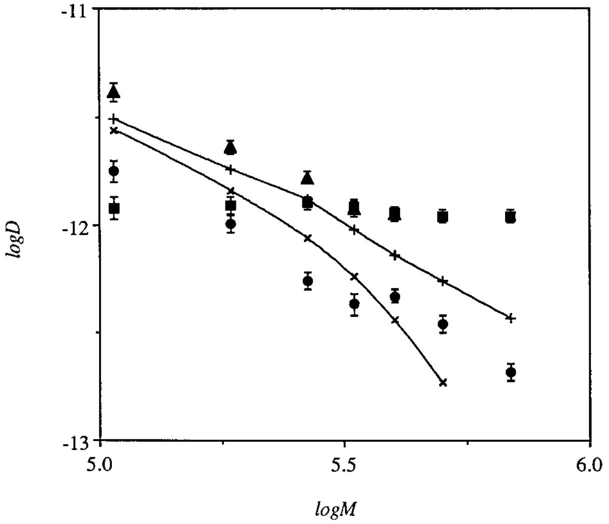

Figure 2. Diffusion coefficients plotted against minority polymer molar mass to logarithmic scales, for solutions formed with 390 000 molar mass polystyrene and poly(methyl methacrylate)s dissolved in deuterated bromobenzene. ▲ and ■ are the measured self-diffusion coefficients of the poly(methyl methacrylate) and the polystyrene, respectively. ● is the measured slow diffusion coefficient. + and × are the theoretical slow diffusion coefficients obtained from the polystyrene self-diffusion coefficients using χ/v = 0.07 and 0.14, respectively. Lines are drawn through the + and × values to guide the eye.

were observed, this graph would be a straight line. A fast decay is not apparent, the amplitude of the fast decay mode being negligible, since the solution approximately satisfied the equal contrast special condition discussed above. Calculations based on the Borsali–Benmouna theory indicate that the ratio of the fast to slow mode amplitudes is less than 1:50 for these solutions. The slow diffusion coefficient of each solution was determined from the decay constant of the observed single exponential decay of the autocorrelation function of the scattered light.

The diffusion coefficients are displayed in graphical form in Figures 2 and 3 together with the Borsali–Benmouna theoretical predictions of the slow diffusion coefficient, estimating χ/v to be 0.07, using data given in the literature.[8,32] Figure 2 also include the theoretical slow diffusion coefficient calculated assuming χ/v to be 0.14. Agreement with experiment is not improved by doubling χ/v; indeed, theory now predicts the solution formed with 690 000 molar mass PMMA to have phase separated, which is not so. Theoretical values of D_- were also calculated for χ/v equal to 0.14 for the data presented in Figure 3, but they are not included since agreement between theory and experiment was not enhanced by this arbitrary doubling of χ/v. It is clear that the Borsali–Benmouna theory fails to account for the observed variation of D_- with minority polymer molar mass. This failure of the theory is caused either by an inherent fault in the theory or by χ or v varying with the minority polymer molar mass, or by a combination of the above.

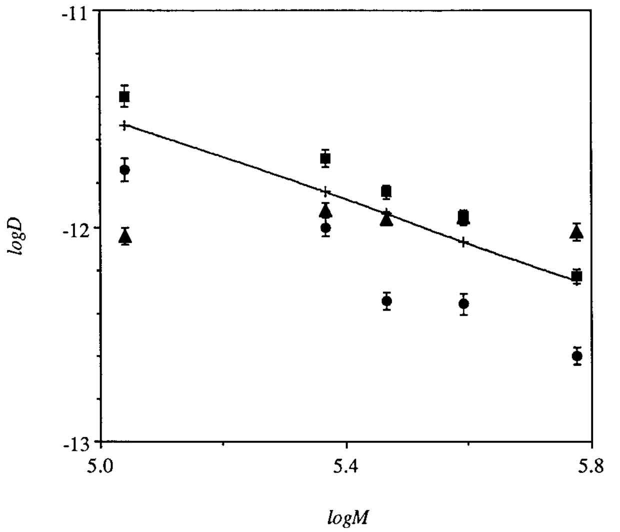

Figure 3. Diffusion coefficients plotted against minority polymer molar mass to logarithmic scales, for solutions formed with 400 000 molar mass poly(methyl methacrylate) and polystyrenes dissolved in deuterated bromobenzene. ▲ and ■ are the measured self-diffusion coefficients of the poly(methyl methacrylate) and the polystyrene, respectively. ● is the measured slow diffusion coefficient. + is the theoretical slow diffusion coefficient obtained from the poly(methyl methacrylate) self-diffusion coefficient using χ/v = 0.07. A line is drawn through the + values to guide the eye.

