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Light Scattering from Dilute Polystyrene in Mixtures of Semidilute Poly(dimethylsiloxane) and Tetrahydrofuran

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ABSTRACT: Ternary solutions of tetrahydrofuran (THF), polystyrene (PS), and poly(dimethylsiloxane) (PDMS) were studied using total low-angle light scattering and dynamic light scattering. The PS concentration, c_2, was varied but was always kept very dilute. The PDMS concentration was held constant at the semidilute concentration of 15 vol %, corresponding to $3c_3^*$, where c_3^* is the entanglement concentration. The range of PS molecular weights investigated was such that $R_{H,2}/\xi_3$, where $R_{H,2}$ is the hydrodynamic radius of PS in pure THF and ξ_3 is the dynamic correlation length of the semidilute PDMS matrix, fell in the "crossover" regime between 0.7 and 3.0. The tracer diffusion coefficient of PS at infinite dilution, $D_{22}(0)$, was determined from the "measured" mutual diffusion coefficient, $\lambda_2(c_2)$, according to $\lambda_2(c_2) = D_{22}(0)(1 + k_Dc_2)$. $D_{22}(0)$ in the examined system scales with molecular weight according to $D_{22}(0) \sim M_{w,2}^{-0.91}$. Similar to a binary mixture, we show that k_D defined above may be represented by two terms, one arising from thermodynamic interactions and the other from hydrodynamic interactions. The dependence of k_D on molecular weight is found to be $k_D \sim -M_{w,2}^{0.57}$ and is dominated here by the thermodynamic term.

I. Introduction

Dynamic light scattering (DLS) measurements on "optically labeled" ternary solutions have been reported,[1-15] in which dilute amounts of polymer chains act as a single "probe" (denoted by the subscript 2) diffusing in an isorefractive solution containing a more concentrated "host" polymer (denoted by the subscript 3) and a solvent. In such systems, under the restriction of $qR_{g,2} < 1$, where q is the scattering wave vector and $R_{g,2}$ is the radius of gyration of the probe, the measured correlation functions have generally been interpreted as reflecting the translational diffusion of the probe chains.[2-15] Data must be analyzed with caution in these systems, as it has both theoretically[16,17] and experimentally[14,15,18] been shown that when $qR_{g,2} < 1$ and $qR_{g,3} < 1$, the DLS spectrum consists of two exponential terms. The diffusion coefficient of the probe determined by DLS for an optically labeled ternary solution will be referred to as a "measured" mutual diffusion coefficient, $\lambda_2(c_2)$. $\lambda_2(c_2)$, which is necessarily determined at a finite probe concentration, c_2, must be extrapolated to $c_2 = 0$ to determine the tracer diffusion coefficient, $D_{22}(0)$. Assuming an analogy with binary dilute polymer solutions,[19] $\lambda_2(c_2)$ has been represented by[6,20]

$$\lambda_2(c_2) = D_{22}(0)(1 + k_Dc_2) \tag{1}$$

where k_D is the concentration coefficient of diffusion. It has often been assumed that for a low c_2 the product k_Dc_2 is small,[1-9] so that any difference between $D_{22}(0)$ and $\lambda_2(c_2)$ at small c_2 is negligible. Although this assumption has recently been experimentally verified for solutions containing a polystyrene (PS) probe and a poly(vinyl methyl ether) (PVME) host, where $k_Dc_2 \leq 0.02$ for $c_2 = 5 \times 10^{-4}$ g·cm^{-3} and $c_3 \leq 0.08$ wt %,[20] the most appropriate manner to obtain $D_{22}(0)$ is by an extrapolation procedure of $\lambda_2(c_2)$ to the limit of $c_2 = 0$.[11,16]

Optically labeled ternary solutions have also been studied using elastic light scattering (ELS). It has been found that the "apparent" second virial coefficient, $A_{2,\mathrm{app}}$, of the probe in the mixture of isorefractive host polymer and solvent always decreases with increasing c_2.[2,21-25] Also, at the point where $A_{2,\mathrm{app}} = 0$, $R_{g,2}$ is much greater than in a Θ-homosolvent. An integration of total intensity results (ELS) into the analysis of diffusion from DLS data has seldom been performed in these ternary systems.[10,23]

In this paper we will examine how excluded volumes and small degrees of nonexact refractive index matching in optically labeled ternary mixtures affect the ELS results. The developed expressions will be applied to the results of elastic low-angle light scattering (LALS) measurements on dilute PS in solution with mixtures of semidilute poly(dimethylsiloxane) (PDMS) and THF. We will also present expressions that separate the effects of thermodynamics and hydrodynamics on probe diffusion; and from the combination of DLS and LALS results, the relative importance of thermodynamics and friction on the magnitude of k_D will be determined. Finally, the molecular weight dependence of $D_{22}(0)$ and of k_D will be obtained and discussed.

II. Low-Angle Elastic Light Scattering

The Rayleigh factor at $\Theta = 0$, $\Delta R_3'$, of a concentrated ternary solution consisting of two polymers and a solvent over that of the pure solvent (component 1) has recently been given as[26]

$$\frac{\Delta R_0'}{N_AK} = \frac{a_2^2x_2 + a_3^2x_3 + (a_2^2\upsilon_{33} + a_3^2\upsilon_{22} - 2a_2a_3\upsilon_{23})x_2x_3}{1 + \upsilon_{22}x_2 + \upsilon_{33}x_3 + (\upsilon_{22}\upsilon_{33} - \upsilon_{23}^2)x_2x_3} \tag{2}$$

where υ_{22}, υ_{33}, and υ_{23} represent concentration-dependent excluded-volume parameters. In eq 2, a_i is a contrast factor of polymer i with the solvent and is equal to ν_im_i/N_A, where N_A is Avogadro's number, m_i is the molecular weight of a monomer of polymer i, and the volume of a monomer is defined as equal to the volume of a solvent molecule. ν_i is the refractive index increment of species i with the solvent at its concentration c_i' in the solution:

$$\nu_i = \lim_{c_i \to c_i'} (\partial n/\partial c_i)_{T,P,c_j} \tag{3}$$

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where n is the refractive index of the solution, T is absolute temperature, P is pressure, and λ_o is the wavelength of incident light in vacuo. x_i is equal to $\sum_n N_{i,n} P_{i,n}^2$, where $N_{i,n}$ is the number of molecules of i having chain length $P_{i,n}$ and the sum is over the different chain lengths of polymer i. The summation takes into account the polydispersity of the polymer. K is a constant equal to $4\pi^2 n^2 \lambda_o^{-4} N_A^{-1}$ at zero scattering angle.

To determine υ_{22}, υ_{33}, and υ_{23} from LALS experiments on mixtures of PS, PDMS, and THF, a reciprocal form of eq 2 is employed, which is similar to Zimm's expression used to analyze ELS data from binary mixtures,[27] except that the "solvent" is now a mixture of components 1 and 3 at $c_3 = c_3^\circ$. The Rayleigh factor, ΔR_0, of the ternary mixture minus that of the binary mixture of solvent and host polymer at c_3° is determined by subtracting the Rayleigh factor due to polymer 3 from eq 2; the result is[28]

$$\frac{N_A K a_2^2 x_2}{\Delta R_0} = \frac{1}{\Omega^2}\left(1 + \upsilon_{22} x_2 - \frac{\upsilon_{23}^2 x_2 x_3}{1 + \upsilon_{33} x_3}\right) \tag{4}$$

where

$$\Omega = 1 - \left(\frac{\upsilon_{23} x_3}{1 + \upsilon_{33} x_3}\right)\left(\frac{a_3}{a_2}\right) \tag{5}$$

Using the definitions of a_i and x_i, eq 4 and 5 become

$$\frac{K\nu_2^2 c_2}{\Delta R_0} = \frac{1}{\Omega^2 M_{w,2}}\left(1 + \frac{N_A}{m_2^2} c_2 M_{w,2} \upsilon_{22} - \frac{(N_A/m_2 m_3)^2 c_2 c_3^\circ M_{w,2} M_{w,3} \upsilon_{23}^2}{1 + (N_A/m_3^2) c_3^\circ M_{w,3} \upsilon_{33}}\right) \tag{6}$$

where

$$\Omega = 1 - \left(\frac{(N_A/m_3^2) M_{w,3} c_3^\circ \upsilon_{23}}{1 + (N_A/m_3^2) M_{w,3} c_3^\circ \upsilon_{33}}\right)\left(\frac{\nu_3 m_3}{\nu_2 m_2}\right) \tag{7}$$

and $M_{w,i}$ is the weight average molecular weight of species i. Equation 6 can be put into the following form

$$\frac{K\nu_2^2 c_2}{\Delta R_0} = \frac{1}{\Omega^2}\left(\frac{1}{M_{w,2}} + 2A_{2,\mathrm{app}} c_2\right) \tag{8}$$

where $A_{2,\mathrm{app}}$, an apparent second virial coefficient, is defined as:

$$2A_{2,\mathrm{app}} = (N_A/m_2^2)\upsilon_{22} - \frac{(N_A/m_2 m_3)^2 c_3^\circ M_{w,3} \upsilon_{23}^2}{1 + (N_A/m_3^2) c_3^\circ M_{w,3} \upsilon_{33}} \tag{9}$$

