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Dynamic Light Scattering Experiments on PVME–Polystyrene–Toluene and PVME–Polystyrene–Carbon Tetrachloride Solutions

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ABSTRACT: The results of dynamic light scattering experiments on poly(vinyl methyl ether)–polystyrene–toluene and poly(vinyl methyl ether)–polystyrene–carbon tetrachloride solutions are presented. In each of these systems, the poly(vinyl methyl ether) (PVME) is approximately isorefractive with the solvent and the polystyrene (PS) is present only as a trace. The results of our experiments on PVME–PS–toluene solutions agree with previous work, giving the self-diffusion coefficient of the PS. However, a change of solvent from toluene to carbon tetrachloride produces much lower values for the effective diffusion coefficients. It is concluded that the true self-diffusion coefficient is no longer measured by this technique due to the solvent being of good quality for one polymer but only marginal for the other. This result is discussed in the context of theoretical studies of dynamic scattering from ternary polymer solutions. The scattering vector dependence of the effective diffusion coefficient obtained from cumulant fits to the DLS data is also studied.

1. Introduction

It has been known for some time[1] that a dynamic ligth scattering (DLS) experiment on a solution containing two macromolecular solutes will, in general, give an autocorrelation function composed to two modes of decay. For dilute ternary solutions, this result is trivial—the two modes of decay correspond to the free particle diffusion coefficients of the two solutes. However, the results become more difficult to interpret when the solutes interact with each other. Phillies[1] showed in 1974 that the two modes of decay are related to combinations of the ternary diffusion coefficients of the solutes.

In recent DLS experiments on ternary polymer solutions, the emphasis has been on solutions in which one solute was isorefractive with the solvent and the other was present only as a trace. Under such conditions, a DLS experiment usually gives a correlation function consisting of a single exponential decay. This convenient simplification has been exploited in many recent studies; see refs 2–8, for examples. Some experiments have concerned nonisorefractive polymer solutions; for example, Daivis et al.[9] investigated aqueous solutions containing two dextran fractions of different molar mass, and Brown et al.[10] investigated solutions of two polystyrenes of differing molar mass in solution with chloroform.

It is often assumed that the self-diffusion coefficient of the visible polymer is obtained from measurements on ternary solutions in which one of the solutes is isorefractive with the solvent, if the concentration of the visible polymer is low; hence, the name "optical tracer" dynamic light scattering. This assumption has been tested experimentally by Chang et al.[11] under a restricted range of experimental conditions. They obtained the diffusion coefficient of the slow mode measured by dynamic light scattering (DLS) experiments and by forced Rayleigh scattering experiments on poly(vinyl methyl ether)–toluene solutions to which a trace amount of polystyrene had been added and found good agreement after extrapolating to zero polystyrene content. Daivis et al.[12] used dynamic light scattering and pulsed field gradient nuclear magnetic resonance (PFGNMR) to study the self-diffusion coefficient of 110 000 molar mass polystyrene (PS) in ternary solution with 110 000 molar mass poly(vinyl methyl ether) (PVME) and toluene at total polymer concentrations as high as 600 kg m^{-3} and polystyrene to total polymer concentration ratios up to 0.25. They found agreement between the diffusion coefficient of the slow mode measured by DLS and the polystyrene self-diffusion coefficient measured by PFGNMR.

Polystyrene and poly(vinyl methyl ether) are compatible and toluene is a good solvent for both of them. This is clearly a special (almost unique) case—most polymer blends are incompatible, and even when compatible polymers are considered, few solvents are isorefractive with one of the polymers and equally thermodynamically good for both. If dynamic light scattering from ternary solutions is to be fully understood, experiments must be performed under a variety of experimental conditions, involving changes in solvent quality, polymer–polymer compatibility, optical contrast, and probe concentration.

Two theories of dynamic light scattering from semidilute ternary polymer solutions have appeared in the literature. One was developed by Benmouna et al.[13-17] Benmouna gave specific results of the theory for two specific cases. In the first, the polymers are assumed to have equal molar masses and sizes, one of them is assumed to have no contrast with the solvent, and the solvent quality is assumed to be the same (in fact good) for both polymers. In the second case, the two polymers are assumed to differ only in their molar masses. We have used Benmouna's theory to derive results that apply to unequal molar mass polymers with a nonzero polymer–polymer interaction parameter and to solvents with unequal solvent quality for the two polymers.

The second theory of dynamic light scattering from ternary polymer solutions was developed by Cohen et al.[18,19] This theory assumes that the majority polymer has no contrast with the solvent, and it further assumes that the concentration of the visible polymer is low and the solution is semidilute. There is no restriction on solvent quality. We use our results to critically examine these theories.

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Two sets of experiments are discussed in this paper. The first set comprises optical tracer DLS experiments similar to those performed by Martin.[4] An important difference between Martin's experiments and ours is that we used a different method of data anlaysis to extract information from the DLS data. Martin used either a single exponential fit to correlation functions from which several to the initial channels had been removed or double exponential fits containing a term accounting for the fast initial decay as well as a diffusion term. Martin did not make any further use of the term relating to the initial fast decay. We used cumulant fits to extract the effective diffusion coefficient, defined as the initial decay rate divided by the squared scattering vector $\mathbf{q}^2$, and found it to be $\mathbf{q}$ dependent, with the extrapolated value at zero scattering vector being equivalent to Martin's long-time diffusion coefficient.