These propositions were tested by employing eq 5 twice. Since the polymer self-diffusion coefficients have been determined for each solution, D_{S2} in eq 5 can be identified with either D_{SPMMA}, the self-diffusion coefficient of PMMA, or with D_{SPS}, the self-diffusion coefficient of polystyrene, as preferred. The two variants of eq 5 were solved as simultaneous equations in χ and v. The value of v (0.07 ± 0.01) was found to be insensitive to the minority polymer molar mass, but the value of χ varied appreciably, this variation is shown in Figure 4. The uncertainties on these χ values are due primarily to the random uncertainties on the diffusion coefficients, yielding a range of values for the coefficients in the two linear equations.

Notice χ strongly decreases with increasing minority polymer molar mass, no matter which polymer is in the minority. The values of χ found for the two solutions of 390 000 polystyrene and 400 000 PMMA dissolved in deuterated bromobenzene are 0.0076 ± 0.0004 and 0.0078 ± 0.0004 where the relative abundance of the PMMA is 0.75 and 0.25, respectively. These values are within the experimental uncertainties, and χ for these solutions can be taken as 0.0077 ± 0.0004. This indicates that if χ does vary with PMMA relative abundance, x, then it does so in a manner such that the χ values at $x = 0.25$ and at $x = 0.75$ are equal. These observations support the assumption that χ varies parabolically with x about 0.50, as indicated by eq 2. This does not agree with the Sun and Wang recalculations of the results reported by Giebel et al.; however, it is not in conflict with Sun and Wang's calculations of their own observations.[29]

There are two aspects of the values of χ that are to be addressed: first, the variation of χ with polymer molar mass and, secondly, the magnitude of χ.

Theory is insufficiently developed to fully describe χ of these solutions. However, we know that χ is a function of several parameters, for example, the nature of the solvent, the total polymer concentration, the polymer relative abundances, the polymer molar masses, the solution temperature, and how far the solution is from phase separation. The second virial coefficients reported by Fukuda et al.[8] indicate that the ratio of the excluded volume parameters of polystyrene and PMMA in bromobenzene is 1:1.38 ± 0.03 this implies that bromobenzene has approximately equal affinities for the two polymers. So χ is expected to be small and none of the bromobenzene solutions studied here is expected to approach phase separation. So the solvent quality, the total polymer concentration, the polymer relative abundances, and the solution temperature were all constant in each set of deuterated bromobenzene solutions. This allowed the variation of χ with polymer molar mass to be discernible since all other parameters governing the behavior of χ were approximately constant. We can appeal to the Flory–Huggins formula (eq 1b) to calculate the variation of the critical value of the polymer–polymer interaction parameter χ_c, with the polymer molar masses. χ_c can then be normalized to 0.0077, the value of χ found for the solutions formed with nearly equal molar mass polymers (400 000 PMMA and 390 000 polystyrene) and written as χ_t. The variation of χ_t is also shown in Figure 4 and is in good agreement with experiment. The absolute value of χ_t is arbitrary here, only its variation with minority polymer molar mass is considered. The good agreement between χ_t and the data indicates that all the solutions were approximately "equally far" from phase separation. The value of χ_c predicted by eq 2 for the solution with equal molar mass polymers is 0.011; it is also included in Figure 4. This value of χ_c is considerably larger than the experimental value (0.0077 ± 0.0004), which would seem to confirm that these solutions are not close to phase separation.