According to eq 8, data analysis for a ternary mixture can proceed in an analogous fashion as for a binary mixture. When $K\nu_2^2 c_2/\Delta R_0$ is plotted against c_2 holding c_3 constant, the slope is equal to $2A_{2,\mathrm{app}}/\Omega^2$ and the y-intercept is equal to $1/\Omega^2 M_{w,2}$. In the special case where polymer 3 is perfectly isorefractive with the solvent, ν_3 is zero, Ω becomes unity, and eq 8 simplifies to

$$\frac{K\nu_2^2 c_2}{\Delta R_0} = \frac{1}{M_{w,2}} + 2A_{2,\mathrm{app}} c_2 \tag{10}$$

In the limit of dilute ternary solutions (dilute in both components 2 and 3), the following identifications can be made[29]

$$\upsilon_{ii} = (V_1/N_A)(g_{c,ii}/k_B T - 1/P_i \phi_i) \tag{11}$$

$$\upsilon_{23} = (V_1/N_A)(g_{c,23}/k_B T) \tag{12}$$

where

$$g_{c,ij} = \left(\frac{\partial^2 G_c}{\partial \phi_i \partial \phi_j}\right)_{T,\phi_k} \tag{13}$$

For a polydisperse polymer, $P_i \phi_i$ in eq 11 is replaced by $\sum_n P_{i,n} \phi_{i,n}$, where the sum is over the different chain lengths of polymer i. G_c is the free energy per "lattice site", given by

$$G_c = \frac{\Delta G^M}{V N_A / V_1} \tag{14}$$

where ΔG^M is the free energy of mixing and V_1 is the molar volume of the solvent. It can be shown[28] using eq 11–13 that eq 6 and 7 reduce properly to the classical results[30] of the excess scattered intensity from a dilute ternary solution over that of the binary solution consisting of components 1 and 3, which is given by

$$\frac{K k_B T \nu_2^2 V_1}{\Delta R_0 \bar{\upsilon}_2^2} = \frac{g_{c,22} - g_{c,23}^2/g_{c,33}}{[1 - (g_{c,23}/g_{c,33})(\bar{\upsilon}_2/\bar{\upsilon}_3)(\nu_3/\nu_2)]^2} \tag{15}$$

where k_B is Boltzmann's constant and $\bar{\upsilon}_i$ is the specific volume of component i. Equations 6 and 7 thus provide the correct limiting behavior at infinite dilution and represent an extension of eq 15 to solutions concentrated in component 3 where the υ_{ij}'s are undetermined quantities.

We can examine the physical significance of the parameter Ω in eq 6 by starting from the following result obtained by Casassa and Eisenberg[31]

$$\lim_{c_2 \to 0} \frac{K c_2 (\partial n/\partial c_2)_{T,P,\mu_3}^2}{\Delta R_0} = \frac{1}{M_{w,2}} \tag{16}$$

One obtains by combining eq 6 and 16

$$\Omega = \lim_{c_2 \to 0} \frac{\left(\frac{\partial n}{\partial c_2}\right)_{T,P,\mu_3}}{\left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3}} = \lim_{c_2 \to 0} \left\{1 + \left(\frac{\partial c_3}{\partial c_2}\right)_{T,P,\mu_3} \frac{\left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2}}{\left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3}}\right\} \tag{17}$$

The quantity $(\partial c_3/\partial c_2)_{T,P,\mu_3}$ may be written in terms of a preferential adsorption parameter, λ_p,[32] such that

$$\Omega = 1 - (\lambda_p/\bar{\upsilon}_3)(\nu_3/\nu_{2_o}) \tag{18}$$

where ν_{2_o} denotes the refractive index increment of species 2 at infinite dilution. λ_p is interpreted as a measure of the preferential adsorption of solvent molecules compared to monomers of polymer 3 on polymer 2 and has units of volume/mass. It can be expressed in terms of the excluded-volume parameters by combining eq 7 and 18:

$$\lambda_p = \lim_{c_2 \to 0} \frac{\bar{\upsilon}_3 m_3}{m_2}\left(\frac{(N_A/m_3^2) M_{w,3} c_3^\circ \upsilon_{23}}{1 + (N_A/m_3^2) M_{w,3} c_3^\circ \upsilon_{33}}\right) \tag{19}$$

Thus, the parameter Ω arises from a combination of two sources: thermodynamic interactions and nonexact refractive index matching. When υ_{23} is zero, there will be no preferential adsorption of solvent according to eq 19, and in this limit Ω will become one. On the other hand, when components 1 and 3 have exactly the same refractive index, ν_3/ν_{2_o} is 0 in eq 18 and Ω also becomes 1. In this limit of exact refractive index matching, the y-intercept of a plot of $K c_2 \nu_{2_o}^2/\Delta R_0$ vs c_2 gives the correct molecular weight and λ_p cannot be calculated.

III. Dynamic Light Scattering

The electric field correlation function, $g^{(1)}(q,\tau)$, for a ternary solution containing a dilute probe polymer and a refractive index matched solvent is given by[16]

$$g^{(1)}(q,\tau) = a_2 e^{-\Gamma_2 \tau} + a_3 e^{-\Gamma_3 \tau} \tag{20}$$

where the decay rates, Γ_2 and Γ_3, are

$$\Gamma_2/q^2 = \lambda_2(c_2) = \frac{1}{2}\{D_{22} + D_{33} + [(D_{22} - D_{33})^2 + 4D_{23}D_{32}]^{1/2}\} \tag{21}$$

$$\Gamma_3/q^2 = \lambda_3(c_3) = \frac{1}{2}\{D_{22} + D_{33} - [(D_{22} - D_{33})^2 + 4D_{23}D_{32}]^{1/2}\} \tag{22}$$

The main mutual diffusion coefficients (D_{22} and D_{33}) and the cross mutual diffusion coefficients (D_{23} and D_{32}) of probe and host macromolecules may be expressed as (see Appendix A)

$$D_{22} = \frac{\phi_2(1 - \phi_2)P_2}{f_2(c_2,c_3)} g_{c,22} \tag{23}$$

$$D_{23} = \frac{\phi_2(1 - \phi_2)P_2}{f_2(c_2,c_3)} g_{c,23} \tag{24}$$

$$D_{32} = \frac{\phi_3(1 - \phi_3)P_3}{f_3(c_2,c_3)} g_{c,23} \tag{25}$$

$$D_{33} = \frac{\phi_3(1 - \phi_3)P_3}{f_3(c_2,c_3)} g_{c,33} \tag{26}$$

where $f_i(c_2,c_3)$ is the friction factor of macromolecule i in the ternary mixture. If we restrict ourselves to solutions in which the host is semidilute and whose cooperative motions occur faster than the translational motion of the probe, D_{33} will be much greater than D_{22}. Under the condition of $D_{33} \gg D_{22}$, expanding the square roots in eq 21 and 22 and keeping only the first-order terms in $D_{23}D_{32}/D_{33}$, one obtains:

$$\lambda_2(c_2) = D_{22} - \frac{D_{23}D_{32}}{D_{33}} \tag{27}$$

$$\lambda_3(c_3) = D_{33} + \frac{D_{23}D_{32}}{D_{33}} \tag{28}$$

When the probe is present at a much lower concentration than the host, $a_2 \gg a_3$[18] and the term containing Γ_3 in eq 20 will have a negligible contribution to $g^{(1)}(q,\tau)$. Examining now only $\lambda_2(c_2)$, it is found that, by substituting eq 23–26 into eq 27, one obtains:

$$\lambda_2(c_2) = \frac{\phi_2(1 - \phi_2)P_2}{f_2(c_2,c_3)}\left(g_{c,22} - \frac{{g_{c,23}}^2}{g_{c,33}}\right) \tag{29}$$

In comparing eq 29 with the expression for LALS intensity (eq 15), it is seen that the thermodynamic contributions to $\lambda_2(c_2)$ and to $(\Delta R_0)^{-1}$ are identical for perfect refractive index matching of the solvent and host polymer.

To analyze the experimental results, we need the explicit dependence of $\lambda_2(c_2)$ on c_2. To this end, the friction factor of the probe chains, $f_2(c_2,c_3)$, will be expanded in a series for small c_2 at a constant value of c_3

$$f_2(c_2,c_3^{\circ}) = f_2(0,c_3^{\circ})(1 + k_{f,2}c_2 + ...) \tag{30}$$

where $f_2(0,c_3^{\circ})$ is the friction factor of 2 at infinite dilution in a 1–3 mixture at a fixed concentration, c_3°, of 3 and $k_{f,2}$ represents the magnitude of the linear dependence of f_2 on c_2 in the 1–3 mixture at c_3°. The $g_{c,ij}$'s in eq 29 can be related to solution composition and to the excluded-volume parameters through eq 11 and 12. When c_2 is small, second and higher order terms in c_2 can be ignored, and one then obtains from eq 29 after using eq 11, 12, and 30 and the definition of $A_{2,\mathrm{app}}$ given in eq 9

$$\lambda_2(c_2) = \frac{k_B T}{f_2(0,c_3^{\circ})}(1 - k_{f,2}c_2 - \bar{v}_2 c_2 + 2A_{2,\mathrm{app}}M_{w,2}c_2) \tag{31}$$

