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Quasielastic Light Scattering from Semidilute Ternary Polymer Solutions of Polystyrene and Poly(methyl methacrylate) in Benzene

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ABSTRACT: A detailed quasieslatic light (QEL) scattering study of the polystyrene−poly(methyl methacrylate) (PS−PMMA)/benzene ternary solution with both polymers in the semidilute concentration regime was carried out. Two types of the PS−PMMA/benzene solution have been studied: one at fixed composition but different total polymer concentrations, and the other at fixed total polymer concentration but different compositions. Two diffusion modes in the intensity−intensity time correlation function of the scattered light were observed in these solutions. These two modes correspond to the eigenmodes of the diffusivity matrix that governs the time evolution of the concentration fluctuations of the polymers in the ternary solution. The concentration and composition dependencies of the relaxation rates and the amplitudes of these modes were investigated. From the relaxation rates and amplitude factors, the elements of the diffusivity matrix were determined as a function of polymer concentration and composition. By using the diffusivity data, the self-diffusion coefficients of PS and PMMA and the Flory−Huggins interaction parameter χ_F, between PS and PMMA were deduced. The concentration and composition dependencies of these quantities were studied. At fixed composition, the self-diffusion coefficients of PS and PMMA were found to decrease with increasing total polymer concentration, whereas at fixed concentration they decreased with decreasing fraction of its own kind. The value of the Flory−Huggins interaction parameter, χ_F, between PS and PMMA was found to range from 0.008 to 0.026, depending on concentration and composition. The χ_F values obtained by our method are in good agreement with those obtained by other techniques, indicating the reliability of our method.

Introduction

The blending of homopolymers is an important method for preparing new materials that display a wide range of properties.[1,2] While some polymer blends are processed in the dry state, many others are processed by adding a small molecular weight solvent. Addition of a solvent to the polymer blend affects the compatibility of the mixture. In the presence of a good solvent, the chain conformation is modified since in the good solvent conditions chains are swollen, hence increasing the entropy of mixing. Moreover, diffusion takes places more rapidly, and this also facilitates mixing. Thus, in the presence of a solvent, the structural and dynamic properties of chains in the polymer blend are modified, and for this reason, the study of solution properties of polymer blends to obtain information about polymer−polymer interactions and polymer diffusion is an active area of polymer research. Experimental techniques such as viscometry,[3−5] neutron scattering,[6] pulsed field gradient NMR,[7,8] forced Rayleigh scattering,[9,10] and static light scattering[11−14] have been used to reveal the properties of polymer blends in solution.

Quasielastic light (QEL) scattering is also an important technique for the study of ternary polymer solutions. Introduction of a solvent into the polymer blend gives rise to concentration fluctuations, in addition to the composition fluctuations present initially. The concentration fluctuations that are absent from the bulk state are sensitive to the polymer−solvent interactions. The QEL scattering (QELS) study of composition fluctuations, which are limited to miscible polymer blends in the solvent-free state, can now be carried out in the ternary solution consisting of immiscible blends, provided that the polymer concentration−composition lies outside the two-phase region.

QEL scattering from ternary polymer solutions has been investigated extensively in the last decade.[15−21] However, the early experiments mainly deal with one polymer in very low concentrations in a polymer of high concentration whose refractive index is matched to that of the solvent. If the visible polymer (i.e., the one that is not refractive index matched) is kept as a trace, then only an interdiffusion mode can be detected in the QELS spectrum. Under such a condition, the interdiffusion coefficient is approximately equal to the self-diffusion coefficient of the visible polymer. By using this method, a number of researchers have investigated the dynamics of the visible polymer chain in the ternary solutions,[15−21] with the objective to test whether the dynamics of single chains assumes the Rouse-like or a reptation mechanism.[22]

QEL scattering experiments from semidilute ternary polymer solutions have also recently been carried out.[23−28] In the semidilute concentration regime, both the interdiffusion and cooperative diffusion modes are present. To facilitate data analysis using the theory developed by Benmouna et al. on the basis of the random phase approximation (RPA),[29−34] the systems chosen in their studies mostly deal with polymers with similar molecular weights. In a recent paper,[35] we proposed a new method using the QEL scattering technique for determining the Flory−Huggins interaction parameter and self-diffusion coefficients of two polymers in the semidilute ternary solution, in which the concentrations of both the invisible and visible polymers are high. Our method does not employ the restrictive assumptions about an identical molecular weight, identical structural factor, and identical solvent quality for both polymers that were previously imposed on polymer systems to utilize the theory.[34] Our method is applicable to a general semidilute or concentrated ternary polymer solution consisting of homopolymers with different molecular weights and solvent interac-

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tions. We have illustrated the applicability of the method in the ternary system solution consisting of poly(methyl mathacrylate) (PMMA) and poly(dimethylsiloxane) (PDMS) in toluene at a fixed polymer concentration.[35] We have determined the Flory−Huggins interaction parameter and self-diffusion coefficients of the individual polymers in this system.