Fukuda et al.[8,9] have also measured χ for ternary solutions of polystyrene and PMMA dissolved in bromobenzene, they used a classical light scattering technique which required the equal contrast condition (eq 10) to be closely satisfied. Consequently, their study was restricted to symmetric systems, that is solutions formed with nearly equal abundances of polymers of nearly equal degrees of polymerization. However, they were able to measure χ over a large range of polymer molar masses and also over polymer concentrations ranging from the dilute to the spinodal. They showed that χ was independent of polymer molar mass but increased strongly with polymer concentration in the semidilute regime.

It is important to realize that Fukuda et al. measured χ for the smaller polymer molar mass solutions at larger polymer concentrations; failure to realize this has led some authors[7,9,25] to misinterpret their results as evidence for χ being polymer molar mass dependent. The Fukuda et al. determinations of spinodal values of χ for polymers within the molar mass range studied here are also shown in Figure 4. The value of χ_c calculated for a solution formed with equal abundances of two polymers having molar masses of 400 000 is 0.0083, the corresponding value interpolated from the data of Fukuda et al. is 0.0063. Thus the spinodal value reported by Fukuda et al. is approximately 30% smaller than the value predicted by eq 2.

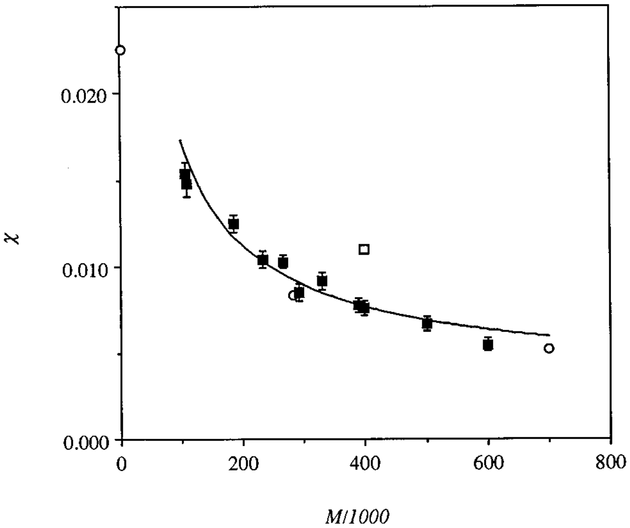

Figure 4. (■) Variation of χ with minority polymer molar mass for solutions formed with deuterated bromobenzene. The spinodal values of χ found by Fukuda et al. for equal molar mass polymers at equal polymer abundances are also shown (○). The line is the variation of χ_t normalized to the value of χ found for the solutions formed with 390 000 molar mass polystyrene and 400 000 molar mass PMMA. The critical value of χ obtained from eq 2 for equal molar mass polymers with polymer abundance ratio 1:3 is indicated by □.

A cursory inspection of Figure 4 implies good agreement between the results presented here and those of Fukuda et al., but this is illusory, for the determinations presented here were made at approximately constant polymer volume fraction (0.060 ± 0.005) whereas the Fukuda et al. measurements were made at larger polymer concentrations for the smaller polymer molar masses. Moreover, Fukuda et al. restricted their study to solutions of equal molar mass polymers in nearly equal relative abundances ($x = 0.5$).

The value of χ found for the two solutions of 390 000 polystyrene and 400 000 PMMA dissolved in deuterated bromobenzene (0.0077 ± 0.0004) is expected to be comparable with that value found by Fukuda et al. (0.0048 ± 0.0002) for similar solutions at the same (interpolated) total polymer volume fraction. But the value found in this study is a factor 1.6 ± 0.1 larger than that interpolated from the Fukuda et al. data.

There are a number of possible reasons for this discrepancy. First, the value of χ used in the Borsali–Benmouna theory is a factor $[m_p\bar{v}_p/m_s\bar{v}_s]^2$ greater than that used by Fukuda et al., where m_p, m_s, $\bar{v}_p$, and $\bar{v}_s$ are the monomer and solvent molar masses and specific volumes, respectively. This introduces a factor of approximately 1.3, which probably accounts for the 30% discrepancy in the spinodal values noted above. Secondly, the polymer relative abundances were 3:1 in the studies reported here but were approximately 1:1 in those reported by Fukuda et al. Benmouna et al.[13] have predicted, and Ould Kaddour and Strazielle[7] have observed, that the critical value of χ increases by a factor of 1.33 as the polymer relative abundance is varied from

1:1 to 1:3. It is likely that χ itself also varies with polymer abundance in a similar manner. Thirdly, Fukuda et al. made their observations at 30 °C, whereas the observations reported here were made at 25 °C. Seils et al.[12] have studied solutions of 980 000 molar mass PMMA and 910 000 molar mass polystyrene dissolved in bromobenzene; they showed that χ increased by a factor of 1.2 as the temperature was reduced from 30 to 25 °C, due to the solution being closer to phase separation at the lower temperature.

