Macromolecules **1997,** *30,* 4939−4944

Light Scattering from Mixtures of Two Polystyrenes in Toluene and Self-Diffusion Coefficients

Z. Sun and C. H. Wang*

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received March 4, 1997; Revised Manuscript Received April 30, 1997[⊗]

ABSTRACT: Experimental light scattering data from solutions consisting of two nearly monodisperse different molecular weight polystyrenes in toluene are interpreted using a theoretical approach recently developed in our laboratory. By allowing polystyrene chains with different chain lengths to have different monomer friction coefficients and different excluded volume parameters, we have provided an excellent theoretical model for this ternary polymer solution over a wide concentration range. The self-diffusion coefficients of two polystyrenes in various concentrations are calculated from diffusivity matrix elements. The results obtained are found to be consistent with those obtained by using different techniques.

Introduction

Light scattering from ternary solutions consisting of two polymers dissolved in a small molecule solvent is a topic of practical and theoretical interest. Experimental studies have been carried out on systems in conditions with one of the two polymers isorefractive with the solvent,[1−6] at an optical θ condition,[4] and with arbitrary solvents.[7,8] Quasielastic light scattering from these solutions gives rise to two modes in intensity auto-time correlation functions. The fast component is often referred to as the cooperative mode, and the slow one, as the interdiffusion mode. These two modes corresponds to the eigenvalues of the diffusive matrix appropriate for the ternary solution and cannot strictly be identified with the cooperative diffusion and interdiffusion coefficients.[9] However, despite the misnomer, we shall use these names in the subsequent discussion. Akcasu, Benmouna, and co-workers have theoretically investigated the scattering function using the random phase approximation (RPA).[10−12] Their work mainly deals with the study of a mixture of two polymers having the same molecular weight and dimension but differing in contrast factors or with a mixture of two polymers having different molecular weights but otherwise identical. Because of such idealization, they have assumed in such systems equal monomer friction coefficients and the same solvent quality for the polymers. We have recently extended the theory without restricting the monomer friction coefficient and the solvent quality for the two polymers. Thus, our theory is capable of dealing with a general polymer system. Using two separate ternary polymer solutions with one polymer isorefractive with the solvent as examples, we have demonstrated how one can obtain the mobility (or self-diffusion coefficient) of each individual polymer and the Flory−Huggins interaction parameter of two polymers in solution.[5,6] We have recently also considered the case with no restriction to the polymer refractive index.[8]

Corrotto et al.[13] have recently published a detailed experimental quasielastic light scattering study of two nearly monodisperse polystyrenes with widely different molecular weights (differing by a factor of about 7.2) in toluene. They have found that over a wide concentration regime the intensity auto-time correlation function of the solution also exhibits a clear bimodal structure. They have extracted D_C and D_I from their experimental data and explained the result in terms of the theory of ternary polymer solutions developed by Benmouna et al.[11] Here D_C and D_I are diffusion coefficients associated with the fast (cooperative diffusion) mode and the slow (interdiffusion) mode, respectively. However, the equation (eq 13 of ref 13) that they used to interpret the D_C/D_I ratio was derived under an assumption that the two polymers have the same excluded volume parameters and also have the same monomer friction coefficient.[11] As mentioned above, these assumptions are not rigorous even for solutions containing two polymers differing only in molecular weight. Thus, it is not clear whether the experimental results indeed quantitatively agree with the theory of Benmouna et al., as is claimed in ref 13.

Nevertheless, ref 13 provides useful D_C and D_I data, with both static and dynamic light scattering data of binary polystyrene solutions given in the paper. These detailed experimental results thus present an excellent candidate for evaluating the consistency of the experiment and theory. In this paper, we use the theory developed in our laboratory to analyze the dynamic light scattering data of the bimodal polystyrene solution published in ref 13. As mentioned above, our theory removes several important approximations made by Benmouna et al.[11] and is expected to be applicable in a general polymer system.

Theory

We describe the theoretical expressions to be used for analyzing the experimental data. Instead of considering the intensity autocorrelation function, we focus on the scattered field autocorrelation function. The scattered field auto-correlation function of a ternary system referenced to the solvent is proportional to

$$C(q,t) = \sum_i \sum_j a_i a_j S_{ij}(q,t) \tag{1}$$

where $S_{ij}(q,t)$ is the ijth element of the dynamic structure matrix, $q = (4\pi n/\lambda)\sin(\theta/2)$ is the amplitude of the scattering wave vector, λ is the wavelength of the incident radiation in vacuum, θ is the scattering angle, a_i and a_j are the refractive index increments of polymers i and j, respectively ($i,j = 1, 2$), and n is the refractive index of the solution. If one of the two polymers (e.g., polymer 2) is isorefractive with the solvent, then $a_2 = 0$, and $C(q,t)$ reduces to $C(q,t) = a_1^2 S_{11}(q,t)$. This simplified case was used in our previous work.[5,6] In this