In this paper, we report new results obtained from a detailed QELS experiment on the polystyrene (PS)−PMMA/benzene ternary system in which the concentrations of both polymers are in the semidilute regime. We investigate the intensity autocorrelation function of the scattered light as a function of total polymer concentration at various scattering angles. The dependence of the autocorrelation function on the polymer composition at a fixed total polymer concentration is also investigated. Benzene is chosen to simplify the data analysis because it is isorefractive with PMMA.[36]

Experimental Section

The PS sample used in this study was purchased from Toya Soda and has an average molecular weight $M_w = 1.85 \times 10^5$ with the polydispersity index $M_w/M_n = 1.05$. PMMA was purchased from Polymer Standards Services (Mainz, Germany) and has an average molecular weight $M_w = 2.85 \times 10^5$ with a polydispersity index M_w/M_n of 1.13. Benzene is a good solvent for both PS and PMMA. Physical properties of the two polymers in benzene that are relevant to the present study are given in Table 1.[37,38] Polymer solutions were prepared by dissolving PS and PMMA in benzene (Fisher, thiophene-free). The solutions were allowed to mix thoroughly (assisted by gentle agitation) over a week. Dust in the solution was removed by filtration through a 0.1 μm Millipore filter into light-scattering cells, which were carefully sealed immediately after filtration. Two sets of samples were prepared and studied: (1) solutions with different concentrations in the semidilute concentration regime ($C^* \approx 0.027$ g/mL for PS and $C^* \approx 0.016$ g/mL for PMMA, estimated by using the formula $C^* = 3M_w/(4\pi R_g{}^3 N_A)$, where R_g is the radius of gyration) at a fixed composition $x = W_{PS}/(W_{PS} + W_{PMMA}) = 0.90$; (2) solutions with different compositions varying from $x = 0.50$ to 0.95 at a fixed total polymer concentration $C_T = 0.042$ g/mL.

QELS measurements at scattering angles ranging from 30 to 150° were carried out using an ALV-5000 correlator and a Spectra-Physics Model-125 He−Ne laser at a wavelength of 632.8 nm. The temperature was controlled at 20 ± 0.05 °C. At these conditions, dn/dc of PMMA in benzene is nearly zero.[36]

The dynamic structure factor that is proportional to the normalized field−field correlation function $g(q,t)$ is obtained via the Sigert relation:

$$\alpha g(q,t) = [G(q,t) - 1]^{1/2} = \int_0^\infty \mathrm{d} \ln \tau A(\tau) \exp(-t/\tau) \quad (1)$$

where $G(q,t)$ is the normalized homodyne intensity autocorrelation function obtained directly from the correlator and α is the contrast factor. The constrained regulation method (CONTIN) developed by Provencher[39] was used to obtain the distribution of relaxation times $A(\tau)$. The distribution function $A(\tau)$ is defined in eq 1.

Results and Discussion

In the present concentration and composition ranges, we observe two diffusion modes. Shown in Figure 1a is the intensity autocorrelation function obtained from the ternary solution at $C_T = 0.05$ g/mL, $x = 0.90$, and $\theta = 110°$. Also shown at the bottom of Figure 1 is the distribution of relaxation times $A(\tau)$ obtained from the CONTIN program. We have also analyzed the data according to the sum of two exponential Kohlrauch−Williams−Watts (KWW) functions:

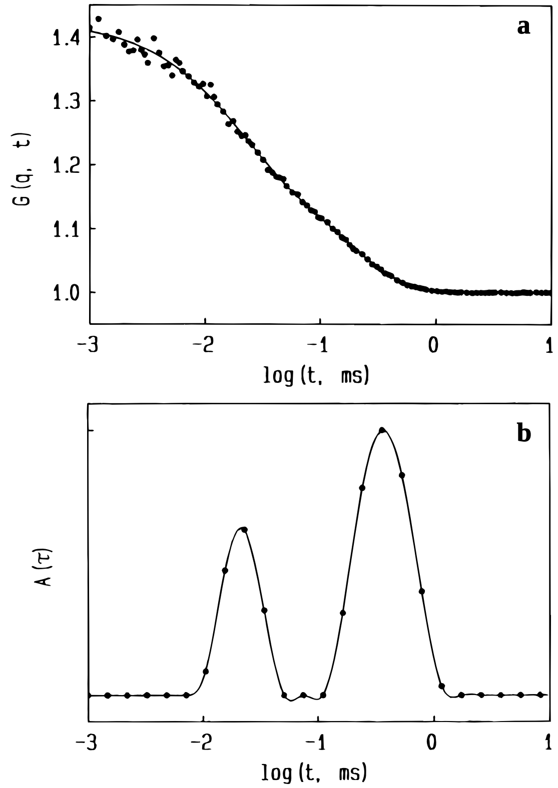

Figure 1. (a) Autocorrelation function measured by QELS for the system PS−PMMA/benzene at $C_T = 0.050$ g/mL, $x = 0.90$ and $\theta = 110°$. The dots represent the experimental data, and the solid line is the two-exponential fit according to eq 2 with parameters $a_c = 0.190$, $\tau_c = 0.0212$ ms, $\beta_c = 0.946$, $a_I = 0.462$, $\tau_I = 0.378$ ms and $\beta_I = 0.885$. (b) Relaxation modes according to CONTIN.

$$ag(q,t) = a_c \exp[-(t/\tau_c)^{\beta_c}] + a_I \exp[-(t/\tau_I)^{\beta_I}] \quad (2)$$

where β_i is the width parameter equal to $0 < \beta_i \le 1$, and τ_i is the intrinsic relaxation time (i = c or I). The KWW function is an empirical function known to give adequate descriptions of the time-dependent data. A good fit using the KWW functions is obtained with the fitting parameters given in the caption of Figure 1a. The relaxation times and amplitudes obtained from the KWW fit are in good agreement with those obtained from CONTIN analysis. In this work, we first use CONTIN as a guide to locate the positions of the relaxation modes and then use the double KWW function (eq 2) to fit the correlation function $g(q,t)$ to obtain the amplitude and relaxation time of each mode. Average relaxation times are calculated by using the equation $\langle \tau_i \rangle = \tau_i \Gamma(\beta_i{}^{-1})/\beta_i$. Since the β_c and β_I values are close to 1, the values of a_c and a_I are not affected if the sum of two exponentials is used. The uncertainty for a_c (and hence for a_I) is about 8%.