The tracer diffusion coefficient of the probe at infinite dilution, $D_{22}(0)$, and the concentration coefficient of diffusion, k_D, may be obtained by fitting experimental data to eq 1. $D_{22}(0)$ and k_D can then be related to the parameters in eq 31 by the following expressions:

$$D_{22}(0) = k_B T/f_2(0,c_3^{\circ}) \tag{32}$$

$$k_D = -k_{f,2} - \bar{v}_2 + 2A_{2,\mathrm{app}}M_{w,2} \tag{33}$$

Assuming that $\bar{v}_2$ is small compared to the other terms in eq 33,[19] k_D may be approximated as:

$$k_D \approx -k_{f,2} + 2A_{2,\mathrm{app}}M_{w,2} \tag{34}$$

Since $A_{2,\mathrm{app}}$ can be extracted from LALS experiments, it is possible to examine the separate contributions of thermodynamic and frictional effects on the concentration dependence of $\lambda_2(c_2)$. First consider the thermodynamic part of k_D, represented by $2A_{2,\mathrm{app}}M_{w,2}$ where $A_{2,\mathrm{app}}$ is given by eq 9. When polymer–solvent interactions are more favorable than the interactions of a polymer with itself, the polymer coil will be expanded and the excluded volume, represented by v_{22} and v_{33}, will increase. This will result in increases in $A_{2,\mathrm{app}}$ and in k_D. On the other hand, a greater magnitude of the excluded volume v_{23} due to an increase in size of the polymer coils will always result in a decrease in k_D, regardless of whether or not the two polymers, 2 and 3, are compatible. The part of k_D due to friction, $k_{f,2}$, is more difficult to predict. In a good solvent with no host polymer, $k_{f,2}$ is positive due to probe–probe hydrodynamic interactions. In the type of ternary mixtures under consideration here, however, we will show that the host polymer screens out these interactions and reduces $k_{f,2}$.

IV. Experimental Section

Materials. Polydisperse, trimethylsiloxy-terminated PDMS from Petrarch Systems, Inc., was fractionated using the solvent/precipitant pair toluene/methanol. Only the coacervate of the first precipitation was kept. This simple fractionation decreased the polydispersity, M_w/M_n, from 2.3 to 1.7 and increased M_w from 108K to 148K. M_w and M_n represent weight and number average molecular weight, and K denotes a multiplication by 10^3. The molecular weight distributions obtained using HPLC indicated that the polydispersity had decreased by the removal of shorter chains within the distribution. Narrow-distribution PS samples from Polysciences, Inc., and from the Pressure Chemical Co. were used as received. The properties of the linear polymers are listed in Table I. THF (Aldrich Chemical Co., 99.9+%, HPLC grade, inhibitor-free) was used as received.

Ternary solutions of PS, PDMS, and THF for use in DLS experiments were prepared by weight. Concentrations were calculated assuming additivity of volumes. The densities at 25 °C were taken to be $\rho_{\mathrm{PDMS}} = 0.9697$ g·cm^{-3},[33] $\rho_{\mathrm{PS}} = 1.0711$ g·cm^{-3},[34] and $\rho_{\mathrm{THF}} = 0.884$ g·cm^{-3}.[35] The mixtures were filtered through 0.45-μm-pore-size filters into dust-free Pyrex 13-

Table I
Properties of Linear PS and Trimethylsiloxy-Terminated PDMS

polymer	designation	M_w	M_w/M_n	source
PS, lot no. 63122	PS3.76K	3.76K[a]	1.08[a]	Polysciences, Inc.
PS, lot no. 16231	PS7.62K	7.62K[a]	1.10[a]	Polysciences, Inc.
PS, lot no. 30420	PS14.1K	14.1K[a]	1.03[a]	Pressure Chem. Co.
PS, lot no. 30811	PS25.5K	25.5K[a]	1.03[a]	Pressure Chem. Co.
PS, lot no. 80317	PS32.1K	32.1K[a]	1.02[a]	Pressure Chem. Co.
PS, lot no. 52790	PS46.7K	46.7K[a]	1.02[a]	Pressure Chem. Co.
PS, lot no. 70929	PS60.1K	60.1K[a]	1.02[a]	Polysciences, Inc.
PDMS, cat. no. PS047	PDMS108K	108K[b]	2.3[a]	Petrarch Systems, Inc.
PDMS, fractionated	PDMS148K	148K[b]	1.7[a]	fractionation of PS047

[a] Obtained by HPLC, PS calibration. [b] Obtained by LALS in toluene.

mm-i.d. centrifuge tubes. As a further precaution for cleanness, the ternary solutions were centrifuged for 90 min at 7000*g*, where *g* is gravitational acceleration. During DLS measurements, the centrifuge tubes were immersed in a refractive index matched glycerol bath contained in a Brice-Phoenix C-105 cylindrical light-scattering cell.

Experimental Apparatus. An LDC/Milton Roy KMX-6 LALS photometer was used to determine the molecular weights of PS and PDMS and to determine the second-virial coefficients of PS when in solution with THF and with mixtures of semidilute PDMS and THF. The temperature of the scattering cell, monitored at the sample, was held at 25 °C by circulating thermostated fluid through the cell. The refractive index increments necessary for the analysis of LALS data were determined by an LDC/Milton Roy KMX-16 differential refractometer. Both the KMX-6 and the KMX-16 used lasers operating at $\lambda_0 = 632.8$ nm as a light source.

The DLS setup used a Lexel Model 85-.7 argon ion laser tuned to $\lambda_0 = 488$ nm as a light source. The light-scattering cell was held by a brass jacket, whose temperature was kept at 25.0 ± 0.1 °C by circulating fluid from a refrigerated bath. Photon counting was performed by an EMI 9789B PMT mounted onto an arm of a rotary table. The PMT signal was put into proper form for the correlator by a Pacific Photometric Instruments Model 3470/AD6 amplifier discriminator. Two correlators were used. For the experiments on solutions of linear PS, linear PDMS, and THF, the normalized photon autocorrelation function, $C(q,\tau)/\beta$, was calculated by a Birnboim correlator. For the experiments investigating solutions of linear PDMS in toluene, a Brookhaven Instruments BI-2030AT correlator was used. Consistency between the results of the two correlators was checked.

Analysis of the Autocorrelation Function. In the homodyne mode of light detection, the following expression relates the photon autocorrelation function, $C(q,\tau)$, to the electric field correlation function, $g^{(1)}(q,\tau)$

$$C(q,\tau) = \beta(1 + \alpha[g^{(1)}(q,\tau)]^2) \tag{35}$$

where β is the base line and α is an empirical factor, which depends on the photon detection optics. For a dilute binary mixture containing a polydisperse polymer, $g^{(1)}(q,\tau)$ is represented by

$$g^{(1)}(q,\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma\tau}\,d\Gamma \tag{36}$$

where Γ is the decay rate and $G(\Gamma)$ is the normalized distribution of decay rates. In a binary polymer solution when $qR_g \ll 1$, no intramolecular motion is probed, and the mean decay rate, defined as

$$\langle\Gamma\rangle = \int_0^\infty G(\Gamma)\,\Gamma\,d\Gamma \tag{37}$$

is related to the *z*-average mutual diffusion coefficient of the polymer molecules by $D_2(c) = \langle\Gamma\rangle/q^2$.[36] An effective way to determine $\langle\Gamma\rangle$ from $g^{(1)}(q,\tau)$ for a polydisperse system is to use a cumulant expansion[37]

$$\ln\,[g^{(1)}(q,\tau)] = -\langle\Gamma\rangle\tau + \frac{\mu_2}{2!}\tau^2 - \frac{\mu_3}{3!}\tau^3 + \ldots \tag{38}$$

where

$$\mu_i = \int_0^\infty (\Gamma - \langle\Gamma\rangle)^i\,G(\Gamma)\,d\Gamma \tag{39}$$

A major requirement for successful application of the above cumulant analysis is that the series in eq 39 converge after only two or three terms. If additional terms are necessary, the reliability of the fitting parameters will be low unless the data is of very high quality.[36]

Although the optically labeled polymer solutions examined in our work were dilute in PS, they were semidilute in PDMS. As a consequence, the diffusive behavior of PS was atypical for a dilute polymer, and the decay rate of $g^{(1)}(q,\tau)$ was nonexponential even when the effect of the host diffusion mode Γ_3 was well separated from Γ_2 and did not contribute significantly to $g^{(1)}(q,\tau)$, which was the case for all the results to be reported here. Lodge et al.[38] have shown that a traditional cumulants analysis is inadequate for extracting $\langle\Gamma\rangle$ of optically labeled polymer solutions, even for probes with polydispersities as low as 1.05. Thus, a different method analyzing $C(q,\tau)$ was employed which utilized the fact that, as $\tau \to 0$, the higher order terms in eq 38 become progressively less important.[36,38] In the analysis procedure, $C(q,\tau)/\beta$ vs τ data were fit using a least-squares routine to the following polynomials in the range $\tau_{\text{init}} \le \tau \le \tau_{\max}$, where τ_{init} is the delay time at $\tau = 1\Delta\tau$, $\tau_{\max}$ is a variable representing the delay time of the last data point in the time correlation to be included in the fit of the data, and $\Delta\tau$ is the sample time interval selected on the correlator:

$$C(q,\tau)/\beta = 1 + A\exp\{2[-\Gamma'_{\text{app}}\tau]\} \tag{40}$$

$$C(q,\tau)/\beta = 1 + A\exp\{2[-\Gamma''_{\text{app}}\tau + (\mu_2/2)\tau^2]\} \tag{41}$$

In eq 40 and 41, A is the product of the amplitude of the relaxation process and the optical constant α, and the Γ_{app}'s are the "apparent" decay rates calculated using each of the above equations. Equations 40 and 41 assume homodyne light detection.