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(97)00290-8 CCC: $14.00

paper, we deal with the case that two polymers differ only in molecular weight; thus $a_1 = a_2 = a$, and the time correlation function $C(q,t)$ is given by the sum of the four S_{ij}'s as

$$C(q,t) = a^2 \sum_i \sum_j S_{ij}(q,t) \tag{2}$$

To calculate the sum of these S_{ij}'s, it is convenient to consider the time dependence of the dynamic structure matrix $\bar{\bar{S}}(q,t)$, which in the diffusion limit is given by

$$\bar{\bar{S}}(q,t) = \mathrm{e}^{-q^2 \bar{\bar{D}} t} \bar{\bar{S}}(q) \tag{3}$$

where $\bar{\bar{D}}(q)$ is the diffusivity matrix

$$\bar{\bar{D}}(q) = \mathrm{kT} \bar{\bar{M}}(q) \cdot \bar{\bar{S}}(q)^{-1} \tag{4}$$

$\bar{\bar{M}}(q)$ is the mobility matrix, and $\bar{\bar{S}}(q)$ is the static structure factor matrix.

The four elements of the diffusivity matrix are given by

$$\bar{\bar{D}}(q) = \begin{bmatrix} D_{11}(q) & D_{12}(q) \\ D_{21}(q) & D_{22}(q) \end{bmatrix} \tag{5}$$

which in general is not symmetric (i.e., $D_{12} \neq D_{21}$). The diffusivity matrix $\bar{\bar{D}}(q)$ can, however, be diagonalized to yield two eigenvalues, labeled as D_{C} and D_{I}. Using the eigenvalues and eigenvectors of the $\bar{\bar{D}}(q)$ matrix, we obtain for each of the dynamic matrix elements, $S_{ij}(q,t)$ as[11]

$$S_{ij}(q,t) = A_{\mathrm{I}}^{ij} \mathrm{e}^{-q^2 D_{\mathrm{I}} t} + A_{\mathrm{C}}^{ij} \mathrm{e}^{-q^2 D_{\mathrm{C}} t} \tag{6}$$

Here the expressions for the eigenvalues D_{I} and D_{C} are given by

$$D_{\mathrm{I}} = D_{\mathrm{av}} - ({D_{\mathrm{av}}}^2 - \Delta(D))^{1/2} \tag{7}$$

$$D_{\mathrm{C}} = D_{\mathrm{av}} + ({D_{\mathrm{av}}}^2 - \Delta(D))^{1/2} \tag{8}$$

where $D_{\mathrm{av}} = (D_{11} + D_{22})/2$ and $\Delta(D) = D_{11}D_{22} - D_{12}D_{21}$. The amplitudes A_{I}^{ij} and A_{C}^{ij} are given by

$$A_{\mathrm{I}}^{11} = \frac{(D_{\mathrm{I}} - D_{22})S_{11}(q) + D_{12}S_{21}(q)}{D_{\mathrm{I}} - D_{\mathrm{C}}} \tag{9}$$

$$A_{\mathrm{C}}^{11} = \frac{(D_{\mathrm{C}} - D_{22})S_{11}(q) + D_{12}S_{21}(q)}{D_{\mathrm{C}} - D_{\mathrm{I}}} \tag{10}$$

$$A_{\mathrm{I}}^{21} = \frac{(D_{\mathrm{I}} - D_{11})S_{21}(q) + D_{21}S_{11}(q)}{D_{\mathrm{I}} - D_{\mathrm{C}}} \tag{11}$$

$$A_{\mathrm{C}}^{21} = \frac{(D_{\mathrm{C}} - D_{11})S_{21}(q) + D_{21}S_{11}(q)}{D_{\mathrm{C}} - D_{\mathrm{I}}} \tag{12}$$

A_{I}^{22}, A_{C}^{22}, A_{I}^{12}, and A_{C}^{12} can be obtained from the above equations by interchanging indices 1 with 2.