Consider first the concentration dependence. The relaxation time distribution functions $A(\tau)$ obtained by using CONTIN for the sample with $C_T = 0.05$ g/mL and $x = 0.90$ at different scattering angles are shown in Figure 2. Three relaxation modes are found in the autocorrelation function covering the dynamic range 10^{-6}−10^2 s at small scattering angles. The fastest mode is assigned as the λ_+ mode, and the intermediate mode is assigned as the λ_- eigenmode, where λ_+ and λ_- are the eigenvalues of the diffusivity matrix. Note that the λ_+ and λ_- modes are not strictly associated with the concentration and composition fluctuations.[40] However,

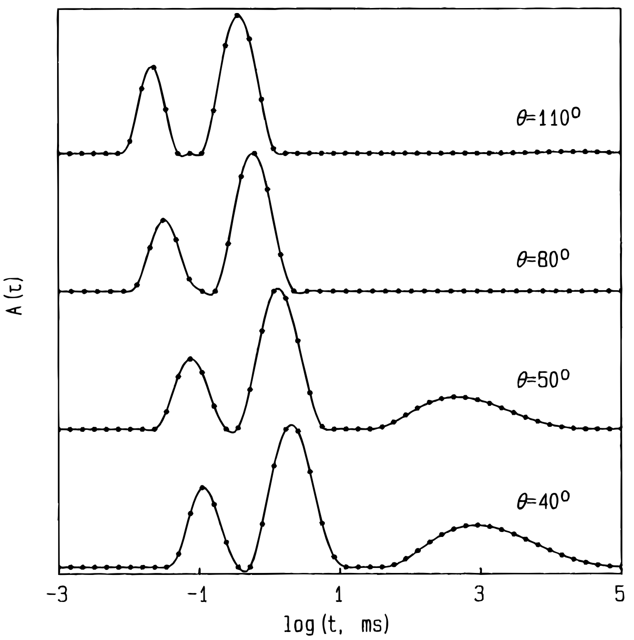

Figure 2. Relaxation time distribution obtained from CONTIN for the ternary system PS−PMMA/benzene of total polymer concentration C_T = 0.050 g/mL at x = 0.90 and different angles.

to facilitate the discussion, we shall equate λ_+ to D_c and λ_- to D_I, where D_c and D_I are the cooperative diffusion coefficient and the interdiffusion coefficient, respectively. The cooperative diffusion made is always faster than the interdiffusion mode. The slowest mode appearing in Figure 2 is rather broad; it has a pronounced amplitude at small scattering angles, but as the scattering angle increases, its amplitude becomes smaller and disappears at large scattering angles (greater than 90° as shown in Figure 2). The nature of the slowest mode in the ternary system is not clear at present, despite the fact that it has been considered to be due to polymer aggregation[41] or long-range density fluctuation.[42] Coupling of the concentration fluctuation to the solution viscoelasticity in a semidilute binary solution has also been shown to give rise to the slow mode;[43,44] however, in contrast to the aggregation mode, which has a q^2 dependence, the viscoelastic mode is q-independent at large scattering angles.[44,45] We have found that the slowest mode does not affect the ratio of the amplitude of the cooperative diffusion to that of the interdiffusion mode. In addition, due to the fact that its position is rather removed from the two eigenmodes, the slowest mode can easily be separated by the CONTIN analysis. Thus, we shall not include the slowest mode in subsequent discussions of the present paper.

To certify these modes, we plot $\langle\tau_c\rangle^{-1}$ and $\langle\tau_I\rangle^{-1}$ versus q^2 in Figures3a,b. Clearly, both sets of data display a q^2 dependence with a zero intercept, signifying that there are diffusive modes. The linear dependencies of $\langle\tau_c\rangle^{-1}$ and $\langle\tau_I\rangle^{-1}$ on q^2 also indicate that the static structure factors of the present system are not q-dependent. This is due to the relatively low molecular weights of PS and PMMA used in the present study. For these polymers, the radii of gyration are 13.7 and 19.1 nm for PS and PMMA, respectively,[21,41] and single chain from factors $P_1(q)$ and $P_2(q)$ are nearly equal to 1 for scattering angles less than 90°.

Having identified the modes to be diffusive, we now proceed to study the concentration dependence of the diffusion coefficients D_c and D_I. The concentration

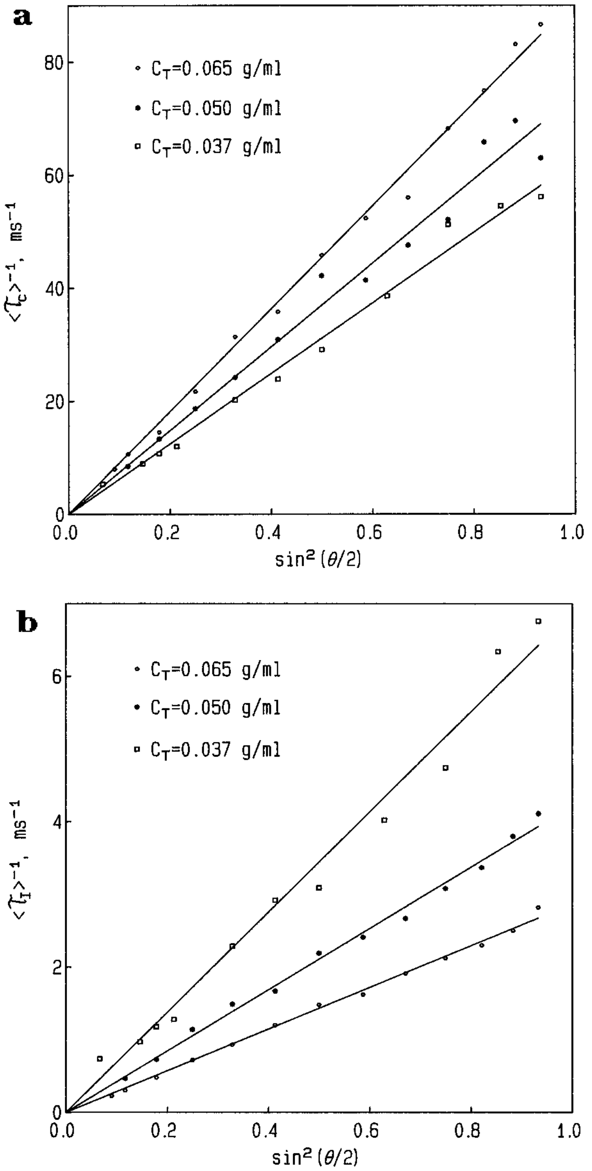

Figure 3. (a) Typical q^2 dependence of relaxation time of cooperative diffusion of PS−PMMA/benzene at x = 0.90 and different concentrations. (b) Typical q^2 dependence of relaxation time of interdiffusion of PS−PMMA/benzene at x = 0.90 and different concentrations.