The second set of experiments deals with similar measurements on the PVME–PS–carbon tetrachloride system. The PVME–PS–carbon tetrachloride system is thermodynamically quite different from the PVME–PS–toluene system because carbon tetrachloride is a good solvent for PVME but only a marginal solvent for PS. We find that the thermodynamic conditions of the solution can have a strong effect on the results of DLS experiments. It is shown that even if the matrix polymer is isorefractive with the solvent the probe polymer is present only as a trace component, and the polymers are compatible in the absence of solvent the self-diffusion coefficient of the probe polymer is not necessarily measured.

2. Theory

Dynamic Light Scattering. The dynamic scattering from infinitely dilute ternary solutions is simply a special case of the polydispersity problem which is discussed in standard texts.[20] The dynamic structure factor for scattering from a system consisting of a solvent and two different interacting spherical solutes was first considered by Phillies.[1] He found that $S(\mathbf{q},\tau)$ consisted of a sum of two exponentials having decay rates related to the ternary diffusion coefficients

$$S(\mathbf{q},\tau) = A_+\exp(-D_+\mathbf{q}^2\tau) + A_-\exp(-D_-\mathbf{q}^2\tau) \qquad (1)$$

$$D_\pm = \frac{1}{2}(D_{11} + D_{22}) \pm \frac{1}{2}[(D_{11} - D_{22})^2 + 4D_{12}D_{21}]^{1/2} \qquad (2)$$

This problem was also considered by Pusey, Fijnaut, and Vrij,[21] who calculated the mode amplitudes A_+ and A_- for hard spheres.

The diffusion coefficients D_+ and D_- represent the rates of decay of two different types of density flucutation. The + mode can be interpreted as a compression–dilation or collective mode, with the relative concentrations fixed ($\delta C_1/C_1 = \delta C_2/C_2$). The − mode can be interpreted as an exchange of species at fixed total number density (i.e., $\delta C_1 + \delta C_2 = 0$).

Scattering from polymer–polymer–solvent systems was considered by Hanley, Balloge, and Tirrell,[3] who obtained the same general form as eq 1.

Foley and Cohen[18] discussed DLS experiments on semidilute ternary polymer solutions. They found two relaxation modes in $S(\mathbf{q},\tau)$, but did not attempt detailed calculations of the decay rates. This theory was further developed by Aven and Cohen,[19] who obtained expressions for the decay rate of the slow mode in terms of the apparent second virial coefficient $A_{2,\mathrm{app}}$ of the minority polymer in the "equivalent solvent" formed by the majority (isorefractive) polymer and the solvent. This theory predicts the measured diffusion coefficient D_I to be dependent on the minority polymer concentration C_1 as follows

$$D_\mathrm{I} = D_\mathrm{m}(0)[1 - k_DC_1] \qquad (3a)$$

where

$$k_D \approx -k_{f,1} + 2A_{2,\mathrm{app}}M_1 \qquad (3b)$$

Here, $k_{f,1}$ and M_1 are, respectively, the friction coefficient and molar mass of the visible polymer. $k_{f,1}$ is expected to be small.

Benmouna et al.[13-17] assumed hydrodynamic interactions to be totally screened and used the random-phase approximation (RPA) to find an approximate expression for the initial slope of ln $[S(\mathbf{q},\tau)]$ for semidilute ternary polymer solutions. For static properties, use of the RPA results in the Flory–Huggins expression for $S(0)$.[15] This theory is only valid above the overlap concentration.[16] They also identified two modes of relaxation in the initial slope of ln $[S(\mathbf{q},\tau)]$.

Benmouna et al. have considered the special case of two interacting polymers with equal molar masses and sizes, one having no contrast with the solvent, in a solvent of the same solvent quality for both polymers. They used the Flory–Huggins theory of polymer solution thermodynamics and assumed that the excluded volume parameters were given by

$$v_{1s} = v_0(1/\phi_s - 2\chi_{1s}) \qquad (4a)$$

$$v_{2s} = v_0(1/\phi_s - 2\chi_{2s}) \qquad (4b)$$

where subscripts 1 and 2 refer to the polymers and subscript s to the solvent, ϕ_s is the solvent volume fraction, and v_0 is a constant.[22] This is a reasonable assumption for our experiments because the monomer molar masses of polystyrene and PVME are similar. The solvent is assumed to be equally good for the polymers, so v_{1s} and v_{2s} can be written as v, and v_{12} can be written as $v + \chi$, where $\chi = v_0\chi'_{12}$. After further assuming x and χ/v to be small, the two initial decay rates reduce to

$$\Gamma_\mathrm{I} = \mathbf{q}^2D_\mathrm{I}(\mathbf{q}) = \Gamma_s(\mathbf{q})[1 - 2x(1-x)\phi NP(\mathbf{q})\chi] \qquad (5)$$

and

$$\Gamma_\mathrm{C} = \mathbf{q}^2D_\mathrm{C}(\mathbf{q}) = \Gamma_s(\mathbf{q})[1 + \phi NP(\mathbf{q})v] \qquad (6)$$