Using these results, we can write the time correlation function $C(q,t)$ given by eq 2 as

$$C(q,t) = A_{\mathrm{I}} \mathrm{e}^{-q^2 D_{\mathrm{I}} t} + A_{\mathrm{C}} \mathrm{e}^{-q^2 D_{\mathrm{C}} t} \tag{13}$$

where

$$A_{\mathrm{I}} = a^2 (A_{\mathrm{I}}^{11} + A_{\mathrm{I}}^{12} + A_{\mathrm{I}}^{21} + A_{\mathrm{I}}^{22}) \tag{14}$$

$$A_{\mathrm{C}} = a^2 (A_{\mathrm{C}}^{11} + A_{\mathrm{C}}^{12} + A_{\mathrm{C}}^{21} + A_{\mathrm{C}}^{22}) \tag{15}$$

In general, the mobility matrix has both diagonal and off-diagonal elements. The off-diagonal elements arise from the hydrodynamic interaction between different chains and the diagonal elements are due to simple chains. The Zimm-type hydrodynamic interactions are present in both the diagonal and off-diagonal elements. However, in the semidilute and concentrated regimes, the hydrodynamic interactions are screened and thus the off-diagonal mobility matrix elements can be neglected.[14] In dilute solution, the Zimm-type hydrodynamic interaction is important; however, in this case the importance of the cross terms of the mobility matrix is reduced because polymer chains are far apart.[15] Thus, in either case, we set $M_{12} = M_{21} = 0$. This approximation is the same as that employed by Benmouna et al.[10] The diagonal elements of the mobility matrix are written as $M_{ii} = \phi_i/\xi_i$, with $i = 1$ or 2. Then one immediately obtains from eq 4 the diffusivity matrix $\bar{\bar{D}}(q)$ as

$$\bar{\bar{D}}(q) = \frac{kT}{\Delta(s)} \begin{bmatrix} \dfrac{\phi_1 S_{22}(q)}{\xi_1} & \dfrac{-\phi_1 S_{12}(q)}{\xi_1} \\ -\dfrac{\phi_2 S_{21}(q)}{\xi_2} & \dfrac{\phi_2 S_{11}(q)}{\xi_2} \end{bmatrix} \tag{16}$$

where $\Delta(S) = S_{11}S_{22} - S_{12}S_{21}$. Here $\phi_i = n_i N_i$ is the number of monomer units per unit volume of type i. N_i is the number of monomer units per chain (i.e., the degree of polymerization), and n_i is the number of chains per unit volume. ξ_i is the friction coefficient of monomer of type i. One notes that in contrast to the theory of Benmouna et al.,[10] we allow the monomer friction coefficient of each polymer to be different. As can be seen later, for the bimodal polystyrene solution, no agreement with the experiment is possible if the monomer friction coefficient is assumed to be the same even for these polymers that are different only in chain length. Equation 16 yields two important equalities between elements of the diffusive matrix and the structure matrix: $D_{11}/D_{12} = -S_{22}/S_{12}$, $D_{22}/D_{21} = -S_{11}/S_{21}$. These equalities are important as they lead to considerable simplification in the calculation of the time correlation function.

Experimentally, one can determine D_{C} and D_{I} as well as the amplitude ratio $A_{\mathrm{I}}/(A_{\mathrm{I}} + A_{\mathrm{C}})$ of the two eigenmodes. Since D_{I} and D_{C} are eigenvalues of the diffusivity matrix, it follows that

$$D_{\mathrm{C}} + D_{\mathrm{I}} = D_{11} + D_{22} \tag{17}$$

$$D_{\mathrm{C}} D_{\mathrm{I}} = D_{11}D_{22} - D_{12}D_{21} = D_{11}D_{22}(1 - XY) \tag{18}$$

where $X = D_{21}/D_{22}$ and $Y = D_{12}/D_{11}$.

In addition, one can show the amplitude ratio to be

$$\frac{A_{\mathrm{I}}}{A_{\mathrm{I}} + A_{\mathrm{C}}} = \frac{\left[(X + Y - 2XY) - D_{\mathrm{I}}\left(\dfrac{Y}{D_{22}} + \dfrac{X}{D_{11}}\right)\right] D_{\mathrm{C}}}{(D_{\mathrm{C}} - D_{\mathrm{I}})(X + Y - 2XY)} \tag{19}$$

In the isorefractive case considered in ref 5, we can obtain D_{11}, D_{22}, and $D_{12}D_{21}$ from the experimental result without requiring further approximations; however, in the present case, additional information regarding the qualities X and Y are required in order to obtain the elements of the diffusivity matrix.