To determine $\langle\Gamma\rangle$, Γ_{app}/q^2 for a fixed q was first plotted against $\Gamma_{\text{app}}\tau_{\max}$, where $\tau_{\max}$ varied from either $2\tau_{\text{init}}$ or $3\tau_{\text{init}}$ for linear or quadratic fits, respectively, to an arbitrary value of τ representing the last data point included in the fit. The data were then extrapolated to $\Gamma_{\text{app}}\tau_{\max} = 0$, with the value of Γ_{app}/q^2 at this point being taken as $\langle\Gamma\rangle/q^2$. Γ_{app}/q^2 vs $\langle\Gamma\rangle\tau_{\max}$ was then repeatedly plotted until the value of $\langle\Gamma\rangle$ converges. Lodge et al.[38] noted that such plots usually have a plateau over a considerable range of $\langle\Gamma\rangle\tau_{\max}$ and suggested that the plateau value be used as the best estimate of $\langle\Gamma\rangle/q^2$. Pusey et al.[36] used a sloping extrapolation of Γ_{app}/q^2 to $\tau_{\max} = 0$ for the linear fit and plateau values of $\langle\Gamma\rangle/q^2$ for the quadratic fit. Assuming that polydispersity was the primary reason for the nonexponential decay of $g^{(1)}(q,\tau)$ and assuming that it can largely be accounted for in the second moment of the cumulant expansion, Pusey et al.'s method of extrapolation was used here. The magnitude of the measured mutual diffusion coefficient, $\lambda_2(c_2)$, was taken to be the average of $\langle\Gamma\rangle/q^2$ obtained using linear and quadratic fits at all measured angles.

Software provided with the BI-2030AT correlator fits $C(q,\tau)/\beta$ vs τ data to polynomials in delay time of first and second order using a weighted least-squares technique. This software was used to analyze the $C(q,\tau)/\beta$ vs τ data for solutions of lin-

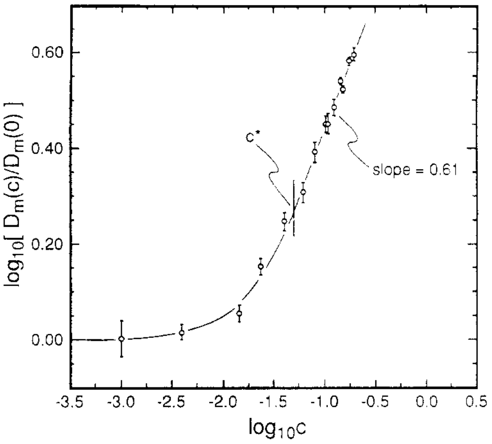

Figure 1. log–log plot of normalized mutual diffusion coefficient, $D_m(c)/D_m(0)$, vs concentration, c, of PDMS148K in toluene at 25 °C.

ear PDMS in toluene. Use of the above-described extrapolation method of data analysis produced results that were identical with those calculated using the BI2030AT software.

V. Results

Dynamic Light Scattering. DLS was first used to determine the mutual diffusion coefficient, $D_m(c)$, of PDMS148K in toluene at 25 °C for several different concentrations between 0.001 and 0.20 g·cm^{-3}. Toluene was used since the refractive index increment of PDMS in THF is too small for this binary mixture to be studied by DLS. Toluene, like THF, is good solvent for PDMS, possessing about the same polymer–solvent interaction parameter with PDMS at infinite dilution as THF.[39] Therefore, PDMS should, to a first approximation, have the same molecular dimensions in toluene as in THF. The purpose of these experiments was 2-fold. First, it was necessary to characterize our semidilute PDMS solution in terms of c^*, taken here as the minimum concentration of polymer in a binary solution at which $D_m(c)$ is independent of chain length.[40] The value of c^* of PDMS in toluene will be assumed to be equal to that in THF. Second, we needed to establish that, in our ternary mixtures, D_{33} (equivalent to $D_m(c)$) was indeed much larger than D_{22} to ensure the validity of the approximations made in obtaining eq 27–34. The results of $D_m(c)/D_m(0)$ vs c for PDMS148K in toluene are shown on a log–log plot in Figure 1. A region of constant slope beginning at $c^* \approx 0.05$ g·cm^{-3} ($\log c^* = -1.3$) is observed. From a least-squares fit of the data for which $c > c^*$, the concentration dependence of the cooperative diffusion coefficient, $D_{\text{coop}}(c)$, is obtained as:

$$D_{\text{coop}}(c) = (5.4 \pm 0.6) \times 10^{-6} c^{0.61\pm0.04}\ \text{cm}^2\cdot\text{s}^{-1}$$
$$0.05\ \text{g}\cdot\text{cm}^{-3} < c < 0.20\ \text{g}\cdot\text{cm}^{-3} \qquad (42)$$

The discrepancy between the power law exponent of 0.61 determined here and the theoretical scaling law value of 0.75[41] or the experimental value of 0.77 determined by Munch et al.[40] on the same system but for PDMS of $M_w = 6.0 \times 10^6$ g·mol^{-1} may be accounted for by the large difference in M_w in the two experiments. As molecular weight decreases at constant polymer mass concentration, the exponent will decrease as the measured $D_{\text{coop}}(c)$ will represent an increasing proportion of chain-end diffusion relative to cooperative diffusion. Thus, other workers, examining PS in toluene,[14] ethyl acetate,[42] and benzene,[42,43] have obtained exponent values of 0.51, 0.66, and 0.67–0.68, respectively, using different ranges of molecular weights.

$D_{\text{coop}}(c)$ for PDMS in THF at 25 °C can be estimated from data for PDMS in toluene by using the proportionality of $D_{\text{coop}}(c)$ to the inverse of solvent viscosity

$$D_{\text{coop,THF}}(c) = (\eta_{\text{tol}}/\eta_{\text{THF}})D_{\text{coop,tol}}(c) = 1.22 D_{\text{coop,tol}}(c) \qquad (43)$$

where, at 25 °C, η_{tol} and η_{THF} have been taken to be 0.554[44] and 0.453 cP,[45] respectively. The dynamic correlation length, ξ, of a semidilute polymer solution, providing a measure of the mesh size of the entangled polymer, can then be obtained from $D_{\text{coop}}(c)$ using an expression due to de Gennes[41]

$$D_{\text{coop}}(c) = \frac{k_B T}{6\pi\eta_s\xi} \qquad (44)$$

where η_s is solvent viscosity.

Tracer diffusion coefficients at infinite dilution, $D_2(0)$, and concentration coefficients of diffusion, k_D, of linear PS in THF at 25 °C have been determined using DLS over a broad range of molecular weights by Mandema and Zeldenrust[46] and by Duval et al.[47] It will be useful to compare the data of k_D and $D_2(0)$ for PS in THF to our results for k_D and $D_{22}(0)$ of dilute PS in mixtures of 15 vol % PDMS and THF. The molecular weights of PS used in our work are at the lower end of the molecular weight ranges at which results on the binary mixtures are available. By combining the DLS data of Mandema and Zeldenrust[46] and of Duval et al.,[47] and excluding points for which $M_{w,2} > 200\,000$ g·mol^{-1} the following relation is found to give a very good fit to the experimental data:

$$D_2(0) = (1.86 \times 10^{-4}) M_{w,2}^{-0.51}\ \text{cm}^2\cdot\text{s}^{-1}$$
$$10\,500\ \text{g}\cdot\text{mol}^{-1} \le M_w \le 182\,000\ \text{g}\cdot\text{mol}^{-1} \qquad (45)$$

The hydrodynamic radius, $R_{H,2}$, of PS in pure THF may be determined from $D_2(0)$ by using the Stokes–Einstein relationship:

$$R_{H,2} = \frac{k_B T}{6\pi\eta_s D_2(0)} \qquad (46)$$

The expected values of $D_2(0)$ and $R_{H,2}$ according to eq 45 and 46 are listed in Table II for the molecular weights of PS tested in this work. Although eq 45 is not necessarily valid for the two lowest molecular weights listed in this table, it should still provide a reasonable approximation of $D_2(0)$.

In ternary solutions of PS, PDMS, and THF, only very small concentrations of PS are soluble at high semidilute PDMS concentrations in THF. Thus, in DLS experiments an acceptable signal to noise (S/N) ratio over a concentration range broad enough to calculate $D_{22}(0)$ and k_D is not achievable. At low semidilute PDMS concentrations, cooperative diffusion of the PDMS host in the optically labeled ternary mixtures occurs at approximately the same rate as the translational diffusion of the probe PS for the lower molecular weights of PS used. Under this condition, k_D cannot be analyzed in terms of eq 34 as the assumptions leading to this expression are not fulfilled. An optimal concentration of PDMS to work at was found to be 0.1455 g·cm^{-3} (15 vol %) PDMS148K in THF. At this concentration according to eq 42 and 43, $D_{\text{coop}}(c) = 20.4 \times 10^{-7}$ cm^2·s^{-1} and $\xi_3 = 2.36$ nm.