where Γ_I is a slow decay rate associated with the interdiffusion mode, Γ_C is a fast decay rate associated with the cooperative diffusion mode, ϕ is the total polymer volume fraction, and N is the degree of polymerization of the polymers. Also, x is the relative concentration of the visible polymer (e.g., $C_1/(C_1+C_2)$), C is the total polymer concentration ($C_1 + C_2$), v is the excluded volume parameter (assumed to be the same for both polymers), and χ is the Flory interaction parameter for polymer–polymer interactions. In the small q limit, the diffusion coefficients D_I and D_C are qualitatively similar to D_- and D_+ in eq 2. Note that $v\phi N/2$ is a measure of C/C^*, where C^* is the overlap concentration.[13] $\Gamma_s(q)$ is the "bare" initial decay rate, i.e., the initial decay rate of the self dynamic structure factor[17] which in this theory is given by

$$\Gamma_s = \mathbf{q}^2\frac{k_\mathrm{B}T}{N\zeta P(\mathbf{q})} = \mathbf{q}^2\frac{D_s}{P(\mathbf{q})} \qquad (7)$$

Unless $P(\mathbf{q}) = 1$, a $\mathbf{q}$-dependent effective diffusion coefficient is obtained from a measurement of Γ_s. In the limit of small, $\mathbf{q}$, $P(\mathbf{q}) = 1$ and the self-diffusion coefficient is measured. The friction factor $N\zeta$ in eq 7 is the Rouse model friction factor, so this theory clearly does not account for the effect of hydrodynamic interactions or entanglements on chain dynamics.

In the limit of zero visible polymer concentration, (i.e., x approaching zero) eqs 5–7 are consistent with the known limits of ternary diffusion coefficients[3,23]

$$D_{12} = 0 \tag{8}$$

$$D_{22} = D_{20} \text{ (mutual diffusion)} \tag{9}$$

$$D_{11} = D_1(C_2) \tag{10}$$

where D_{20} represents the binary mutual diffusion coefficient and $D_1(C_2)$ the self-diffusion coefficient of a trace of component 1 in the presence of a variable concentration C_2 of component 2. Equation 10 is analogous to eq 5 with x approaching zero. This is the condition which must be satisfied in order to perform an "optical tracer" dynamic light-scattering experiment. However, a note of caution must be made at this point. Equation 5 indicates that the degree to which D_I approximates D_s depends not only upon the value of x but also upon the thermodynamic quantities χ and v, if we consider a fixed value of $v\phi N$. An interesting limit of eq 5 is found when χ/v tends to zero. Then Γ_I becomes equal to $\Gamma_\mathrm{s}(\mathbf{q})$ regardless of the value of x. Such a situation is realized when the polymers are compatible and the solvent is good for both of them. On the other hand, a large value of χ/v will result in a discrepancy between D_I and D_s, even for small values of x.

Expressions for the mode amplitudes are given by Borsali et al.[17] In the limit as x approaches zero, the amplitude of the cooperative mode also approaches zero, so that only the interdiffusion mode is measured. When x is large both modes are expected to contribute to $S(\mathbf{q},\tau)$, even though one of the polymers is "invisible". (These considerations apply to solutions of interacting polymers, not dilute solutions.)

We have extended the analysis to include polymers of unequal molar mass. Writing the degree of polymerization of the visible polymer as N_1 and that of the isorefractive polymer as N_2, the slow decay rate reduces to

$$\Gamma_\mathrm{I} = \frac{\mathbf{q}^2 k_\mathrm{B} T}{2\zeta N_1 P_1}\{F_1 - \sqrt{(F_1{}^2 - F_2)}\} \tag{11}$$

where

$$F_1 = 1 + \frac{N_1P_1}{N_2P_2} + N_1P_1\phi v$$

and

$$F_2 = \frac{4N_1P_1}{N_2P_2} + 4[N_1P_1\phi v]^2 x(1-x) + 4N_1P_1\phi v\left[\frac{xN_1P_1}{N_2P_2} + (1-x)\right] - 4x(1-x)[N_1P_1\phi v]^2\left[1 + \frac{\chi}{v}\right]^2$$

Neither x nor χ/v is assumed to be small in eq 11. One of the important predictions of the Flory–Huggins theory is that there is a single, simple criterion for polymer compatibility, which is that two polymers are compatible if the value of χ is negative or at worst small and positive. However, the Flory–Huggins theory has been shown to be incomplete because the theory introduces χ as a constant, independent of polymer composition, concentration, or temperature which is contrary to experiment.[24,25] The polymer–polymer interaction parameter also depends on the thermodynamic properties of the solution[25]—indeed, Saeki et al.[26] have shown that χ can assume large positive values for the "compatible" polymers polystyrene and poly(α-methylstyrene) when in ternary solution with solvents of unequal quality. Extensions to the Flory–Huggins theory have been proposed but these have not been incorporated in the Benmouna theory.

Applications of the Benmouna theory to systems in which the solvents are of unequal solvent quality for the two polymers must be viewed with considerable circumspection as the Flory–Huggins theory cannot account for the challenge to polymer compatibility posed by such a solvent. Notwithstanding this caveat we have used the Benmouna theory to derive results for solutions with solvents of unequal quality for the two polymers.