The additional information that we resort to is the random phase approximation (RPA). The RPA[16,17] is the generalization of the Zimm condition[18] for the scattering intensity of a binary solution to the multichain system. It is given by equation

$$\bar{\bar{S}}(q)^{-1} = \bar{\bar{S}}_0(q)^{-1} + \bar{\bar{v}} \tag{20}$$

where $\bar{\bar{S}}_0(q)$ is the structure matrix for a single noninteracting chain and $\bar{\bar{v}}$ is the excluded volume interaction matrix with elements given by v_{ij}. The RPA allows the multichain static structural factor S_{ij} to be expressed in terms of single chain dynamics and the binary interaction parameter. Using the RPA, it is easy to show from eq 20 that

$$X = D_{21}/D_{22} = \frac{v_{21}S_{22}^0}{1 + v_{22}S_{22}^0} \tag{21}$$

and

$$Y = D_{12}/D_{11} = \frac{v_{12}S_{11}^0}{1 + v_{11}S_{11}^0} \tag{22}$$

where S_{12}^0 and S_{21}^0 vanish and S_{11}^0 and S_{22}^0 are given by

$$S_{11}^0(q) = x\phi N_1 P_1(q) \tag{23}$$

$$S_{22}^0(q) = (1 - x)\phi N_2 P_2(q) \tag{24}$$

ϕ is the total number of polymer chains per unit volume in solution and x is the fraction of polymer 1 of the total polymer. $P_i(q)$ is the form factor of a single chain, and for $qR_g \ll 1$, it reduces to unity. Here R_g is the radius of the gyration.

If two polymer chains only differ in molecular weight, such as the bimodal polystyrene solution considered here, then one has

$$v_{12} = \frac{1}{2}(v_{11} + v_{22}) = v_{21} \tag{25}$$

where v_{11} and v_{22} are related to the second virial coefficients by

$$v_{ii}\phi_i N_i = 2A_{2,ii}M_iC_i \qquad i = 1, 2 \tag{26}$$

Here $A_{2,11}$ and $A_{2,22}$ are the second virial coefficients with respect to the solvent for polymer 1 and polymer 2, respectively. M_i and C_i are the molecular weight and concentration (grams per unit volume) of chain i, respectively.

Substituting the above results into eq 4, we obtain

$$D_{11} = \frac{kT}{N_1\xi_1P_1(q)}[1 + 2xA_{2,11}M_1C_TP_1(q)] \tag{27}$$

$$D_{22} = \frac{kT}{N_2\xi_2P_2(q)}[1 + 2(1 - x)A_{2,22}M_2C_TP_2(q)] \tag{28}$$

and

$$X = \frac{D_{21}}{D_{22}} = \frac{(A_{2,11} + A_{2,22})(1 - x)M_2C_TP_2(q)}{1 + 2A_{2,22}(1 - x)M_2C_TP_2(q)} \tag{29}$$

$$Y = \frac{D_{12}}{D_{11}} = \frac{(A_{2,11} + A_{2,22})xM_1C_TP_1(q)}{1 + 2A_{2,11}xM_1C_TP_1(q)} \tag{30}$$

where C_T is the total polymer concentration (in grams per unit volume). If the molecular weight of polymer i (proportional to N_i) is less than the entangled molecular weight, then the quantity $kT/N_i\xi_i$ is the self-diffusion coefficient D_{si} of a single chain undergoing Brownian motion in the multichain solution.

In dilute solution, ξ_i is influenced by hydrodynamic interactions, which must be included in the calculation of D_{si}. One may use the Kirkwood–Riseman operator to calculate ξ_i that includes the hydrodynamic interaction. The result based on the Oseen hydrodynamic tensor for D_{si} is[15]

$$D_{si} = \frac{kT}{N_i\xi_R}\left(1 + \frac{\xi_R}{6\pi\eta_o N_i}\sum_{\alpha,\beta}\left\langle\frac{1}{R_{\alpha\beta}}\right\rangle\right) \tag{31}$$

where ξ_R is the friction coefficient of a Rouse chain, η_o is the solvent viscosity, and $R_{\alpha\beta}$ is the distance between segments α and β on the same chain. The angular brackets indicate taking an ensemble average. Equation 31 suggests that if the hydrodynamic interaction is included, then in order to express D_{si} in the form $kT/N_i\xi_i$, one needs to introduce a chain length (N_i) dependent friction coefficient ξ_i given by

$$\xi_i^{-1} = \xi_R^{-1}\left(1 + \frac{\xi_R}{6\pi\eta_o N_i}\sum_{\alpha,\beta}\left\langle\frac{1}{R_{\alpha\beta}}\right\rangle\right) \tag{32}$$

It is noted that in addition to the specific N_i factor, $\langle 1/R_{ij}\rangle$ also depends on N_i. Explicit calculations of this quantity[14] show that $\xi_i \sim N_i^{\gamma-1}$. For good solvents, $\gamma = 0.6$, hence suggesting that ξ_i decreases with increasing molecular weight, which is consistent with the present result.