The measured mutual diffusion coefficient, $\lambda_2(c_2)$, was determined at several PS concentrations for the seven different molecular weights of PS listed in Table I in mixtures of 15 vol % PDMS148K and THF. The mean

Table II
Hydrodynamic Properties of PS in Solution with THF and with Mixtures of 15 vol % PDMS148K and THF at 25 °C

$M_{w,2} \times 10^{-3}$, g·mol^{-1}	$D_{22}(0) \times 10^7$, cm^2·s^{-1}	k_D, cm^3·g^{-1}	$D_2(0) \times 10^7$,[a] cm^2·s^{-1}	$R_{H,2}$,[b] nm	$D_{22}(0)/D_2(0)$
3.76	13.69 ± 0.64	−28.0 ± 7.7	27.9	1.73	0.491
7.62	7.53 ± 0.36	−39.8 ± 7.0	19.5	2.47	0.386
14.1	4.410 ± 0.231	−52.3 ± 12.5	14.2	3.40	0.311
25.5	2.686 ± 0.136	−72.0 ± 16.1	10.5	4.59	0.256
32.1	2.255 ± 0.146	−105 ± 16	9.36	5.15	0.241
46.7	1.433 ± 0.128	−115 ± 61	7.73	6.24	0.185
60.1	1.028 ± 0.130	−187 ± 180	6.80	7.09	0.151

[a] According to eq 45. [b] According to eq 46.

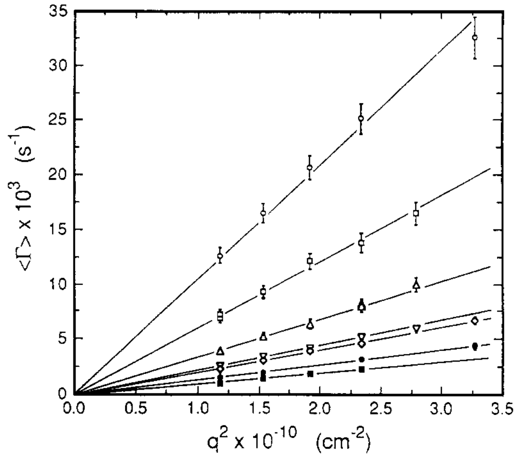

Figure 2. q^2 dependence of $\langle\Gamma\rangle$ for different molecular weights of PS in 15 vol % PDMS148K/THF at 25 °C: (○) PS3.76K; (□) PS7.62K; (△) PS14.1K; (▽) PS25.5K; (◇) PS32.1K; (●) PS46.7K; (■) PS60.1K.

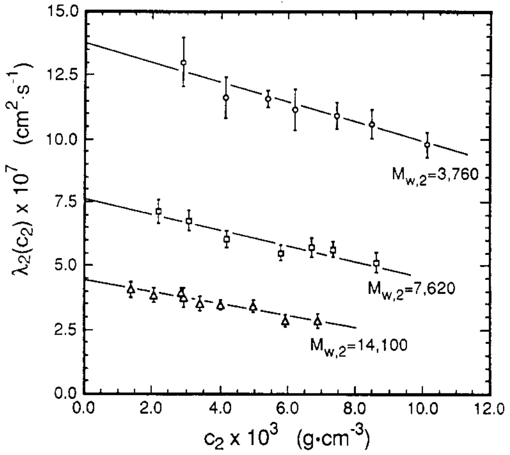

Figure 3. Measured mutual diffusion coefficient, $\lambda_2(c_2)$, vs concentration, c_2, of PS in solution with 15 vol % PDMS and THF at 25 °C.

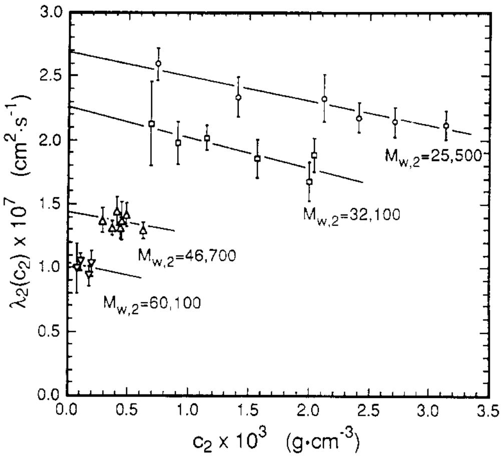

Figure 4. Measured mutual diffusion coefficient, $\lambda_2(c_2)$, vs concentration, c_2, of PS in solution with 15 vol % PDMS and THF at 25 °C.

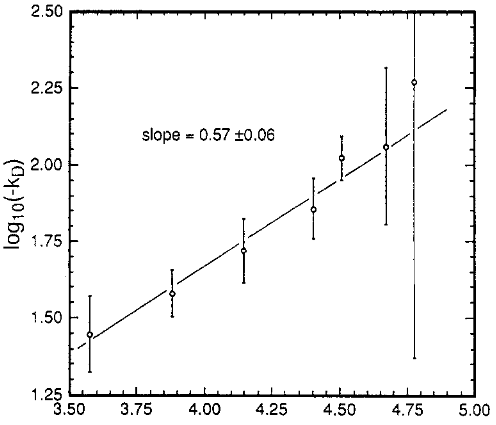

Figure 5. Dependence of the concentration coefficient of diffusion, k_D, on molecular weight for PS in 15 vol % PDMS and THF at 25 °C.

decay rate $\langle\Gamma\rangle$ measured at different angles exhibited a q^2 dependence (Figure 2), which allowed the calculation of $\lambda_2(c_2) = \langle\Gamma\rangle/q^2$ and its dependence on c_2 which is plotted in Figures 3 and 4. The lines in these figures correspond to a linear least-squares fit of the data. $D_{22}(0)$ and k_D are obtained from the y-intercept and slope of the fit, respectively. A linear dependence of $\lambda_2(c_2)$ on c_2 is observed for all molecular weights. Values of $D_{22}(0)$ and k_D calculated from the least-squares fit are listed in Table II. When c_2 is increased to close to the cloud point concentration for PS3.76K and PS7.62K and the delay time interval $\Delta\tau$ is decreased from that normally used, the Γ_3 decay mode representing cooperative diffusion of the semidilute matrix was evident at short delay times. The Γ_3 mode has also been observed for the same system when $c_2/c_3 = 1.2$.[18] In the results presented here, the sample time interval $\Delta\tau$ was always chosen such that the decay of the Γ_3 mode would occur within a delay time $\tau < 1\Delta\tau$ of the correlation. Furthermore, the amplitude of the Γ_3 mode was always negligible compared to the amplitude of the Γ_2 mode due to the very small relative concentration c_2/c_3.[26] Therefore, we can assume that the Γ_3 mode did not affect our results.

The molecular weight dependence of k_D is illustrated in Figures 5 and 6. Figure 5 is a log–log plot illustrating the dependence of k_D on $M_{w,2}$. Omitting the data point for PS60.1K because of the very large uncertainty associated with it, a least-squares fit of the data gives:

$$k_D = -(0.23 \pm 0.07)M_{w,2}^{0.57\pm0.06} \qquad (47)$$

Our results for k_D are compared to literature results for binary mixtures of PS in THF and cyclohexane in Figure 6.

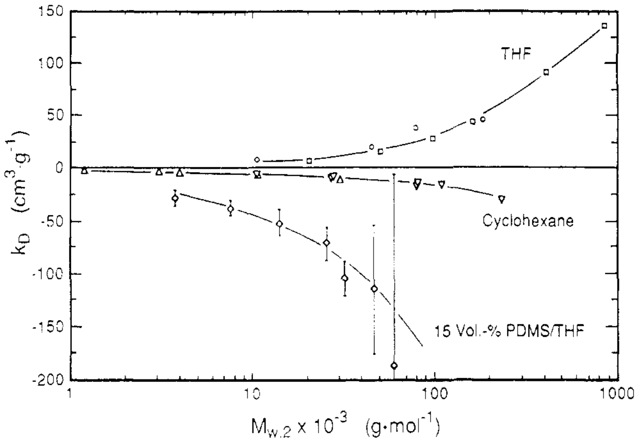

Figure 6. Dependence of k_D on PS molecular weight in various solvents: (□) THF at 25 °C;[46] (○) THF at 25 °C;[47] (△) CH at 34.5 °C;[51] (▽) CH at 34.5 °C;[52] (◇) 15 vol % PDMS/THF at 25 °C.

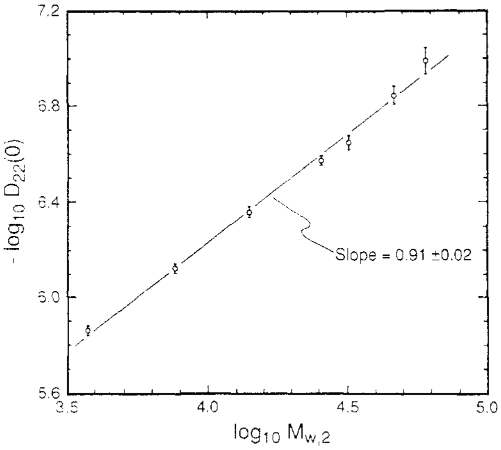

Figure 7. log–log plot of the tracer diffusion coefficient of infinitely dilute PS, $D_{22}(0)$, in 15 vol % PDMS148K/THF at 25 °C vs the molecular weight of PS.