This can be done in either of two ways. The simplest procedure is to assume that the major effect of the use of such a solvent is an increase in the effective value of the polymer–polymer interaction parameter. This implies that χ/v cannot be assumed to be small, and eq 11 must be used.

The second procedure explicitly incorporates the variation in the polymer-excluded volume parameters. We present results for two special cases only. Equation 12a gives the slow (or interdiffusion) decay rate for a ternary solution in which the solvent is poor for polymer 1 and good for polymer 2. We have assumed $v_{1\mathrm{s}} = 0$ and $v_{2\mathrm{s}} = v$, giving $v_{12} = (v + 2\chi)/2$. Ould Kaddour et al.[22] caution that higher order terms should be included in the expansion of A_2 as a function of concentration when the excluded volume parameter approaches zero. However, such a detailed analysis is not available. Equation 12b gives the slow decay rate for a ternary solution in which the solvent is poor for polymer 2 and good for polymer 1 (here $v_{2\mathrm{s}} = 0$ and $v_{1\mathrm{s}} = v$, giving $v_{12} = (v + 2\chi)/2$). In this case, neither x nor χ/v can be considered small.

$$\Gamma_\mathrm{I} = \frac{\mathbf{q}^2 k_\mathrm{B} T}{2\zeta N_1 P_1}\{R - \sqrt{(S^2 + U)}\} \tag{12a}$$

$$\Gamma_\mathrm{I} = \frac{\mathbf{q}^2 k_\mathrm{B} T}{2\zeta N_1 P_1}\{W - \sqrt{(Y^2 + U)}\} \tag{12b}$$

where

$$R = \frac{N_1P_1}{N_2P_2} + (1-x)N_1P_1\phi v + 1$$

$$S = \frac{N_1P_1}{N_2P_2} + (1-x)N_1P_1\phi v - 1$$

$$U = x(1-x)\{N_1P_1\phi v(1 + 2\chi/v)\}^2$$

$$Y = \frac{N_1P_1}{N_2P_2} - xN_1P_1\phi v - 1$$

and

$$W = \frac{N_1P_1}{N_2P_2} + xN_1P_1\phi v + 1$$

The ternary solutions formed with carbon tetrachloride approximate the conditions specified for the derivation of eq 12a.

3. Experimental Section

The dynamic light scattering experiments were performed using an apparatus which has been described previously,[27] except for a few modifications which will now be briefly mentioned. The light source is a Spectra Physics 165–08 argon ion laser operated at 488.0 or 514.5 nm. The correlator is connected to a computer which is used for remote control of the correlator and data collection and analysis. A printer and plotter are connected to the computer to provide printed output.

DLS Experiments on PS–PVME–Toluene. These experiments were similar to a set of optical tracer dynamic light scattering experiments reported by Martin.[4]

The PVME used for our PS–PVME–toluene experiments was an unfractionated sample (Gantrez M-555) kindly donated by ISP (GAF) (Australasia) Pty Ltd, Auckland, New Zealand.

Gantrez M-555 is supplied as a 50% solution in toluene with η_{sp} = 0.77 at 1% w/v in benzene. The molar mass estimated using the equation for the intrinsic viscosity of PVME in benzene at 30 °C given by Manson and Arquette[28] was 102 000 g mol^{-1}. The PVME used by Martin (Gantrez M-556) which has a slightly higher molar mass than that used here was not available for these experiments. The polystyrene was a narrow fraction with M_W = 929 000 g mol^{-1} and M_W/M_n = 1.10 obtained from Polysciences (lot no. 23590). The PVME concentration was varied, and the polystyrene mass fraction (mass of polystyrene per unit mass of solution) was kept at approximately 0.2 × 10^{-3}.

The PVME was used as received from the manufacturer. The concentration of the stock material was determined by weighing. Several diluted samples of the PVME stock were made and slowly filtered into cleaned scattering cells using 0.2-μm pore size Teflon filters (Millipore). The mass of solution in each cell was determined by weighing and the appropriate amount of a filtered stock solution of the polystyrene (PS mass fraction = 24.41 × 10^{-3}) was added to each cell to give an overall polystyrene mass fraction of 0.0002.

The mass fractions were converted to mass/volume concentrations and volume fractions by taking the partial specific volumes $\bar{v}$ of PVME, PS, and toluene at 25 °C to be 0.98 × 10^{-3} m^3 kg^{-1}, 0.916 × 10^{-3} m^3 kg^{-1}, and 1.154 × 10^{-3} m^3 kg^{-1},[29] respectively.

The measurements were made at a temperature of 25 °C.

Diffusion coefficients were obtained from second-order cumulant fits to correlation functions. Whenever it was possible, several measurements were averaged at each of two or three different angles between 27° and 120°.

As was also noted by Martin, the intensity of the light scattered by the PVME–toluene solutions was not measurably greater than that scattered by the pure solvent.