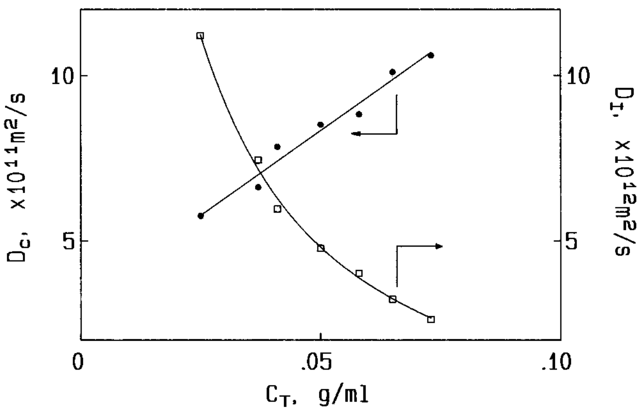

Figure 4. Concentration dependencies of cooperative diffusion coefficient and interdiffusion coefficient of PS−PMMA/benzene of x = 0.90.

dependencies of D_C and D_I are shown in Figure 4. It should be noted that the size of the symbols does not represent the relative uncertainty of the data. The

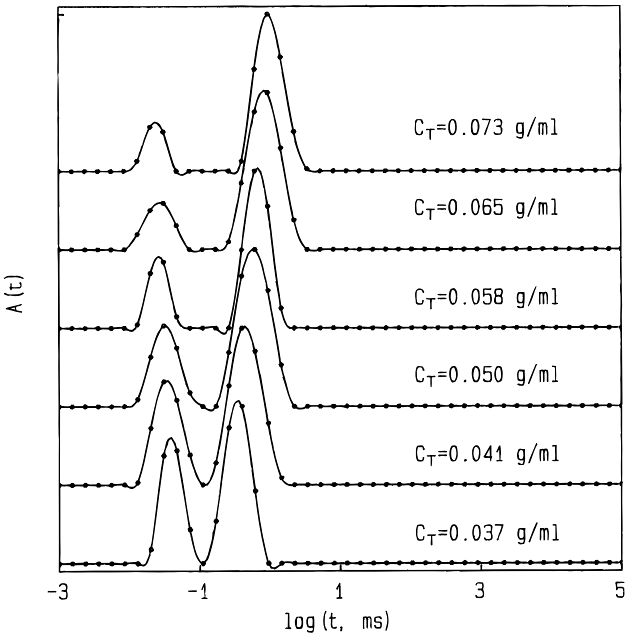

Figure 5. Relaxation time distribution obtained from CONTIN for the PS−PMMA/benzene systems at $x = 0.90$, scattering angle 80°, and different concentrations.

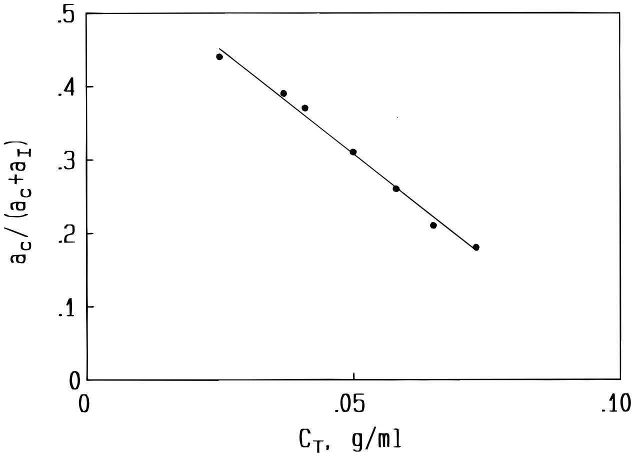

Figure 6. Variation of the relative amplitude of the cooperative diffusion as a function of concentration at $x = 0.90$.

Table 1. Properties of Polymer Samples

sample	$10^{-3} M_w$	$I = M_w/M_n$	$10^4 A_2$ (mol cm^3 g^{-2})
PS	186	1.05	4.67(37)
PMMA	285	1.13	2.91(38)

Table 2. Diffusivity Matrix Elements for PS−PMMA/Benzene at Different Polymer Concentrations

C (g/mL)	D_{11} ($\times 10^{12}$ m^2/s)	D_{22} ($\times 10^{12}$ m^2/s)	$(D_{12}D_{21})^{1/2}$ ($\times 10^{12}$ m^2/s)
0.025	48.3	20.4	18.5
0.037	57.4	16.2	21.0
0.041	70.1	14.3	23.1
0.050	76.2	13.7	25.2
0.058	78.6	13.7	26.8
0.065	90.5	13.7	30.3
0.073	93.7	14.9	33.5

uncertainties in the various quantities are given whenever they arise in the text. The results show that, over the concentration range studied, the cooperative diffusion coefficient D_c increases nearly linearly with increasing total polymer concentration, whereas D_I decreases nonlinearly with increasing polymer concentration.