Clearly, just these considerations are more than sufficient to account for the discrepancy between the results presented here and those previously reported by Fukuda et al. However, there other possible sources of systematic differences between these experiments. For example Ould Kaddour and Strazielle[7] have shown that χ is strongly solvent dependent and Fukuda et al. used bromobenzene whereas these studies were required to use deuterated bromobenzene to facilitate the nmr studies, the effects of a deuterated solvent on the slow diffusion coefficient are unknown. Finally, the validity of the various approximations made in the Borsali–Benmouna theory is unproven. Indeed, the assumption that the polymers have equal excluded volume parameters was not met in this study. The ratio of the excluded volume parameter of polystyrene to that of PMMA in bromobenzene can be estimated from the second virial coefficients obtained by Fukuda et al.,[8] this ratio is 1.38 ± 0.03 over the range of molar masses used in this study. The Borsali–Benmouna theory strictly applies to solvents in which this ratio is unity, this may account for the calculated value of v being insensitive to the minority polymer molar mass.

Deuterated Toluene Solutions. Deuterated toluene was chosen as a solvent because its refractive index is nearly equal to that of PMMA, so ternary solutions of PMMA and polystyrene dissolved in deuterated toluene approximately satisfy the isorefractive condition. The relative abundance of the visible polymer was 0.25 in all of these solutions so the slow decay mode is expected to dominate the dynamic light scattering investigations. Calculations based on the Borsali–Benmouna theory indicate the ratio of the fast to slow mode amplitudes was always less than 1:10 and the ratio of the decay rates was always greater than 8. This means that observations of any fast decay would be confined to the first few channels of the autocorrelation function which could be disregarded if necessary and the slow mode decay rate could be obtained without difficulty. No fast decay mode was observed for any of the solutions formed with deuterated toluene. It was found that ternary solutions formed with deuterated toluene were less stable than those formed with deuterated bromobenzene; consequently, solutions were formed with a smaller total polymer volume fraction (0.051 ± 0.001), and the solutions were formed with majority polymers of smaller molar mass. These ternary polymer solutions suffer polymer–polymer phase separation rather than polymer–solvent phase separation, so two binary phase solutions are formed on phase solution. This means that the relative amplitude of the fast mode is not enhanced as phase separation is approached. However, Seils et al.[12] have confirmed the predictions of Benmouna et al.[13] that an additional slow mode can be engendered close to phase separation. They observed the relative amplitude of this additional slow mode to increase as the scattering vector was reduced and also as phase separation was approached. No additional slow mode was resolved in this work.