A log–log plot of $D_{22}(0)$ vs $M_{w,2}$ is shown in Figure 7. From a least-squares fit of the data, one obtains

$$D_{22}(0) = (2.6 \pm 0.6) \times 10^{-3} M_{w,2}{}^{-0.91\pm0.02} \qquad (48)$$

A check on the validity of the results has been performed by calculating $C(q,\tau)$ as a function of τ, given the experimentally determined values of M_w/M_n for PS, $\langle\Gamma\rangle$, and the scaling exponent in eq 48 and comparing with experimental $C(q,\tau)$ vs τ data.[28] The results demonstrate excellent agreement between the experimental and calculated data for small τ. For large τ a small disparity exists and may be due to a difference between the actual chain length distribution of the PS sample and the assumed Schulz distribution.

Low-Angle Light Scattering. We found using differential refractometry that ν_{2_0} (PS/THF) = 0.1885 cm^3·g^{-1} and that ν_{3_0} (PDMS148K/THF) = 0.00654 cm^3·g^{-1}. No dependence of either ν_2 or ν_3 on polymer concentration was observed. At such a high ratio of the refractive index increments, $\nu_{2_0}/\nu_{3_0} = 29$, it is legitimate[16] to consider PDMS148K and THF an isorefractive system for the dynamic light scattering from the ternary PS/PDMS/THF system. However, the refractive index mismatch will have a large effect on the low-angle light-scattering results from this ternary system as we shall find Ω^2 in eq 6 to deviate by about 15% from the value of 1, which it would have if we assume perfect matching.

In LALS experiments on PS in THF and in mixtures of 15 vol % PDMS148K and THF, data were taken at two different scattering angles, θ = 3.6° and 4.6°. An average of at least six readings at each angle was used to calculate ΔR_θ. The average of $K/\Delta R_\theta$ at 3.6° and at 4.6° was utilized in further data analysis. This average is denoted $K/\Delta R_0$, since it is nearly identical with $K/\Delta R_\theta$ at $\theta = 0$. ΔR_0 represents the increase in scattered intensity of a solution infinitely dilute in polymer 2 over that of the solvent and is proportional to $c_2 M_{w,2} \nu_2{}^2$ (cf. eq 8). Low scattering due to low polymer molecular weights or small refractive index increments and limited solubility due to incompatibility of polymers will thus restrict the use of LALS measurements on optically labeled polymer solutions. In our ternary systems, the low molecular weight PS samples scattered insufficient light, and the too high molecular weight PS samples were insufficiently soluble to cover a range of c_2 broad enough to reliably calculate the slope and y-intercept of the data so that apparent molecular weights and second-virial coefficients could be determined. Thus, PS25.5K and PS32.1K were the only samples used in DLS experiments for which LALS measurements could be done with some degree of confidence. Note that the condition of $D_{33} \gg D_{22}$ used in developing eq 29–34 is well satisfied as D_{33} is about 1 order of magnitude larger than D_{22} for these samples.

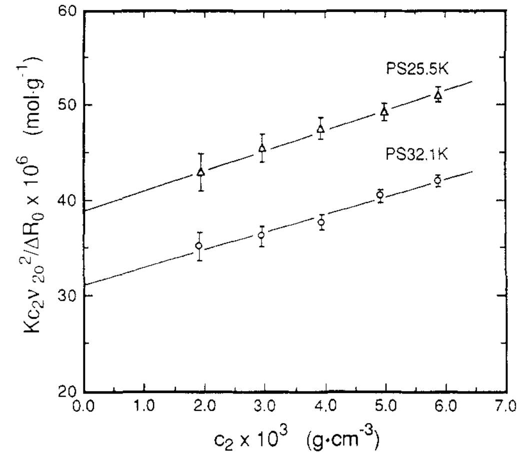

Figure 8. $K\nu_{2_0}{}^2 c_2/\Delta R_0$ vs c_2 for PS in THF at 25 °C.

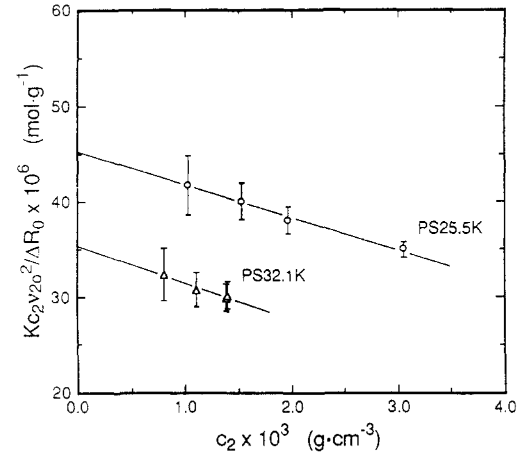

Figure 9. $K\nu_{2_0}{}^2 c_2/\Delta R_0$ vs c_2 for PS in 15 vol % PDMS148K/THF at 25 °C.

Plotted in Figure 8 is $Kc_2\nu_{2_0}{}^2/\Delta R_0$ vs c_2 for PS25.5K and PS32.1K in THF. Plots of $Kc_2\nu_{2_0}{}^2/\Delta R_0$ vs c_2 for PS25.5K and PS32.1K in 15 vol % PDMS148K/THF are shown in Figure 9. Comparison of the results in Figures 8 and 9 corresponding to PDMS concentrations of 0 and 0.1455 g·cm^{-3}, respectively, shows that the slopes of $Kc_2\nu_{2_0}/\Delta R_0$ vs c_2 plots become negative and the y-in-

Table III
LALS Results of PS in THF and in 15 vol % PDMS/THF at 25 °C

	LALS in THF				LALS in PDMS/THF			
polymer	$M_{w,2} \times 10^{-3}$, g·mol^{-1}	$A_2 \times 10^4$, mol·cm^3·g^{-2}	$\upsilon_{22}N_A$, cm^3·g^{-1}	χ_{12}	$\Omega^2 M_{w,2} \times 10^{-3}$, g·mol^{-1}	$A_{2,app} \times 10^4$, mol·cm^3·g^{-2}	Ω^2	λ_p, cm^3·g^{-1}
PS25.5K	25.75	10.52	16.06	0.401	22.2	−14.7	0.862	1.85
	±1.10	±0.20	±0.52	±0.003	±0.9	±3.9	±0.035	±0.49
PS32.1K	32.09	9.07	13.84	0.415	28.3	−17.1	0.881	1.72
	±1.28	±0.15	±0.39	±0.002	±1.8	±9.1	±0.055	±0.80

Table IV
Thermodynamic and Frictional Parameters of PS in CH at 34.5 °C and for PS in THF at 25 °C

	experimental						random flight model[a]	
$M_{w,2} \times 10^{-3}$, g·mol^{-1}	$[\eta]_{THF}$,[b] cm^3·g^{-1}	$[\eta]_{CH}$,[b] cm^3·g^{-1}	$A_2 \times 10^4$(THF),[c] cm^3·mol·g^{-2}	$2A_2M_{w,2}$, cm^3·g^{-1}	$k_{f,2}$(THF),[c] cm^3·g^{-1}	$k_{f,2}$(CH),[d] cm^3·g^{-1}	$k_{f,2}$(THF), cm^3·g^{-1}	$k_{f,2}$(CH), cm^3·g^{-1}
10.5	9.36	8.4	11.0	23.1	17.4	5.7	15.7	1.7
45.0	26.2	17.4	8.04	72.4	52.4	11.7	48.7	3.5
79.5	39.1	23.1	6.61	105.1	66.7	15.5	70.6	4.6
182.0	70.4	35.0	4.62	168.2	122.2	23.3	115.0	7.0

[a] $k_{f,2} = 1.2A_2M + 0.2[\eta]$.[19] [b] $[\eta]_{THF} = 1.344 \times 10^{-2} M_w^{0.707}$ cm^3·g^{-1}.[57] $[\eta]_{CH} = 8.2 \times 10^{-2} M^{0.50}$ cm^3·g^{-1}.[58] [c] Data of Duval et al.;[47] $k_{f,2} = -k_D + 2A_2M_{w,2}$. [d] Data of Huber et al.[51] and Hadziioannou et al.;[52] $k_{f,2} = -k_D$.

tercepts are shifted upward, indicating that $A_{2,app}$ is negative and Ω^2 is less than one for this system. Results for the factor due to nonexact refractive index matching, Ω^2, the second-virial coefficient of 2 in the 1–3 mixture, $A_{2,app}$, and the preferential adsorption parameter, λ_p, are listed in Table III. The uncertainty in the slope, and hence in $A_{2,app}$, is large due to the narrow range of c_2 which could be examined.

λ_p is a measure of the volume of THF that is preferentially adsorbed into the environment of each added gram of PS. The values of $\lambda_p \approx 1.8$ cm^3·g^{-1} are comparable in magnitude to the results of van den Esker et al.[48] for PS probes in polyisobutylene/toluene mixtures, where 2.4 cm^3·g^{-1} $\leq \lambda_p \leq$ 3.1 cm^3·g^{-1}. For polymers in solution with two low molecular weight solvents, it has been found that λ_p is generally less than 0.5 cm^3·g^{-1}.[39,49,50] The large value of λ_p quantifies how strongly the thermodynamic interactions between PS and PDMS affect the solution structure by showing that, on a microscopic scale, the surroundings of PS contain a much higher proportion of THF than on average in the solution. The thermodynamic interactions leading to the negative values of $A_{2,app}$ and large degree of preferential adsorption in the PS/PDMS/THF mixtures may be investigated by determining the excluded-volume parameters υ_{22}, υ_{33}, and υ_{23}. For concentrated polymer solutions, these parameters can be determined using eq 7 and 9 only by assuming a relation between them or by making an assumption about one of them. Such assumptions will be considered in the discussion.