Figure 5 shows the concentration dependence of the two relaxation modes obtained from the CONTIN analysis for the time correlation functions observed at $\theta = 80°$. As can be seen from this representation, the amplitude of the cooperative diffusion mode decreases with the increase in total polymer concentration, whereas the amplitude of the interdiffusion mode is found to increase when the total polymer concentration increases. The relative amplitudes of the two modes are nearly independent of the scattering angle due to the low molecular weights of the polymers used, as mentioned earlier. In Figure 6, we plot the amplitude of the cooperative mode relative to the sum of the amplitudes of these two modes, represented by $a_c/(a_c + a_I)$, as a function of concentration at a fixed composition $x = 0.90$. The result shows that $a_c/(a_c + a_I)$ decreases nearly linearly with the increase in total polymer concentration.

As previously shown,[33,34] the time evolution of the concentration of two polymers in a solvent is governed by the diffusivity matrix, which is given by

$$\mathbf{D} = q^2\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \tag{3}$$

In the semidilute and concentrated ternary polymer solutions, the intermolecular hydrodynamic interaction is screened,[46] and one can neglect the effect of intermolecular coupling on the mobility tensor between the two polymers (the intrachain hydrodynamic coupling is still kept). By using this approximation, we have recently shown that if polymer 2 is isorefractive with the solvent, it then follows that[35]

$$\frac{a_c}{a_c + a_i} = \left(\frac{D_c D_I}{D_{22}} - D_I\right)/(D_c - D_I) \tag{4}$$

Thus, from the amplitude factor data given in Figure 6 and the diffusion coefficients given in Figure 4, we can calculate the diffusivity element D_{11} from eq 4. By knowing D_{11}, we can obtain the element D_{22} and the product $D_{12}D_{21}$ from the equations

$$D_c + D_I = D_{11} + D_{22} \tag{5}$$

and

$$D_c D_I = \Delta^2 \tag{6}$$

where $\Delta^2 = D_{11}D_{22} - D_{12}D_{21}$. Equations 5 and 6 are the properties of the diffusivity matrix given in eq 3. Values of D_{11}, D_{22}, and $D_{12}D_{21}$ obtained are given in Table 2 for different total polymer concentrations. One notes that D_{11} is significantly larger than D_{22}. Near C^* (the overlap concentration), D_{11} is more than a factor of 2 larger than D_{22}, and at about 3 times C^*, it is more than 6 times larger. In addition, the product of the off-diagonal elements, D_{12} and D_{21}, is not negligible. The value of $(D_{12}D_{21})^{1/2}$ also increases rapidly as the total polymer concentration is increased. The large D_{11} element is due to the fact that more PS is present in the ternary solution ($x = 0.9$) and also that benzene is a better solvent for PS than for PMMA, as indicated by a large second virial coefficient A_2 shown in Table 1. The large value of the off-diagonal diffusivity matrix elements clearly shows the importance of the PS−PMMA interaction, and the coupling between them is also rather important.

By neglecting the off-diagonal mobility matrix elements (due to screening of the intermolecular hydrodynamic interaction in the semidilute polymer solution), one can show that the diffusivity matrix elements are simply given by

$$D_{ij} = kTM_{jj}(\mathbf{S}^{-1})_{ij} \qquad i,j = 1 \text{ or } 2 \tag{7}$$

where k is the Boltzmann constant, T is the absolute temperature, M_{jj} is the jj element of the mobility matrix, and $\mathbf{S}^{-1}$ is the inverse of the multichain static structure matrix $\mathbf{S}(q)$.

If one invokes the random phase approximation (RPA),[30−34] then one can relate the multichain static structure matrix $\mathbf{S}(q)$ needed in eq 7 to the excluded volume interaction parameter. The RPA is

$$\mathbf{S}(q)^{-1} = \mathbf{S}_0(q)^{-1} + \boldsymbol{v} \tag{8}$$

where $\boldsymbol{v}$ is the excluded volume interaction matrix with elements v_{ij}, $\mathbf{S}_0(q)$ is the structure matrix for single chains having only elements $\mathbf{S}^0{}_{11}(q)$ and $\mathbf{S}^0{}_{22}(q)$. By using eqs 7 and 8, one obtains, after some algebra that

$$D_{11} = \frac{D_{s1}}{P_1(q)}[1 + 2x_1A_{2,11}M_{w1}C_TP_1(q)] \tag{9a}$$

$$D_{22} = \frac{D_{s2}}{P_2(q)}[1 + 2x_2A_{2,22}M_{w2}C_TP_2(q)] \tag{9b}$$

$$D_{12} = (D_{s1}x_1C_T)(2A_{2,12}M_{w1}(m_2/m_1)) \tag{9c}$$

$$D_{21} = (D_{s2}x_2C_T)(2A_{2,12}M_{w2}(m_1/m_2)) \tag{9d}$$

where $D_{si} = kT/N_i\xi_i$, where N_i is the number of the segments and $\xi_i \sim M_{ii}{}^{-1}$, the friction coefficient of polymer i. D_{si} and m_i are, respectively, the self (or tracer) diffusion coefficient and the monomer molecular weight of polymer i. $A_{2,ij}$'s are the second virial coefficients associated with the interaction of the molecules (or segments) i and j; they are related to the excluded volume parameters v_{ij} . From the D_{11} and D_{22} data given in Table 2 and the second virial coefficient data given in Table 1, we can use eqs 9a,b to calculate the tracer diffusion coefficients D_{s1} and D_{s2}. By knowing D_{s1}, D_{s2}, and the value of $D_{12}D_{21}$, as given in Table 2, we can next calculate the quantity $A_{2,12}$ with the help of eqs 9c,d. $A_{2,12}$ is related to the Flory−Huggins polymer−polymer interaction parameter χ_F by

$$\chi_F = \frac{2V_s}{\bar{v}_1\bar{v}_2}A_{2,12} - \frac{V_s}{\bar{v}_1{}^2}A_{2,11} - \frac{V_s}{\bar{v}_2{}^2}A_{2,22} \tag{10}$$

where $\bar{v}_i$ is the specific volume of polymer i and V_s is the molar volume of the solvent. The results obtained for $A_{2,12}$ and χ_F are shown in Figure 7 and the concentration dependencies of D_{s1} and D_{s2} are given in Figure 8.