DLS Experiments on PS–PVME–Carbon Tetrachloride. The refractive index of carbon tetrachloride at a wavelength of 589 nm and temperature 20 °C is 1.460,[29] which actually provides a better refractive index match with PVME (n = 1.467) than does toluene (n = 1.496). The match is still not quite as good as that provided by o-fluorotoluene which has a refractive index of 1.468.[29]

The PVME used in these experiments was a fractionated sample, PVME fraction B2, which was prepared by methods described elsewhere.[28,30,31] The weight-averaged molar mass of a fraction prepared using the same procedure and having the same value of D_0 within experimental errors was determined by sedimentation and diffusion measurements combined with Svedberg equation as 110 000 g mol^{-1}.[31] The PS was the same as that used for the experiments in the preceding section. The carbon tetrachloride was a spectroscopic-grade solvent which was used as received.

The sample preparation technique for this series of experiments was slightly different from that used for the PVME–PS–toluene experiments. Only a limited quantity of the PVME B2 fraction was available, so the most concentrated sample was made first and then diluted as required to cover the desired concentration range. After each dilution, a small quantity (less than 100 μL) of the stock polystyrene solution (mass fraction = 3.28 × 10^{-3}) was added to maintain the total polystyrene mass fraction at 0.2 × 10^{-3}. The PVME concentration was varied from 94 to 36 kg m^{-3}. Evaporation of solvent during the course of the measurements was checked by weighing and found to be negligible.

The technique used in the DLS experiments was the same as that described in the previous section, except that a more systematic examination of the **q** dependence was made. Experiments were performed at 27°, 60°, 90°, and 120°. Several runs were made, often over a period of a few days, at each angle. Normalized correlation functions measured at a given angle under identical experimental conditions were averaged after adjusting the quadratic cumulant fit intercept of each run to the same value. The small adjustment was required to allow for the effects of minor variations in count rate and normalization on the intercept. Quadratic cumulant fits to the averaged data were then used to extract the effective diffusion coefficient and second moment at each angle.

The measurements were made at a temperature of 30 °C.

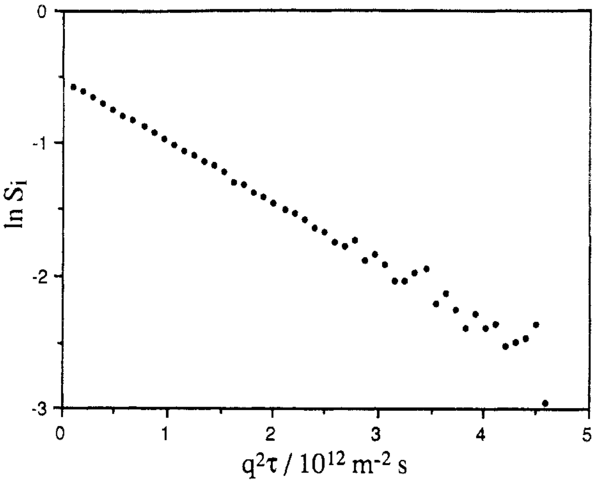

Figure 1. Typical correlation function for the PVME–polystyrene–toluene system. S_i is the experimental estimate of the normalized electric field autocorrelation function. The measurement was made at an angle of 27° with a sample time of 1.5 ms. The total polymer volume fraction was 0.144, and the polystyrene mass fraction was 0.000 18.

The depolarized component of the scattered light was weak, indicating the absence of multiple scattering.

4. Results and Discussion

DLS Experiments on PS–PVME–Toluene. The PVME volume fraction was varied from 0.056 up to 0.246 in these measurements. The variation of R_G with molar mass for PVME in toluene is not known, so C^* is difficult to calculate, but an approximate value of C^* (assumed here to be given by $M/N_A R_G{}^3$) can be estimated by the following method. The molar mass dependence of the unperturbed mean square end to end distance of PVME is given in ref 29. The expansion factor of a polystyrene molecule with the same number of monomers as 110 000 g mol^{-1} of PVME can be estimated as 1.3 in toluene at 25 °C. Assuming that the PVME used here has the same expansion factor, a C^* of 45 kg m^{-3} (or ϕ^* = 0.044) is found. This seems to be a reasonable figure because the value of C^* for 110 000 g mol^{-1} of polystyrene in benzene is around 60 kg m^{-3} and a PVME molecule has a larger radius of gyration than a polystyrene molecule of the same molar mass. If this estimate of ϕ^* is correct, the PVME is semidilute for all of the measurements on this system.

There was no sign of any significant deviation from single exponential behavior in the measured correlation functions for these samples, as is evident in Figure 1.

The values of the effective diffusion coefficient, D_{eff}, given by $\langle\Gamma\rangle/q^2$, extracted from cumulant fits to the averaged data typically varied by less than 10% over the angular range covered. Within this variation, there was a weak tendency for the lower values to occur at lower angles. Figure 2a,b shows the dependence of the measured effective diffusion coefficient on scattering vector (i.e., angle) for the two cases in which measurements were extended to angles greater than 90°. Even for these samples, the **q** dependence of the effective diffusion coefficient is weak. In the first instance this effect was neglected, so the diffusion coefficients obtained at different angles were averaged to produce the values plotted in Figure 3. Martin's results are also plotted for comparison. The scattering vector dependence of the effective diffusion coefficient will be considered in more detail later.