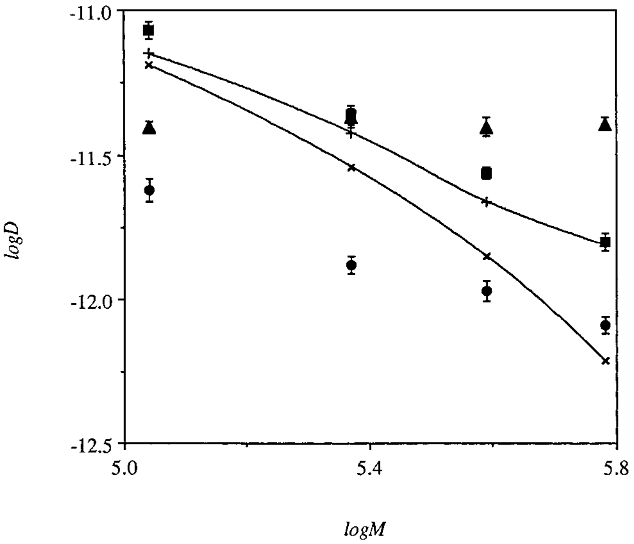

Figure 5. Diffusion coefficients plotted against minority polymer molar mass to logarithmic scales, for solutions formed with 265 000 molar mass poly(methyl methacrylate) and polystyrenes dissolved in deuterated toluene. ▲ and ■ are the measured self-diffusion coefficients of the poly(methyl methacrylate) and the polystyrene, respectively. ● is the measured slow diffusion coefficient. + and × are the theoretical slow diffusion coefficients obtained from the poly(methyl methacrylate) self-diffusion coefficient using $\chi/v = 0.05$ and 0.10, respectively. Lines are drawn through the + and × values to guide the eye.

Solutions were formed with 265 000 molar mass PMMA and 110 000, 233 000, 390 000, and 598 000 molar mass polystyrenes. The total polymer volume fraction was 0.051 ± 0.001, and the mass ratio of PMMA to polystyrene was 3:1 (relative abundance of visible polymer was 0.25). The self-diffusion coefficients and slow mode diffusion coefficients for these solutions were determined by pfg nmr and dynamic light scattering, respectively, they are shown in Figure 5. Note the solution formed with 598 000 molar mass polystyrene was close to phase separation; indeed, it did phase separate when the temperature was not maintained at 25 °C. A solution formed with 929 000 molar mass polystyrene phase separated at 25 °C, and no observations on this solution are presented here. The experimental and fitted autocorrelation functions for the solution formed with 265 000 molar mass polystyrene and 598 000 molar mass PMMA are compared in Figure 6 plotted to logarithmic ordinate scales. The fitted autocorrelation function was obtained in the manner described above. Solutions formed with 265 000 PMMA and 598 000 polystyrene exhibited a small scattering vector dependence (see Figure 7). The value of D_- quoted was obtained by extrapolation to zero scattering angle.

The variation of χ with minority polymer molar mass is compared with χ_t in Figure 8. The variation of χ with polymer molar mass is similar to that of χ_t, although the agreement is poorer than that found for the deuterated bromobenzene solutions, and the values of χ are larger despite the deuterated toluene solutions having a smaller polymer content. The value of χ predicted by eq 2 for the equal polymer molar mass solution is 0.05; it is not included in Figure 8.

Solutions were also formed with 107 000 molar mass PMMA and 110 000, 233 000, 390 000, 598 000, and 929 000 molar mass polystyrenes. These solutions were

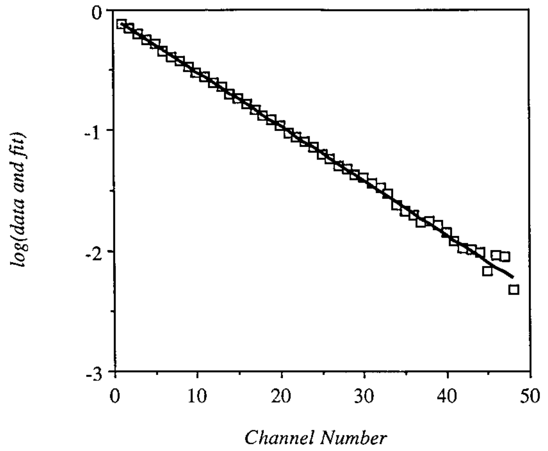

Figure 6. Comparison between dynamic light scattering data (□) and the theoretical single exponential fit (line) for the solution formed with 265 000 molar mass PMMA and 598 000 molar mass polystyrene dissolved in deuterated toluene. The time scale for the collelator channels was 240 μs, the scattering angle was 45°, and the temperature was 25 °C. The single exponential fit gave D^*, the apparent diffusion coefficient to be 0.86(±0.01) × 10^{-12} m^2 s^{-1}.