One notes that the χ_F value is positive, suggesting that PS−PMMA is immiscible in the dry state, which is consistent with the results reported previously.[1,2,47,48] The concentration dependence of $A_{2,12}$ or χ_F as given in Figure 7 shows that χ_F (or $A_{2,12}$) increases with increasing total polymer concentration. This results is in agreement with Fukuda's results in different systems.[14] At the lowest concentration ($C_T = 0.025$ g/mL), we have $\chi_F = 0.017$, but it increases to $\chi_F = 0.021$ at the highest concentration ($C_T = 0.073$ g/mL). These results should be compared with the value $\chi_F = 0.021$ obtained by Callaghan and Paul[49] on the basis of the measurement of the cloud point from mixtures of PS with PMMA for different compositions of the two components. A value of $\chi_F = 0.025$ from neutron scattering of an isotope-substituted PS and PMMA diblock copolymer has also been reported by Russell.[50]

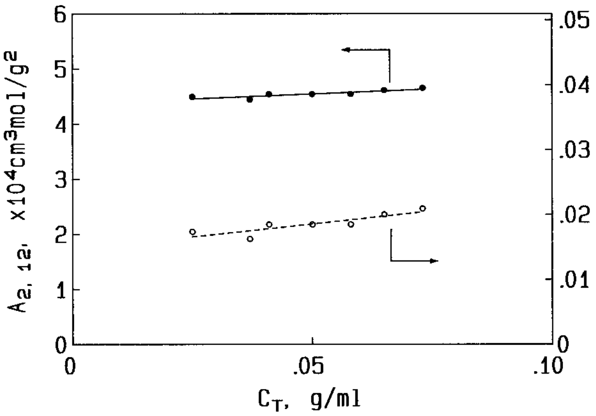

Figure 7. Concentration dependence of $A_{2,12}$ and χ_F between PS and PMMA in benzene at fixed composition.

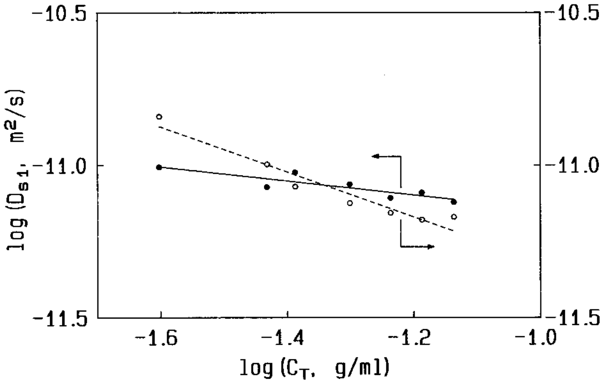

Figure 8. Concentration dependence of the self diffusion coefficient of PS (D_{s1}) and that of PMMA (D_{s2}) in benzene at a fixed composition.

The tracer or self-diffusion coefficient of single PS chains in isorefractive solutions of PMMA/benzene was previously studied by Numasawa and co-workers[20,21] to determine the molecular weight and concentration dependencies of the self-diffusion coefficient of PS. In the present work, the relative concentration of PS (x) is rather high ranging from 0.50 to 0.95 with respect to PMMA. Concentration and molecular weight dependencies of the self-diffusion coefficient D_s of polymer in binary polymer solutions have been widely studied by various techniques[51] for high molecular weight polymers, and the results have been discussed in terms of the reptation model,[21] which predicts $D_s \propto M^{-2}C^{-1.75}$ in good solvents. Various values for the power law exponent have been observed, depending on the concentration and molecular weight ranges.[9,50−53] Moreover, instead of the power law, a stretched exponential type of the concentration dependence has also been proposed.[54] By using the optical labeling QELS technique, Martin[16] observed a continuous change in the slope of the log D_s versus log C plot in a ternary polymer system. At a fixed composition ($x = 0.90$), our results for D_s of PS (D_{s1}) and PMMA (D_{s2}) show a decrease with increasing total polymer concentration. This is consistent with the previous results reported in the literature. If we force a power law fit to the D_{s1} and D_{s2} data with respect

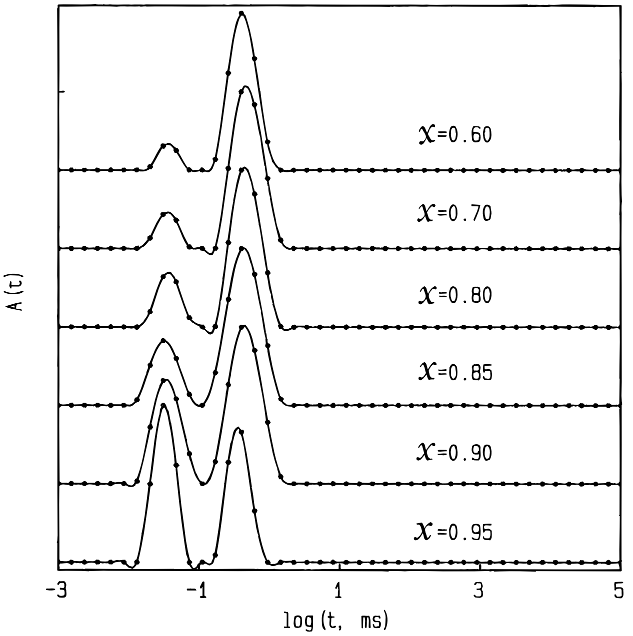

Figure 9. Relaxation time distribution obtained from CONTIN for the ternary system PS−PMMA/benzene at total polymer concentration C_T = 0.042 g/mL, θ = 80° and the compositions shown.

to their concentration dependencies, we obtain exponents of −0.23 and −0.74 for D_{s1} and D_{s2}, respectively. The experimental uncertainties for D_I, D_c, and a_c are 1.4, 2.7, and 8.0%, respectively. Thus, the relative errors for D_{s1} and D_{s2} are estimated to be 3.8 and 5.3%, respectively.