The values of the normalized variance of the distribution of decay rates, $\mu_2/\langle\Gamma\rangle^2$, were typically 0.05 ± 0.02. These very low values confirm that the polystyrene had a narrow molar mass distribution and that the correlation function

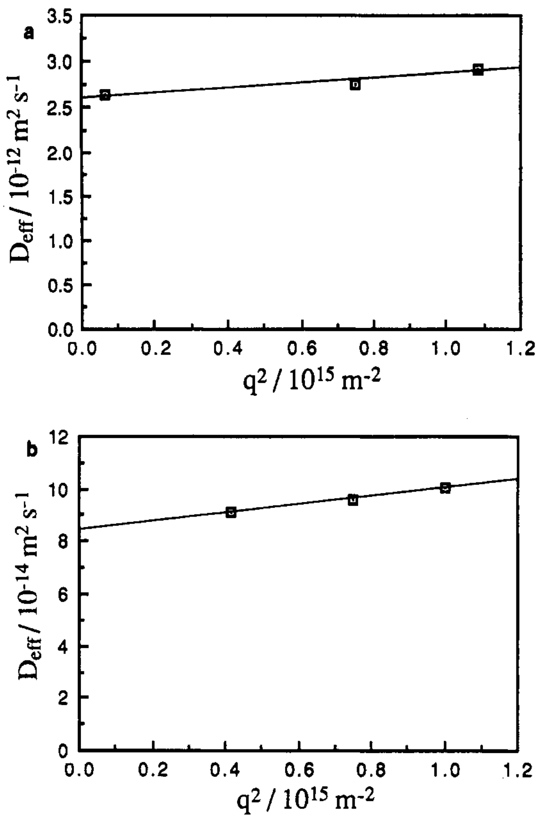

Figure 2. Scattering vector dependence of the effective diffusion coefficient, $D_{\rm eff} = \langle\Gamma\rangle/q^2$ obtained from second-order cumulant fits to DLS data for two samples of PVME–PS–toluene solutions. (a) The polymer volume fraction was 0.056. The slope of the linear fit gives R_G = 32±5 nm, using eq 15. (b) The polymer volume fraction was 0.246. The slope of the linear fit gives R_G = 43 ± 2 nm.

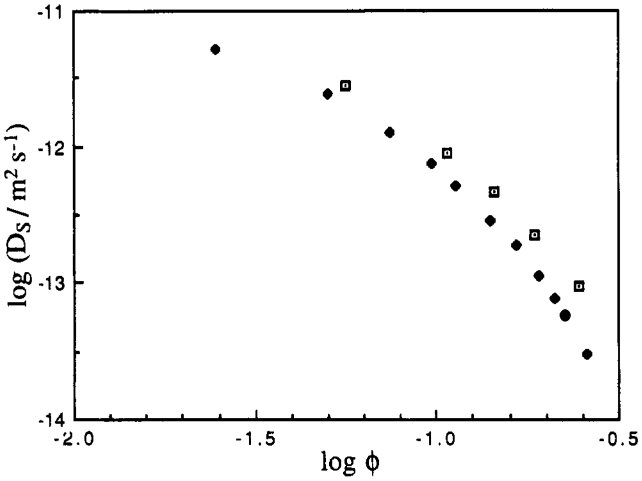

Figure 3. Concentration dependence of the polystyrene self-diffusion coefficient in PVME–polystyrene–toluene solutions obtained from DLS experiments: this work, ⊡; and Martin, ◆. The PVME and polystyrene molar masses were 102 000 and 929 000 g mol^{-1} in our experiments and 110 000 and 990 000 g mol^{-1} in Martin's.

was effectively a single exponential over the concentration range covered by these measurements.

The intensity of light scattered from a polymer in a solvent at infinite dilution is proportional to $CM(\partial n/\partial C)^2$, where $(\partial n/\partial C)$ is the refractive index increment.[32] The refractive index increment of PVME in toluene can be estimated to be $\bar{v}\Delta n$ using the approximation given by Huglin,[33] where Δn is the difference between the polymer and solvent refractive indices. At a temperature of 20 °C and a wavelength of 589 nm, the refractive indices of PVME and toluene are 1.467 and 1.496, respectively,[29] giving a refractive index increment of −0.028 cm^3 g^{-1}. The refractive index increment of polystyrene dissolved in toluene is 0.111 cm^3 g^{-1},[33] so the ratio of the intensities scattered by PS and PVME molecules with equal molar masses and concentrations in a dilute solution is approximately 10:1. The higher PS molar mass used in these experiments increases this ratio to 80:1. These considerations suggest that the scattering from PS dominates the scattering from PVME in very dilute ternary solutions, provided that the PS concentration remains greater than approximately one tenth of the PVME concentration.