VI. Analysis of Results and Discussion

Dominance of Thermodynamic Effects on k_D. For the purpose of comparison, the data of k_D from the diffusion of PS in 15 vol % PDMS148K/THF at 25 °C versus the molecular weight of polystyrene are plotted in Figure 6 along with the corresponding data for PS in pure THF at 25 °C[46,47] and in pure cyclohexane (CH)[51,52] at 34.5 °C (a Θ-solvent for PS). The origin of the differences in k_D may be obtained by employing eq 1 and 34 to calculate the hydrodynamic ($-k_{f,2}$) and thermodynamic ($2A_{2,app}M_{w,2}$) contributions to k_D for the ternary mixtures and comparing with the analogous quantities for the binary systems. For a dilute binary solution, the following equations may be employed to evaluate DLS data:[19]

$$D_m(c_2) = D_2(0)(1 + k_Dc_2) \tag{49}$$

$$k_D = -k_{f,2} + 2A_2M_{w,2} \tag{50}$$

The relative contributions of hydrodynamics and thermodynamics to k_D can be calculated from a combination of DLS and LALS results. k_D, $2A_2M_{w,2}$ and $k_{f,2}$ for the binary mixtures are listed in Table IV for the molecular weights of PS for which A_2 data is available.[47] Since CH at 34.5 °C is a Θ-solvent for PS, $A_2 = 0$ and k_D arises totally from hydrodynamics and must be negative. For PS in THF, k_D is positive because its hydrodynamic contribution is smaller in magnitude than its thermodynamic contribution. Also listed in Table IV is $k_{f,2}$ calculated using available experimental data for $[\eta]$ according to an expression derived by Yamakawa using a random flight model of monodisperse polymer chains:[19]

$$k_{f,2} = 1.2A_2M_{w,2} + 0.2[\eta] \tag{51}$$

The value of $k_{f,2}$ from eq 51 is in very good agreement with the value of $k_{f,2}$ extracted experimentally from eq 49 and 50 for the THF data but is less good for the CH data. In any event, eq 51 shows how frictional and thermodynamic effects are coupled and can explain at least qualitatively the large difference in $k_{f,2}$ between PS in CH and in THF.

Turning to the ternary system of dilute PS in 15 vol % PDMS/THF, the thermodynamic and frictional contributions to k_D will change from those for PS in pure THF due to the presence of the PDMS matrix. Experimentally, k_D changes from positive to negative when the solvent becomes richer in PDMS, as can be surmised from the results in Figure 6. For mixtures of PS25.5K and PS32.1K in 15 vol % PDMS148K/THF for which both DLS and LALS measurements were performed, values of k_D and $2A_{2,app}M_{w,2}$ are listed in Table V. It is apparent that, as PDMS is added to the PS/THF mixture, $k_{f,2}$ must decrease and become negligible compared to the thermodynamic effects ($2A_{2,app}M_{w,2}$), which now dominate k_D. The decrease in $k_{f,2}$ from its value in pure THF can be physically explained in terms of hydrodynamic screening of the velocity perturbations arising from diffusing PS coils by the PDMS chains in between the coils.

Table V
Thermodynamic and Frictional Parameters for Solutions of PS in 15 vol % PDMS/THF at 25 °C

$M_{w,2} \times 10^{-3}$, g·mol^{-1}	k_D, cm^3·g^{-1}	$2A_{2,app}M_{w,2}$, cm^3·g^{-1}
25.5	-72 ± 16	-75 ± 20
32.1	-105 ± 16	-110 ± 52

Table VI
Comparison of Solutions of PS in 15 vol % PDMS and THF Investigated by Authors to Solutions of PS in 0.432 vol % PMMA and Benzene Investigated by Numasawa et al.[10,23]

quantity	PS/PDMS/THF	PS/PMMA/benzene
$M_{w,3} \times 10^{-3}$	148	12 000
c_3^*,[a] g·cm^{-3}	0.040	0.0016
c_3^0, g·cm^{-3}	$0.1455 = 3.6c_3^*$	$0.0047 = 2.3c_3^*$
ξ_3, nm	2.36[b]	30[c]
range of $R_{H,2}$,[d] nm	1.7–7.0	23–110
range of $R_{H,2}/\xi_3$	0.72–2.97	0.76–3.67
range of $qR_{g,2}$	0.02–0.11[e]	0.2–5.3
ν_H	−0.91	−0.91

[a] $c_3^* = M_{w,3}/N_AR_{g,3}^3$. [b] Dynamic correlation length (eq 44). [c] Static correlation length.[23] [d] In pure solvent. [e] $R_{g,2}$ of PS in toluene.[52]

Molecular Weight Dependence of $A_{2,app}$ and Evaluation of υ_{22}, υ_{33}, and υ_{23}. As shown in Figure 5, the relationship between k_D and $M_{w,2}$ is well described by the equation: $k_D \sim -M_{w,2}^{0.57\pm0.06}$, where $\sim$ denotes a proportionality. The similar $M^{1/2}$ dependence of k_D that exists for a binary Θ-solution is due entirely to frictional effects, where $k_D \approx -k_f \sim [\eta] \sim M^{1/2}$ (see eq 50 and 51). On the other hand, we have seen that in the ternary systems investigated here k_D is dominated by the thermodynamic term $2A_{2,app}M_{w,2}$. The dependence of $A_{2,app}$ on $M_{w,2}$ may be obtained by taking $k_{f,2}$ to be negligible in eq 34 and substituting $-M_{w,2}^{0.57}$ for k_D, thus

$$A_{2,app} \approx \frac{k_D}{2M_{w,2}} \sim \frac{-M_{w,2}^{0.57}}{M_{w,2}} \sim -M_{w,2}^{-0.43} \qquad (52)$$

Benoit and Benmouna's model of polymer interactions,[26] on which the expression for $A_{2,app}$ given in eq 9 is based, can be used as the starting point to assess whether the power law observed in eq 52 may be predicted. Since thermodynamic properties of semidilute solutions must be independent of the chain length of the semidilute polymer,[41] eq 9 must lose its $M_{w,3}$ dependence when component 3 is semidilute to be a valid representation of $A_{2,app}$. We shall indeed find later from estimates of υ_{33} extracted from LALS results that $(N_A/m_3^2)c_3M_{w,3}\upsilon_{33} \gg 1$. Hence, eq 9 loses its $M_{w,3}$ dependence and simplifies to:

$$2A_{2,app} = (N_A/m_2^2)\upsilon_{22}\left(1 - \frac{\upsilon_{23}^2}{\upsilon_{22}\upsilon_{33}}\right) \qquad (53)$$

Determining the $M_{w,2}$ dependence of $A_{2,app}$ now involves predicting the $M_{w,2}$ dependence of υ_{22} and of the quotient $\beta' \equiv \upsilon_{23}^2/(\upsilon_{22}\upsilon_{33})$.

First consider a dilute binary mixture of PS and THF. When $c_3^0 = 0$ in eq 9, $A_{2,app}$ becomes A_2 and one obtains:

$$2A_2 = (N_A/m_2^2)\upsilon_{22} \qquad (54)$$

Using the relationship $\upsilon_{22} = u_2/P_2^2$, where P_2 is the chain length of polymer 2 and u_2 is the excluded-volume parameter per polymer molecule,[53] assuming that the polymer molecules interact like hard spheres with a radius proportional to $R_{g,2}$, and postulating a scaling relationship of the form $R_{g,2} \sim M_2^{\nu}$, one obtains:[41]

$$A_2 \sim M_2^{3\nu-2} \qquad (55)$$

Assuming that $R_{H,2}$ goes like $R_{g,2}$ for scaling exponents near 0.5[41] and using the molecular weight dependence of $R_{H,2}$ given by eq 45 and 46, a relationship between A_2 and M_2 for PS in THF is obtained:

$$A_2 \sim M_2^{\{3(0.51)-2\}} = M_2^{-0.47} \text{ (prediction)} \qquad (56)$$

A least-squares fit of the A_2 vs $M_{w,2}$ data for PS in THF of Duval et al.[47] and that obtained here (see Table III) yields the following relationship

$$A_2 \sim M_{w,2}^{-0.40\pm0.06} \text{ (experimental)} \qquad (57)$$

where the datum for $M_w = 10\,500$ g·mol^{-1} was excluded from the fit since A_2 values from LALS measurements have a high degree of uncertainty at molecular weights this low. The small disparity between eq 56 and 57 may arise from the fact that the polymers used in the experiments were not perfectly monodisperse.