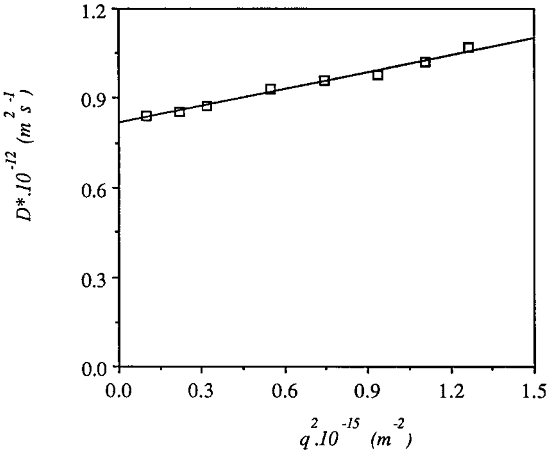

Figure 7. Variation of D^*, the apparent diffusion coefficient (□), with the square of the scattering vector. The linear least squares fit gave the intercept, and hence D_-, to be 0.82(±0.01) × 10^{-12} m^2 s^{-1}.

made to the same total polymer volume fraction 0.051 ± 0.001, and the mass ratio of PMMA to polystyrene was 3:1. The diffusion coefficients of these solutions are shown in Figure 9. Solutions formed with 598 000 polystyrene and with 929 000 polystyrene also exhibited a small scattering vector dependence, and the quoted value of D_- was obtained by extrapolation to zero scattering angle.

The values of χ obtained for the 107 000 PMMA solutions are shown in Figure 10 together with the appropriately calculated χ_t. The χ values are significantly larger, and there is no agreement between χ_t and the data at large molar masses. Interpolating the Fukuda et al. data and applying the systematic corrections discussed above indicate that χ is expected to be 0.009 for solutions formed with equal molar mass polystyrene and PMMA dissolved in bromobenzene at a polymer volume fraction of 0.051. The value of χ found here for solutions formed with deuterated toluene at this concentration is 0.016 ± 0.001. The value of χ_c predicted by eq 2 for the equal molar mass solutions is also included in Figure 10.

The scattering vector dependence observed for solutions formed with the large molar mass polystyrenes has been noted before by Daivis and Pinder[33] in their investigations of ternary solutions formed with 110 000 molar mass PVME and 929 000 molar mass polystyrene dissolved in toluene and in carbon tetrachloride. They attributed the effect to internal modes and used their observations to estimate R_g, the radius of gyration of the polystyrene after making due allowance for the finite time scale of the observations. They predicted a value of R_g which was smaller than expected, such a shrinking of the coil radius of gyration is predicted close to the critical point.[34,35] Using the Borsali−Benmouna theory, the values of R_g found here are 25 ± 1 and 30 ± 1 nm for solutions formed with 107 000 PMMA and

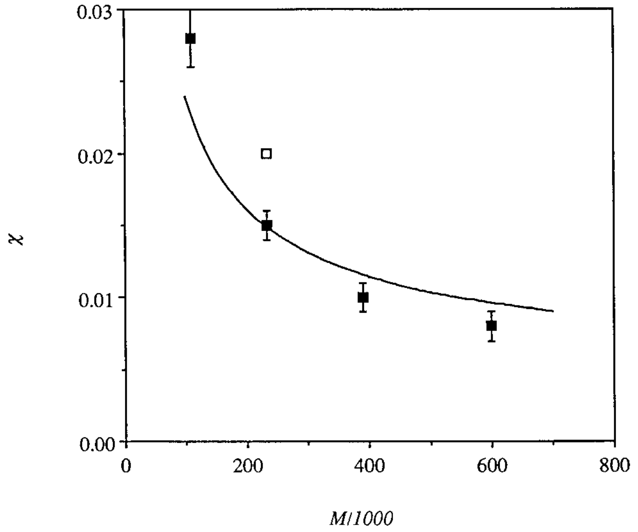

Figure 8. (■) Variation of χ with minority polymer molar mass for solutions formed with 265 000 molar mass PMMA and polystyrenes dissolved in deuterated toluene. The values of χ were obtained from the data reported in Figure 5. The line is the variation of χ_t normalized to the value of χ found for the solution formed with 233 000 molar mass polystyrene. □ represents the critical value of χ for equal molar mass polymers with relative abundances 1:3.