The same simple arguments cannot be used to predict the ratio of intensities scattered by the two polymer components in more concentrated solutions. The scattered intensity is more generally proportional to $C(\partial\Pi/\partial C)^{-1}(\partial n/\partial C)^2$ for a solution of a polymer in a solvent.[32] As was mentioned earlier, the intensity scattered by PVME alone in toluene is small, even at high concentrations. This is not only due to the small refractive index increment. The substitution of the scaling law for $(\partial\Pi/\partial C)$ for a polymer in a good solvent into the above expression shows that the scattered intensity decreases as $C^{1-5/4} = C^{-1/4}$ as the concentration increases. Concentration fluctuations are suppressed and the scattered intensity therefore decreases. Similarly, the amplitudes of the two modes measured in a DLS experiment on a ternary system depend on thermodynamic factors and diffusion coefficients, as well as the refractive index increments.[3,13,18]

There is now considerable theoretical[13–19] and experimental[11,12] evidence that an optical tracer DLS measurement on a semidilute compatible polymer–polymer–solvent system such as the PVME–PS–toluene system studied here does in fact yield the self-diffusion coefficient of the trace component. The theoretical results of Benmouna et al.[13] show that the amplitude of the cooperative mode is zero in the limit of zero tracer concentration for an isorefractive solution of the matrix polymer. In addition, the result for the decay rate of the interdiffusion mode (eq 11 calculated for the case of unequal molar mass polymers approaches $D_s q^2$ in the limit of zero tracer concentration provided that the polymers are compatible, the solvent is good for both of them (i.e., $\chi/\upsilon < 1$) and the molecular form factor $P(q)$ is close to 1.

The compatibility of PS and PVME in toluene has been well verified.[34] Although measurements of the composition and temperature dependence of χ in PVME–PS blends,[34] concentrated benzene solution,[35] and dilute chlorobenzene[36] have been reported, no measurements of χ in semidilute solutions are available. Kwei et al.[35] found that χ was independent of benzene concentration for benzene volume fractions less than 0.2 and also that χ tended to zero in the limit of high PVME to polystyrene ratios. Shibayama et al.[24] found χ to be -2.74×10^{-2} at room temperature in PVME–polystyrene blends composed of 10% polystyrene. Klotz et al.[36] found that χ varied between −0.018 and −0.006 for dilute solutions of PS and PVME in chlorobenzene. It is therefore reasonable to assume that χ is small and negative for the samples discussed here. Cotts[2] has measured the apparent second virial coefficient $A_{2,\rm app}$ of polystyrene in the equivalent solvent PVME and toluene. Cotts found that $A_{2,\rm app}$ was positive and varied as the reciprocal of the total polymer concentration, approaching zero for semidilute solutions.

Chang et al.[11] have recently made a direct comparison of results obtained from optical tracer DLS and forced Rayleigh scattering experiments on the PVME–PS–o-fluorotoluene system. They concluded that the diffusion coefficients from optical tracer DLS were equal, within experimental errors, to the self-diffusion coefficients of the trace component measured by forced Rayleigh scattering (FRS), although the DLS values were consistently marginally higher than the FRS values. They also studied the effect of small departures from true optical tracer conditions by varying the concentration of polystyrene between 0.5 and 3.0 kg m^{-3} in their DLS measurements. Only a weak dependence on PS concentration was found, and they concluded that little error is introduced by assuming that the measured diffusion coefficient is equal to D_s in this concentration range. In the experiments reported here, the polystyrene concentration was 0.2 mg g^{-1} (approximately 0.2 kg m^{-3}), and the polystyrene concentration as a fraction of the total polymer concentration (expressed as mass fractions) varied from 0.0055 down to 0.0007. According to the conclusions of Chang et al.,[11] these concentrations are low enough for the diffusion coefficient measured here to be within 2% of the self-diffusion coefficient of the polystyrene. This conclusion is consistent with the Aven and Cohen theory since C_1 is small and $A_{2,\text{app}}$ is close to zero, as was shown by Cotts.

The **q** dependence of the effective diffusion coefficient is shown in Figure 2. It is instructive to compare our results with those of Martin.[4] Martin commented that two modes of relaxation were present in the correlation functions measured at higher angles throughout the entire concentration range, with the fast component having its smallest amplitude at the highest concentrations. Martin attributed the fast decays to internal modes. He used two different methods of data analysis to account for their effect. The first was to delete several of the initial channels from the data analysis, and the second was to fit a sum of two exponentials to the data, including a term accounting for the relaxation of the internal modes and a diffusive term. The diffusion coefficients obtained by these two methods of data reduction agreed to within 3%.

The method of data analysis used in the work presented here, in contrast to Martin's emphasizes the short time data in the calculation of the effective diffusion coefficient, $D_{\text{eff}} = \langle \Gamma \rangle / \mathbf{q}^2$. Martin's data analysis method effectively eliminated the **q** dependence by calculating the diffusion coefficient from the long time part of the correlation function rather than the initial slope which contains small, rapidly decaying contributions due to internal relaxations. When measured at sufficiently long times so that the internal modes have decayed completely, Martin's diffusion coefficients are equivalent to the zero scattering vector limit of the effective diffusion coefficients measured here.