One assumption in the theory of dynamic scattering from the ternary solution consisting of two homopolymers and a solvent is that the second virial coefficient $A_{2,ii}$ ($i = 1$ or 2) for the i polymer in the ternary solution remains the same as that in the binary solution, consisting of the solvent and the i polymer alone. Using this assumption, one can then determine X and Y from eqs 29 and 30, employing the static light scattering (or intensity) data of binary solutions consisting of only polymer 1 or 2. With the availability of X and Y, one can then calculate D_{11} and D_{22} from the experimental values of D_C and D_I using eqs 17 and 18. From the determined D_{11} and D_{22}, one can further calculate the amplitude ratio by using eq 19. Comparison of the calculated ratio with the experimental one would provide a consistency test of the experimental result and theory, provided that the amplitude ratio is accurately measured.

Results and Discussion

The PS samples used in ref 13 were characterized by the static light scattering technique and obtained M_w for PS-1 and for PS-2 to be equal to $6.3(\pm 0.6) \times 10^5$ and $0.88(\pm 0.03) \times 10^5$, respectively. The molecular weight data obtained are consistent with the specification provided by the manufacturer. Both samples are also nearly monodisperse (M_w/M_n equals 1.05 for PS-1 and equals 1.01 for PS-2). From the binary solution light scattering measurements, the second virial coefficients

Table 1. Concentrations (in g/mL)[20] and QELS Data of PS-1/PS-2/Toluene Ternary Solutions

solution no.	10^3C(PS-1), g/mL	10^3C(PS-2) g/mL	10^8D_I, cm^2/s	10^7D_C, cm^2/s	$A_I/(A_I + A_C)$ at 90° (exptl)	X (q = 0)	Y (q = 0)
1	4.92	35.47	2.3 ± 0.19	8.7 ± 0.6	0.05	0.73	0.81
2	2.84	19.32	3.7 ± 0.5	6.4 ± 0.8	0.10	0.61	0.69
3	1.92	13.04	4.6 ± 0.3	6.7 ± 0.4	0.10	0.53	0.59
4	1.42	9.65	8.6 ± 0.7	5.8 ± 0.5	0.15	0.46	0.51
5	0.481	3.251	12.7 ± 1.0	5.1 ± 0.4	0.30	0.23	0.25
6	0.277	2.151	17.9 ± 0.1	5.2 ± 0.4	0.30	0.17	0.16

Table 2. Calculated Diffusivity Matrix Elements, Amplitude Ratios, and Self-Diffusion Coefficients at Different Polymer Concentrations[a]

		solution no.					
		1	2	3	4	5	6
10^7D_{11}, cm^2/s (q = 0)	I	0.59	0.67	0.69	1.18	1.37	1.86
	II	8.3	6.10	6.47	5.48	5.00	5.13
10^7D_{12}, cm^2/s (q = 0)	I	0.48	0.46	0.41	0.60	0.34	0.30
	II	6.79	4.20	3.80	2.77	1.24	0.81
10^7D_{21}, cm^2/s (q = 0)	I	6.06	3.74	3.41	2.50	1.14	0.85
	II	0.43	0.41	0.36	0.54	0.31	0.31
10^7D_{22}, cm^2/s (q = 0)	I	8.34	6.10	6.47	5.48	5.00	5.13
	II	0.59	0.67	0.69	1.18	1.37	1.86
$A_I/(A_I + A_C)$ (θ = 90°)		0.12	0.16	0.19	0.18	0.28	0.27
10^7D_{s1}, cm^2/s		0.15	0.24	0.32	0.63	1.06	1.59
10^7D_{s2}, cm^2/s		1.83	2.08	2.80	2.78	3.77	4.22
$\eta = \xi_2/\xi_1$		0.50	0.74	0.71	1.43	1.77	2.38

[a] The concentration in the solution number column is the same as that given in Table 1.

are found to be equal to 4.9 × 10^{-4} and 5.7 × 10^{-4} mL·mol·g^{-2} for PS-1 and PS-2, respectively. Thus, the excluded volume parameter ratio of PS-2/PS-1 differs by a factor of $v_{22}/v_{11} = 1.16$. To maintain approximately equal contribution to the total scattering intensity, the authors of ref 13 prepared concentrations of the ternary solution with the relative composition of PS present in the sample having approximately C(PS-1)/C(PS-2) = M_w(PS-2)/M_w(PS-1).

The experimentally determined values of D_C, D_I, and $A_I/(A_I + A_C)$ are listed in Table 1. Using second virial coefficients and other needed data, we have calculated X and Y according to eqs 29 and 30. The X and Y values calculated for different concentrations are also listed in Table 1. For each data set of D_C, D_I, X, and Y, we have then calculated D_{11} and D_{22} for each concentration using eqs 17 and 18. These results also provide the values of D_{12} and D_{21}. Since eqs 17 and 18 are quadratic equations, we obtain two solutions. Using the values obtained for D_{11}, D_{22}, X, and Y and with the help of eq 19, we then calculate the amplitude ratio $A_I/(A_I + A_C)$. The two solutions for D_{11}, D_{22}, D_{12}, and D_{21} are given in Table 2 and judicious choice is needed to select the physical solution.