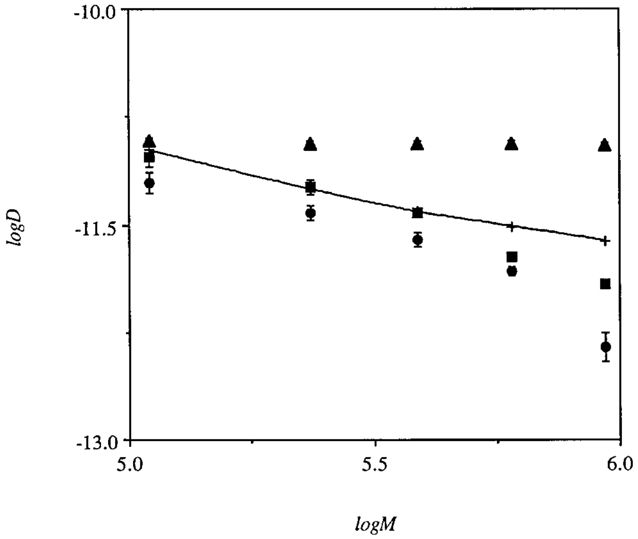

Figure 9. Diffusion coefficients plotted against minority polymer molar mass to logarithmic scales, for solutions formed with 107 000 molar mass poly(methyl methacrylate) and polystyrenes dissolved in deuterated toluene. ▲ and ■ are the measured self-diffusion coefficients of the poly(methyl methacrylate) and the polystyrene, respectively. ● is the measured slow diffusion coefficient. + is the theoretical slow diffusion coefficient obtained from the poly(methyl methacrylate) self-diffusion coefficient using $\chi/v = 0.05$. A line is drawn through the + values to guide the eye.

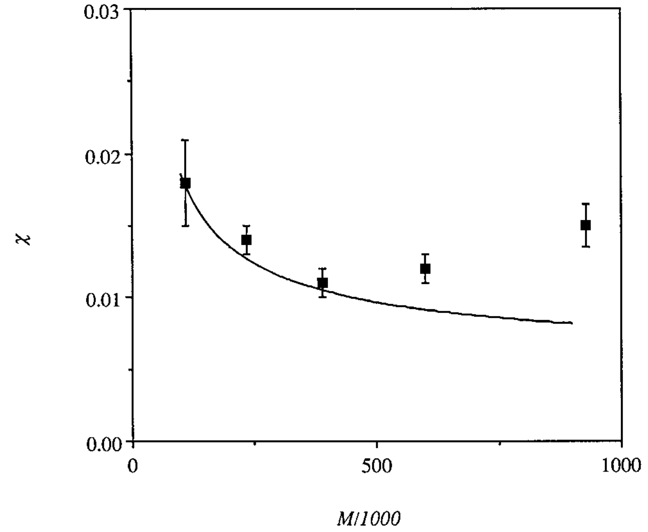

Figure 10. Variation of χ with minority polymer molar mass for solutions formed with 107 000 molar mass PMMA and polystyrenes dissolved in deuterated toluene. The values of χ were obtained from the data reported in Figure 9. The line is the variation of χ_t normalized to the value of χ found for the solution formed with 110 000 molar mass polystyrene.

598 000 and 929 000 polystyrenes, respectively. R_g was found to be 26 ± 1 nm for solutions formed with 265 000 PMMA and 598 000 polystyrene. The values of R_g for 598 000 and 929 000 molar mass polystyrenes in dilute solution are 42 and 54 nm, respectively.[36] It should be noted that the Benmouna theory of the behavior of symmetric critical solutions predicts a similar scattering vector dependence in the critical region, so these observations may not be a measure of R_g, but rather a manifestation of the onset of critical behavior. However, this possibility could not be investigated further because the Benmouna theory has not been sufficiently developed to apply to the unsymmetric toluene solutions.

Assuming these values of χ are valid, there are two aspects of the observations to be explained. First, the χ values calculated from the observations of the deuterated toluene solutions are significantly larger than those obtained from observations on the deuterated bromobenzene solutions. Secondly, χ obtained for solutions formed with 107 000 molar mass PMMA and polystyrenes dissolved in deuterated toluene does not vary with polymer molar mass in a manner similar to χ_t.