To understand such a concentration dependence, we apply a simple scaling argument involving blob self-diffusion theory.[22] The self-diffusion coefficient D_s in the semidilute solution in the Rouse regime is given by $D_s(N,C) \approx kT/(N\eta_s\zeta/g)$, where g is the number of links per blob, and $\zeta(=bg^{\nu})$ is the correlation length of the solution. Scaling argument gives $g \sim C^{-\nu/(3\nu-1)}$, and this gives $D_s \sim C^{(\nu-1)/(3\nu-1)}$. If we set $\nu = 0.6$ for good solvents, then we expect $D_s \sim C^{-0.5}$, which is between the two exponents that we have found. The values of these two exponents are far from the prediction of the reptation model due to the small chain lengths of the polymers used, and the reptation model is not applicable in the present system. Another cause for the discrepancy is that, in ternary systems, the effects of composition and the polymer−polymer interaction also play important roles. Because of this, the result derived from binary solutions is not expected to apply to ternary solutions. Nevertheless, considering the presence of various sources of uncertainty, the concentration dependence found in D_{s1} and D_{s2} is reasonable.

We next consider the composition dependence. Relaxation time distribution functions $A(\tau)$ obtained for time correlation functions at scattering angle 80° for samples with a total polymer concentration of C_T = 0.042 g/mL are shown in Figure 9 for different compositions. The values of D_c and D_I derived from the angular dependent measurement of these solutions are shown in Figure 10 as a function of composition x. The amplitude factor $a_c/(a_c + a_I)$ is shown in Figure 11 as a function of x. One notes that both the interdiffusion and cooperative diffusion coefficients depend on the composition. D_I first decreases and then increases slightly with increasing PS fraction, whereas D_C decreases slightly with increasing fraction of PS. On the other hand, upon an increase in the PS fraction, the relative amplitude of cooperative diffusion greatly increases. By using these results, we have deduced the values of D_{11}, D_{22}, and $(D_{12}D_{21})^{1/2}$ with the help of eqs 4−6. The composition dependence of these diffusivity matrix elements is shown in Table 3. One notes that, at large x (more PS), D_{11} is several times larger than D_{22}. However, as x decreases, D_{11} decreases and D_{22} increases, accompanied by an increase in $(D_{12}D_{21})^{1/2}$. Near $x = 0.5$ (symmetric composition), $D_{11} \approx D_{22}$. This result suggests that for symmetric composition the concentration fluctuation and the composition fluctuation become nearly true eigenfuctions of the diffusivity matrix having eigenvalues $D_c = \lambda_+ \approx D_a + (D_{12}D_{21})^{1/2}$ and $D_I = \lambda_- \approx D_a - (D_{12}D_{21})^{1/2}$, with $D_a = (D_{11} + D_{22})/2$.[34]

By following the procedures as outlined earlier, and by using the data given in Table 3, we have calculated the values of D_{s1}, D_{s2}, $A_{2,12}$, and χ_F as a function of the

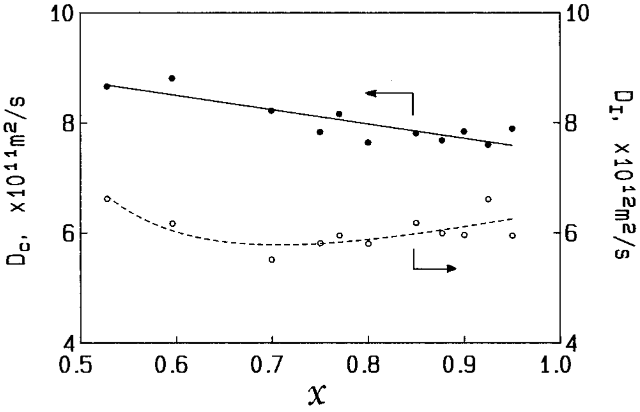

Figure 10. Variation of the cooperative diffusion and interdiffusion coefficients as a function of the composition at C_T = 0.042 g/mL.

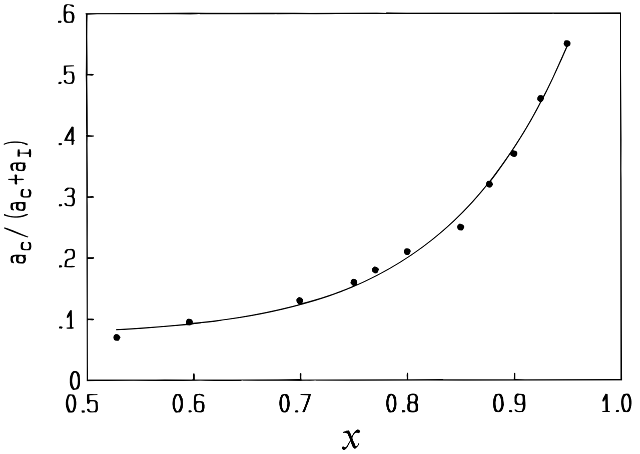

Figure 11. Variation of the relative amplitude of cooperative diffusion $a_c/(a_c + a_I)$ as a function of the composition at C_T = 0.042 g/mL.