In both sets of the solution (sets I and II), the off-diagonal diffusivity elements D_{12} and D_{21} decrease as the total polymer concentration decreases. This is reasonable since in the limit of infinite dilution, D_{12} and D_{21} should vanish. For set I (except for a reversal in the two lowest concentrated solutions, solutions 5 and 6), D_{11} increases with decreasing total polymer concentration, whereas D_{22} decreases with decreasing total polymer concentration. This result is reversed in set II. Because, in the limit of infinite dilution, D_{11} and D_{22} should respectively become the self-diffusion coefficients of PS-1 and PS-2, results obtained in solution set I are chosen to be the physical solution, due to the fact that PS-1 has a greater molecular weight.

Corrotto et al.[13] also reported the amplitude $A_I/(A_C + A_I)$ of the interdiffusion mode (referred to in ref 13 as the slow mode) relative to the total intensity obtained at 90° scattering angle for each solution given in Table 1. Quantitative comparison of the amplitude ratio $A_I/(A_C + A_I)$ requires the amplitude of the cooperative and interdiffusion modes to be accurately known. The amplitude ratio calculated using set I for each concentration is listed in Table 2. It increases with decreasing polymer concentration, although their $A_I/(A_C + A_I)$ data have a large experimental uncertainty,[21] they are consistent with the trend of the variation of $A_I/(A_C + A_I)$ with the polymer concentration reported in ref 13.

As mentioned above, Corrotto et al.[13] have compared the D_C/D_I ratio using the theoretical expressions for D_C and D_I derived by Benmouna et al.[11] The equation (eq 13 of ref 13) that is used to interpret the concentration dependence of D_C/D_I is determined only by the excluded volume parameter, structural data, and concentrations of the polystyrene; the monomer frictional coefficient does not enter in the equation. This is due to the fact that the expressions for D_C and D_I given by Benmouna et al. were derived by assuming that both polymers have the same monomer friction coefficient and the same excluded volume parameter. Equation 13 of ref 13 is thus an idealization, and, as to be shown shortly, it is not applicable even in the bimodal polystyrene solution.

One can remove the assumptions by allowing PS-1 and PS-2 to have different monomer friction coefficients and different excluded volume parameters. From eqs 7 and 8, we can write D_C/D_I as

$$\frac{D_C}{D_I} = \frac{(1 + D_{11}/D_{22}) + \{(1 - D_{11}/D_{22})^2 + 4XYD_{11}/D_{22}\}^{1/2}}{(1 + D_{11}/D_{22}) - \{(1 - D_{11}/D_{22})^2 + 4XYD_{11}/D_{22}\}^{1/2}} \tag{33}$$

where D_{11}, D_{22}, X, and Y are given by eqs 27–30. We define $\eta = \xi_2/\xi_1$, and $\nu = 2M_2(A_{2,22}C_2 + A_{2,11}C_1)$; after substituting eqs 27–30 into eq 33 and working out some algebra, we obtain (for the case with $P_1(q) = P_2(q) = 1$)

$$\frac{D_C}{D_I} = [(1 + \nu + \eta/z) + \{(1 - \eta/z + \nu)^2 - 4\eta a(1 - 1/z) + 4\eta b(A_{2,11} - A_{2,22})^2\}^{1/2}]/[(1 + \nu + \eta/z) - \{(1 - \eta/z + \nu)^2 - 4\eta a(1 - 1/z) + 4\eta b(A_{2,11} - A_{2,22})^2\}^{1/2}] \tag{34}$$

where $z = M_1/M_2$, $a = 2A_{2,11}M_2C_1$, and $b = M_2{}^2C_1C_2$.