The second virial coefficients reported by Konak et al.[32] indicate that the ratio of the excluded volume parameters of polystyrene and PMMA in toluene is 1:(1.60 ± 0.02); this implies that toluene is a solvent with different affinities for the two polymers. This causes χ to be larger for solutions formed with toluene (as was observed), and this in turn causes these solutions to be closer to phase separation. Indeed, solutions formed with the larger molar mass polystyrenes were appreciably closer to phase separation than those formed with the smaller molar mass polystyrenes. Consequently, χ for the deuterated toluene solutions varies under the influence of two parameters: first, χ decreases with polystyrene molar mass in the normal way, and secondly, χ increases with polystyrene molar mass because such solutions are closer to phase separation. These competing influences on χ are manifest in the graph presented in Figure 10. The net result is that χ does not vary as χ_t.

It is possible that the values of χ calculated for the deuterated toluene solutions are in error. There are two reasons to suspect these χ values. First, the data have been analyzed using the Borsali–Benmouna theory which assumes the solvent to have equal affinities for the polymers. It is possible that whereas the theory is able to accommodate solvents whose excluded volume parameters differ by 38% as in the case of the deuterated bromobenzene solutions, the theory fails when the excluded volume parameters differ by as much as 60%, as is the case of deuterated toluene. Although this is a possibility, it would seem to be unlikely that the Borsali–Benmouna theory failure would be so dependent on polymer molar mass. Pinder et al.[37] have shown (in studies of ternary solutions formed with the compatible polymers PVME and polystyrene) that the theory gives predictions in agreement with experiment for solvents which are equally poor solvents, but not for solvents of greatly differing quality.

The second reason to suspect the χ values is the possibility that a second slow decay mode was present in the autocorrelation functions of the scattered light. Benmouna et al. have proposed and Seils et al. have observed that a second slow decay mode can be engendered in the autocorrelation function of scattered light. This additional slow mode is significant only as phase separation is approached, and its amplitude is scattering vector dependent. This additional slow mode is not included in either the Borsali–Benmouna or the Sun and Wang theory. It is possible that this additional slow mode was affecting the observations of some of the deuterated toluene solution observations without it being resolved as a separate mode. This would have had the effect of decreasing the value assigned to D_-, so leading to an erroneous calculation of χ. The Benmouna et al. theory cannot be applied to the deuterated toluene solutions, for it describes symmetric solutions only, that is solutions formed with equal molar mass polymers at equal abundances satisfying the equal contrast condition. Nevertheless, if such a mode does exist in symmetric solutions it probably also exists in isorefractive solutions. No evidence for a resolvable second slow mode was found in any of the data presented here, but if an unresolved second slow mode were present it could have adversely affected the calculation of χ.

Conclusions

This study has shown that the polymer–polymer interaction parameter, χ, can be obtained from measurements of diffusion coefficients of ternary polymer solutions formed with deuterated bromobenzene. Dynamic light scattering is required to measure the slow diffusion coefficient, and pulsed field gradient nmr is required to obtain the self-diffusion coefficients of both polymers. The values of χ obtained are in good agreement with those found from classical light scattering studies of similar solutions provided due attention is paid to systematic differences in the experimental protocols. The same technique has been applied to ternary polymer solutions formed with deuterated toluene, and the value of χ is found to be significantly enhanced in this solvent, as is to be expected, for toluene is a solvent with unequal affinities for the two polymers. χ for the deuterated toluene solutions was also observed to have a more complex variation with polymer molar mass than for the deuterated bromobenzene solutions; this was discussed in terms of the phase stability of the solutions. However, the data extracted from the deuterated toluene solutions should be regarded with some skepticism, for the applicability of the Borsali−Benmouna theory is in doubt for such solutions.

This new technique is complementary to that introduced by Sun and Wang. It is applicable to a wide range of polymer solutions because there is no need to closely meet refractive index or molar mass conditions. This is a considerable advantage over classical light scattering techniques. But each polymer is required to have at least one magnetic resonance in the pfg nmr spectrum that is sufficiently resolved, which is a stringent condition, for not only must the polymer resonances be sufficiently separated but also the minority polymer must be present in sufficient quantity for the collection of reliable data. The present studies have been limited to solutions formed with PMMA and polystyrene in which the polymer relative abundance has not been less than 0.25.

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