Table 3. Diffusivity Matrix Elements for PS−PMMA/Benzene at Different Polymer Compositions

x	D_{11} ($\times10^{12}$ m^2/s)	D_{22} ($\times10^{12}$ m^2/s)	$(D_{12}D_{21})^{1/2}$ ($\times10^{12}$ m^2/s)
0.95	75.6	10.2	17.2
0.93	69.6	13.0	20.1
0.88	66.7	16.1	24.7
0.85	64.3	20.0	28.3
0.77	62.7	24.8	32.7
0.75	58.0	26.1	32.6
0.70	58.5	29.3	35.5
0.60	55.3	39.0	40.1
0.53	46.3	46.9	40.0

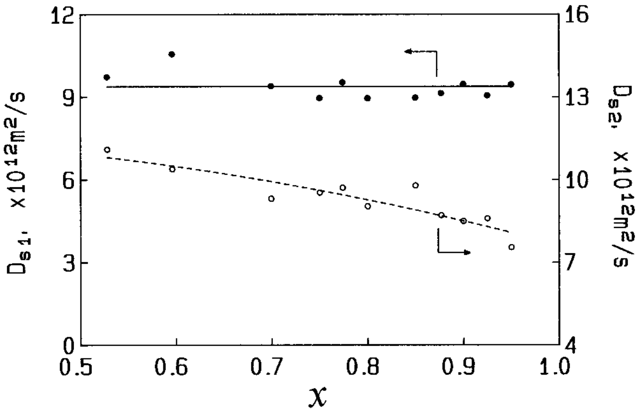

Figure 12. Composition dependencies of the self-diffusion coefficients of PS and of PMMA in benzene at fixed total polymer concentration of 0.042 g/mL.

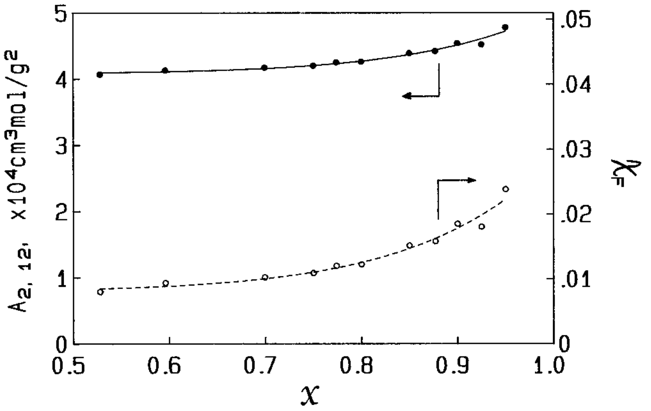

Figure 13. Composition dependencies of $A_{2,12}$ and χ_F between PS and PMMA at fixed concentration $C_T = 0.042$ g/mL.

PS fraction. The uncertainty for $A_{2,12}$ is about 3%, but χ_F has 15% uncertainty due to compound errors involving several quantities. Figure 12 shows the composition dependencies of self-diffusion coefficients of PS and PMMA. While the self-diffusion coefficient of PS is nearly independent of composition, the self-diffusion coefficient of PMMA decreases with increasing PS fraction, especially in the range of high x value. The composition dependence of D_{s2} is consistent with the previous results found in the PMMA−PDMS/toluene system in which the self-diffusion coefficient of PMMA is found to decrease with increasing PDMS composition.[35]

We plot in Figure 13 the composition dependencies of $A_{2,12}$ and χ_F. $A_{2,12}$ increases slightly with increasing PS fraction. One notes that χ_F increases by about 3 times, from 0.008 at $x = 0.50$ to 0.024 at $x = 0.95$. By using static light scattering, Stockmayer and Stanley reported that the χ_F value of PS and PMMA in bromobenzene is 0.014 ± 0.010.[10] Stockmayer and Stanley's work was further extended by Fukuda et al., who used the technique of optical θ conditions (or zero average contrast) and obtained values of 0.004−0.011 for PS and PMMA in bromobenzene to be dependent on the molecular weights of PS and PMMA.[14] The results of both Stockmayer−Stanley and Fukuda et al. are obtained from static intensity measurements, using the dilute solution light-scattering theory for analysis. From the compatibility measurements on solutions of these two polymers in benzene, the χ_F is estimated to be 0.008−0.015.[47,48] Our results obtained for $C_T = 0.042$ g/mL are within this range.

Summary and Conclusion

We have carried out a detailed QEL scattering study of the PS−PMMA/benzene ternary solution with both polymers in the semidilute concentration regime. The QEL scattering measurements at different scattering angles ranging from 30 to 150° have been made. Two types of the PS−PMMA/benzene solution have been studied: one at fixed composition ($x = 0.90$) but different total polymer concentrations, and the other at fixed total polymer concentration ($C_T = 0.042$ g/mL) but different compositions ranging from $x = 0.50$ to 0.95. We have observed, in these solutions, two diffusion modes in the intensity−intensity time correlation function of the scattered light. These two modes correspond to the eigenmodes of the diffusivity matrix that governs the time evolution of the concentration fluctuations of the polymers in the ternary solution. We have measured the concentration and composition dependencies of the relaxation rates and the amplitudes of these modes. With the help of theory, we have determined, by using the relaxation rates and amplitude data, the elements of the diffusivity matrix as a function of polymer concentration and composition. From the diffusivity data, we have further deduced the self-diffusion coefficients of PS and PMMA and the Flory−Huggins interaction parameter χ_F between PS and PMMA, with the help of the RPA. The concentration and composition dependencies of these quantities have been studied. We have found that at fixed composition, the self-diffusion coefficients of PS and PMMA decrease with increasing total polymer concentration, and at fixed concentration they decrease with decreasing fraction of its own kind. We have found that the value of the Flory−Huggins interaction parameter χ_F between PS and PMMA ranges from 0.008 to 0.026, depending on concentration and composition. This result shows that the interaction between PS and PMMA chains in the benzene solution is repulsive. The χ_F values obtained by our method are in good agreement with those obtained by other techniques, indicating the reliability of this method of analysis.

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