One notes in eq 34 the presence of an extra term proportional to the square of the difference in the excluded volume parameters (or second virial coefficients) of two polymer chains. This term is absent in Benmouna's calculation and is important because it is proportional to η. It is easy to see that for the special case with $\eta = 1$ (i.e., $\xi_1 = \xi_2$) and $A_{2,11} = A_{2,22}$, eq 32 reduces to eq 13 of ref 13. The friction coefficient ratio η has an important effect on the value of D_C/D_I. In Figure 1, we show D_C/D_I as a function of total polymer

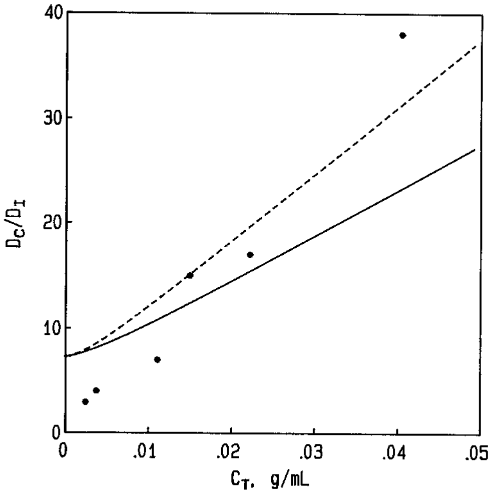

Figure 1. Comparison of measured (dots) D_C/D_I of the PS-1/PS-2/toluene system and calculated values (the solid line) using eq 32 with $\eta = 1$. This comparison shows the lack of agreement. The dashed line represents the calculated values based on the modification of the Benmouna equation as given by Corroto et al.[13]

concentration calculated using eq 32 by assuming $\eta = 1$. The result is compared with the experimental D_C/D_I ratio of ref 13. The calculated value is smaller for solution nos. 1 and 2 (high concentration) and is larger for solution nos. 5 and 6 (low concentration). Clearly, there is no agreement between the theoretical calculated and experimental D_C/D_I ratios, in contrast to the conclusion reached by Corroto et al.[13] It should be pointed out, however, that in ref 13, Corroto et al. have modified the Benmouna equation by introducing $M_{-1} = 2/(M_1^{-1} + M_2^{-1})$ and substituting it for M_2 in the expression of ν, again assuming $\eta = 1$. The calculated result based on this modification is also shown in Figure 1. Althogh the deviation based on this modification is less at higher concentrations, the disagreement for solutions at lower concentrations is still large. However, the substitution of M_{-1} for M_2 is not consistent with the hypothesis of Benmouna's theory.

We have recalculated the D_C/D_I ratio using eq 34 by allowing the friction coefficient ratio to deviate from 1. The η values that bring the calculated D_C/D_I ratio to agree with the experimental one for each solution are given in Table 2. The result shows that $\xi_2 > \xi_1$ in the dilute concentration regime, whereas the reverse is true in the semidilute regime. One can compare the result in the dilute concentration with the dilute solution results for PS-1 and PS-2. As given in Table 2 of ref 13, D_0 are (1.60 ± 0.05) × 10^7 and (5.3 ± 0.05) × 10^7 cm^2/s, for PS-1 and PS-2, respectively. Here D_0 is the translational diffusion coefficient at infinite dilution, and for PS-1 it is equal to $kT/N_1\xi_1^0$ and for PS-2, $kT/N_2\xi_2^0$, where ξ_1^0 and ξ_2^0 are the friction coefficients at infinite dilution of PS-1 and PS-2, respectively; N_1 and N_2 are the chain length (or the degree of polymerization) of PS-1 and PS-2, respectively. These results give an η value of 2.16 ± 0.10 at infinite dilution, which is in good agreement with the η value given in Table 2 extrapolated to the zero polymer concentration ($\eta = 2.49 \pm 0.29$). The larger ξ value for a shorter chain in the dilute concentration regime is consistent with the solvent hydrodynamic draining effect.[15] As the polymer concentration increases, one would expect the hydrodynamic interaction to be screened and we expect to obtain $\eta = 1$, in contrast to the $\eta < 1$ that is obtained here. This is due to the fact that PS-1 has a high molecular weight and additional friction owing to chain entanglement is present in the semidilute regime. In fact, according to the tube model due to entanglement coupling, at large chain lengths, ξ is proportional to the chain length.[19] Consequently, we expect $\xi_1 > \xi_2$ in the regime where chain entanglement becomes important. This result is indeed born out in the present analysis.

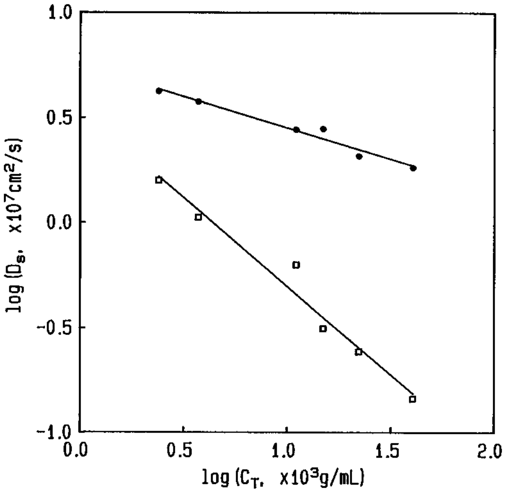

Figure 2. Self diffusion of PS-1 (□) and that of PS-2 (●), as a function of total polymer concentration deduced from the diffusivity matrix.