Turning to the ternary mixture of PS in 15 vol % PDMS and THF, υ_{22} can be calculated in an analogous fashion as for a binary mixture if one again assumes that the probe molecules interact like hard spheres. We shall assume that the scaling of $R_{g,2}$ with $M_{w,2}$ in the ternary system remains unchanged from that in the binary PS/THF system. This is supported by the following observations. Numasawa et al.[10,23] used DLS and ELS to study optically labeled ternary polymer solutions consisting of PS probes in isorefractive mixtures of semidilute PMMA and benzene. As shown in Table VI, their system was analogous to ours except that the polymers they examined were of greater molecular weight. They observed that $R_{g,2}$ of the PS probe did not decrease from its value in pure benzene when semidilute PMMA was added. For both binary and ternary mixtures, it was found that $R_{g,2} \sim M_{w,2}^{0.60}$.[23] Also, Moon and Baumgärtner conducted Monte Carlo simulations of a pearl-necklace chain diffusing within a matrix of infinitely long, randomly spaced rods.[54] Although this system is quite different from ours and that of Numasawa et al., they also found that $R_{g,2}$ did not change from its value in absence of the rods.[54] Finally, unlike large molecular weight chains that decrease in size appreciably with the quality of a solvent near the Θ temperature, the size of low molecular weight chains changes only very negligibly with solvent quality.[55] Given the above observations, we expect the $R_{g,2}$ of our PS chains to remain practically unchanged from their value in pure THF when the PDMS concentration is increased to 15 vol %. In our ternary system, therefore, we shall take the same molecular weight dependence of υ_{22} as that for PS in pure THF, namely

$$\upsilon_{22} \sim M_2^{-0.47} \qquad (58)$$

To obtain the $M_{w,2}$ dependence of $A_{2,app}$ in eq 53, we also need to know something about the ratio $\beta' \equiv \upsilon_{23}^2/\upsilon_{22}\upsilon_{33}$. Kaddour and Strazielle have investigated the behavior of the quotient β' for the exact same mixtures of PS, PDMS, and THF.[56] They found that β' is independent of molecular weight and is only a function of the relative concentrations of probe and host species; that is

$$\beta' = \frac{\upsilon_{23}^2}{\upsilon_{22}\upsilon_{33}} = f\left(\frac{c_2}{c_2 + c_3}\right) \qquad (59)$$

From an extrapolation of their results, one obtains in the limit of $c_2/(c_2 + c_3)$ going to zero that $\beta' = 2.30$. Since the conditions of our experiments are such that $c_2 \ll c_3$, we use this value of β' and eq 58 in eq 53 to obtain the

Table VII
Values of the Excluded-Volume Parameters, v_{ij}, for PS in Mixtures of 15 vol % PDMS148K and THF at 25 °C

$M_{w,2} \times 10^{-3}$, g·mol^{-1}	approximation	$N_A v_{22}$, cm^3·mol^{-1}	$N_A v_{33}$, cm^3·mol^{-1}	$N_A v_{23}$, cm^3·mol^{-1}	β'
25.5	$\beta = 2.3^a$	18.2 ± 6.0	7.4 ± 2.4	17.6 ± 5.8	
	constant v_{22}	16.1 ± 0.5^b	7.0 ± 2.4	16.6 ± 3.6	2.47 ± 0.52
32.1	$\beta = 2.3^a$	20.9 ± 9.8	12.0 ± 5.6	24.0 ± 11.3	
	constant v_{22}	13.8 ± 0.4^b	10.1 ± 4.2	20.4 ± 9.5	2.96 ± 0.93

[a] Extrapolated from the results of Kaddour and Strazielle.[56] [b] Determined for PS in THF at infinite dilution.

molecular weight dependence of $A_{2,\mathrm{app}}$ as:

$$A_{2,\mathrm{app}} \sim M_2^{-0.47}(1 - 2.30) \sim -M_2^{-0.47} \text{ (prediction)} \qquad (60)$$

When we compare eq 60 with eq 52, it is seen that the dependence of $A_{2,\mathrm{app}}$ on $M_{w,2}$ calculated from experimental data is in good agreement with that which can be predicted using simple scaling arguments and independent data for the size of the probe polymer and the magnitude of β'. However, this agreement should be regarded with caution since the condition, $D_{33} \gg D_{22}$, which is necessary for the validity of eq 34 and 42, is not fulfilled for the two lowest molecular weights examined.

The arguments presented in the above discussion (eq 34, 53, and 60) indicate that k_D of the probe in the optically matched ternary mixtures examined is independent of host concentration when the host is semidilute and $c_2 \ll c_3$. The experimental data of Chang et al.[8] on optically matched mixtures of PS (probe), PVME (host), and *o*-fluorotoluene also support a similar conclusion. These data show a large initial decrease in k_D with increasing c_3 when the host was dilute but only a very small change in k_D with increasing c_3 when the host was semidilute.

From the experimental results of Ω^2 and $A_{2,\mathrm{app}}$ and the extrapolated value of $\beta' = 2.30$, we can calculate the values of the three excluded volumes v_{22}, v_{33}, and v_{23} using eq 7 and 9. The results are listed in Table VII. We have also listed the values of v_{33} and v_{23}, if instead of taking β' as a constant, we assume that v_{22} retains, in the ternary mixtures, its value at infinite dilution in the binary PS/THF mixtures. This last assumption would be consistent with the argument that the size of the PS molecules remain unchanged upon addition of component 3 to the solution. Comparison of the results from the two approximations leads indeed to very close values for both v_{33} and v_{23} (Table VII). Note that, from the values of v_{33} tabulated, it is easy to verify that $(N_A/M_{w,3}^2)c_3M_{w,3}v_{33} \gg 1$, leading to the fact that $A_{2,\mathrm{app}}$ will be independent of $M_{w,3}$ (see eq 9 and 53). The values in the table have a high degree of uncertainty propagated from the determination of Ω^2 and $A_{2,\mathrm{app}}$. No trends with PS molecular weight may be inferred from the results, as the difference in each parameter that the change in molecular weight appears to cause is within the experimental uncertainty.

Tracer Diffusion Coefficient of PS at Infinite Dilution. Tracer diffusion coefficients, $D_{22}(0)$, of PS in 15 vol % PDMS/THF for the seven molecular weights of PS tested are shown in Table II. For a comparison, the tracer diffusion coefficients, $D_2(0)$, of PS in THF calculated according to eq 45 are also listed. $D_{22}(0)$ is much smaller than $D_2(0)$, and the ratio $D_{22}(0)/D_2(0)$ decreases as $M_{w,2}$ increases. The motion of the PS molecules is not governed by the macroscopic viscosity of the solution. If the decrease in the diffusion coefficient were due solely to a change in macroscopic viscosity, Stokes' law would predict the following relationship between the diffusion coefficients and solution viscosities:

$$D_{22}(0)/D_2(0) = \eta_{\mathrm{THF}}/\eta_{\mathrm{PDMS/THF}} \qquad (61)$$

An Ubbelohde viscometer was used to obtain $\eta_{\mathrm{PDMS/THF}}$ $\approx$ 300 cps for 15 vol % PDMS148K/THF at 25 °C. Using $\eta_{\mathrm{THF}} = 0.453$ cps[45] and assuming that molecular size and shape do not change appreciably upon adding the PDMS,[23,54] one would expect from eq 61 that $D_{22}(0)/D_2(0) = 0.0016$. However, the ratio $D_{22}(0)/D_2(0)$ falls between 0.15 and 0.49 and depends appreciably on $M_{w,2}$.

The molecular weight exponent, ν_H, of -0.91 that we observed for $D_{22}(0)$ does not match any of the expected scaling behavior for chains undergoing Stokes–Einstein diffusion, Rouse diffusion dynamics, or reptation. It is interesting to note that our value for ν_h is the same as that found by Numasawa et al.[10,23] for PS probes in semidilute PMMA/benzene solutions. Therefore, it is worthwhile to compare the different parameters of the two systems that are listed in Table VI. Although the systems differ in host polymer type, solvent, and polymer molecular weights, the range of ratios of $R_{H,2}/\xi_3$ spanned in the two studies are similar, from about 0.75 to 3.0 and appears to be the critical factor affecting ν_H. $R_{H,2}$ is the hydrodynamic radius of the probe, and ξ_3 is the correlation length of the host. Thus, for both studies the range investigated falls in the crossover region between Stokes–Einstein behavior and "reptation" behavior. Numasawa et al.[10] interpreted their results by postulating that the semidilute host polymer matrix screens the hydrodynamic interactions between different segments of a probe polymer coil and that ν_H is approaching the value of -1.0 expected for a free-draining molecule. However, the fact that $\nu_H = -0.91$ persisted from values of $R_{H,2}/\xi_3$ less than unity to values several times great than unity does not support such a suggestion. Furthermore, Wheeler et al.[6] examined the molecular weight dependence of the diffusion coefficient of dilute PS probe polymers in mixtures of isorefractive PVME host polymers (compatible) and *o*-fluorotoluene as a function of host concentration and found that ν_H decreased smoothly from -0.55 to -1.9 as the PVME concentration was increased from 0 to $30c_3^*$. At $c_3 = 3c_3^*$, ν_H had the value of -0.85. To model the diffusion mechanism in the crossover regime, one must take into account the interaction of the probe with the strongly fluctuating host medium and incorporate the fact that the fast cooperative diffusion coefficient of the host affects the character of the diffusion of the probe. Some attempts have been made in this direction.[59,60]

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Supplementary Material Available: Appendix A consisting of the main and mutual diffusion coefficients in ternary systems (2 pages). Ordering information is given on any current masthead page.

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