Allowing the chain length dependence for the monomer friction coefficient, we designate the quantity $kT/N_i\xi_i$ to be the self-diffusion coefficient D_{si}, for PS chains. Using eqs 27 and 28, we can then calculate the self-diffusion coefficients for PS-1 and PS-2 from the values of diffusivity matrix elements D_{11} and D_{22}. The calculated D_{s1} and D_{s2} at different polymer concentrations are shown in Figure 2 and also listed in Table 2.

The concentration and molecular weight dependence of the self-diffusion coefficient of polymer in solutions has been studied extensively by various techniques. In semidilute and concentrated regimes with very high molecular weight polymers, the reptation model predicts $D_s \sim C^{-1.75}$, whereas, in the semidilute regime involving relatively low molecular weight polymers, simple arguments involving blob diffusion predict the self-diffusion coefficient D_s to depend on the polymer concentration according to $D_s \sim C^{\alpha}$, where $\alpha = (\gamma - 1)/(3\gamma - 1)$, with $\gamma = 0.5$ for Θ solvent, $\gamma = 0.6-0.8$ for good solvent, and α is negtive.[19] In either case, D_s decreases with the increase of polymer concentration.

The values of D_{s1} and D_{s2} deduced from the present theory are found to decrease with the increase of total polymer concentration. This result is consistent with the above model and is similar to the results dealing with ternary systems of PS/PMMA/benzene[5] and PS/PMMA/dioxane.[8] If the concentration dependence of D_{s1} and D_{s2} is forced to a power law fit with respect to the total polymer concentration (Figure 2), we obtain exponents of −0.84 for PS-1 and −0.30 for PS-2, respectively, which gives $\gamma = 0.52$ for PS-1 and $\gamma = 0.68$ for PS-2, indicating that γ is strongly affected by the chain length. However, the −1.75 exponent corresponding to the asymptotic limit of entangled chains is yet to be reached here.

Acknowledgment. This work is supported by a grant from NSF Polymer Division (DMR9112993). We thank Professor J. J. Freire for providing the original data published in ref 13.

References and Notes

(1) Lodge, T. P. *Macromolecules* **1983**, *16*, 1393; **1986**, *19*, 2986.
(2) Borsali, R.; Duval, M.; Benoit, H.; Benmouna, M. *Macromolecules* **1987**, *20*, 1112.
(3) Borsali, R.; Duval, M.; Benmouna, M. *Macromolecules* **1989**, *22*, 816.
(4) Giebel, L.; Borsali, R.; Fisher, E. W.; Benmouna, M. *Macromolecules* **1992**, *25*, 4379.
(5) Sun, Z.; Wang, C. H. *Macromolecules* **1996**, *29*, 2011.
(6) Sun, Z.; Wang, C. H. *J. Chem. Phys.* **1995**, *103*, 3762.
(7) Desbrieres, J.; Borsali, R.; Rinaudo, M.; Milas, M. *Macromolecules* **1993**, *26*, 2592.
(8) Sun, Z.; Wang, C. H. *J. Chem. Phys.* **1997**, *106*, 3775.
(9) Akcasu, A. Z.; Nagele, G.; Klein, R. *Macromolecules* **1991**, *24*, 4408.
(10) Akcasu, Z.; Benmouna, M.; Hammouda, B. *J. Chem. Phys.* **1984**, *80*, 2762.
(11) Benmouna, M.; Benoit, H.; Duval, H.; Akcasu, Z. *Macromolecules* **1987**, *20*, 1107.
(12) Akcasu, Z. In *Dynamic Light Scattering*; Brown, W., Ed.; Oxford University Press: Oxford, U.K., 1993; p 1.
(13) Corrotto, J.; Ortega, F.; Vazquez, M.; Freire, J. J. *Macromolecules* **1996**, *29*, 5948.
(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Science Publishers: Oxford, U.K., 1986.
(15) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(16) Farnoux, B. *Ann. Phys. (Paris)* **1978**, *39*, 77.
(17) Benoit, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
(18) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(19) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(20) In table 3 of ref 13, the composition columns labeled for PS-1 and PS-2 appear to be reversed. PS-1, which has a higher M_w than PS-2, should have a smaller concentration in order to maintain the relation $C(\text{PS-1})M(\text{PS-1}) \cong C(\text{PS-2})M(\text{PS-2})$, as the authors of ref 12 intended to maintain.
(21) Private communication with Prof. J. J. Freire.

MA970290C