Equations 7 and 11 indicate that the effective diffusion coefficient, $\langle \Gamma \rangle / \mathbf{q}^2$, measured in an optical tracer DLS experiment should be **q** dependent unless $P(\mathbf{q})$ is equal to 1. Note that $P(\mathbf{q})$ may differ appreciably from 1 before the amplitudes of the internal modes become sufficiently large for the internal modes to be resolvable as a separate decay process. For example, even when $P(\mathbf{q})$ has dropped to 0.75, the amplitude of the first significant internal mode is still only 0.01 in dilute solutions.[20]

The **q** dependence of the effective diffusion coefficient in ternary systems can be discussed in terms of the theoretical treatment of Benmouna.[13] Equation 7 can be simplified by assuming that

$$\frac{1}{P(\mathbf{q})} = 1 + \frac{1}{3} R_G^{\,2} \mathbf{q}^2 \tag{13}$$

which is valid for $\mathbf{q}R_G < 1$, independent of particle shape.[20] Substitution of this equation into eq 7 gives

$$D_{\text{eff}} = D_s\left(1 + \frac{1}{3} R_G^{\,2} \mathbf{q}^2\right) \tag{14}$$

which predicts a linear dependence of D_{eff} on $\mathbf{q}^2$. This analysis is equally valid when applied to eq 11 in the limit as x approaches zero, so the difference between the PS and PVME molar masses is inconsequential. Only the PS molar mass and $P(\mathbf{q})$ are relevant. Figure 2 shows that we do indeed obtain a linear lot within the range of scattering vectors studied. The radius of gyration obtained from the slope of equation 14 is 20 ± 4 nm. This value appears to be unreasonably small. The radius of gyration of polystyrene with M = 929 000 g mol^{-1} in toluene at infinite dilution is 45 nm (using a relationship given by Appelt and Meyerhoff[37]). The radius of gyration of the same molar mass polystyrene in cyclohexane at the θ temperature is of the order of 30 nm.[38] Two factors are likely contributors to this discrepancy; hydrodynamic interactions and an underestimation of the initial decay rate of the dynamic structure factor.

Equation 5 shows that the self-dynamic struture factor of the visible polymer (component 1) is obtained when component 2 is isorefractive with the solvent and the polymers are compatible and the solvent is good for both polymers or in the limit as x approaches zero. This corresponds to the disappearance of the "interaction" term in the random-phase approximation, (eqs 3 and 4 of ref 13) so that the full dynamic structure factor reduces to the bare (or self) dynamic structure factor of component 1. Hydrodynamic interactions are completely absent in Benmouna's treatment, leading to the appearance of Rouse mobilities in the final results. However, it is reasonable to assume that the bare dynamic structure factor is also obtained in the small x limit when hydrodynamic interactions are included. Equation 17 is identical in form to the result for the first cumulant of a polymer chain in the free-draining approximation at infinite dilution, although in the present application, the friction factor ζ should be seen as the friction factor for a polymer moving through a ternary solution of concentration C and polymer composition x. The **q** dependence of the effective diffusion coefficient at infinite dilution has been calculated, taking hydrodynamic interactions into account, by Burchard et al.,[39] who obtained

$$D_{\text{eff}} = D_s(1 + K R_G^{\,2} \mathbf{q}^2) \tag{15}$$

where K is a constant depending on polydispersity, chain stiffness, and to a lesser extent, excluded volume. For a monodisperse solution, K has been calculated to be 0.173, far less than the value of 0.33 found for the free-draining case. We will assume that the self-dynamic structure factor of a large PS molecule in our PVME–toluene solutions has the same form as that obtained in dilute solution and that hydrodynamic interactions are not screened at the concentrations studied here. Support for our assumption of the absence of hydrodynamic screening is provided by Martin's[40] study of internal modes in PS–PVME–toluene solutions, with PS and PVME molar masses of 48 000 000 and 110 000 g mol^{-1}, respectively. Martin found that the first cumulant scaled as $\mathbf{q}^3$, indicative of Zimm dynamics (no hydrodynamic screening) rather than Rouse dynamics (free-draining) over a wide range of PVME matrix concentrations.

The second reason for our low values of R_G is that our values of D_{eff} are probably underestimates of the values that would be obtained from the true initial slope of the correlation function. It is notoriously difficult to obtain an accurate estimate of the zero time first cumulant when rapidly decaying components are present. In real measurements, the value of K therefore depends on the experimental time scale. This problem has been discussed by Bantle et al.,[41] who plotted the experimental value of K against correlator sample time, showing that the apparent value of K falls with increasing sample time. The value of K is estimated to be 0.10 ± 0.01 for the finite time scales used in this study.

We can now estimate the radius of gyration of the polystyrene from the observed $\mathbf{q}$ dependence of the effective diffusion coefficient using eq 15 with K taken as 0.10. The slopes observed for the three cases in which the data were of sufficient quality (including those shown in Figure 2) are consistent with an R_G of 36 ± 6 nm. The data are neither detailed nor precise enough to allow a more definite conclusion to be reached, but it appears that the radius of gyration of polystyrene in our PVME–PS–toluene solutions is probably only slightly less than it is in the pure solvent.

Nose[42] has derived expressions for the radius of gyration of a probe molecule in ternary solutions consisting of a dilute probe of degree of polymerization N in a semidilute solution of a matrix polymer of degree of polymerization P. The solvent was assumed to be equally good for the polymers. The small χ case treated by Nose is appropriate to the PVME–PS–toluene solutions. Nose's results[42] show that the radius of gyration of the probe molecule is expected to decrease as ϕ increases, with the onset of the change occurring at lower values of ϕ as N/P increases until N/P reaches 10. The change in R_G is predicted to be small and asymptotes to a constant value which depends on χ. As χ approaches zero, the change in dimensions increases and approaches the behavior expected of a bimodal distribution of chemically identical polymers. Our results for the toluene solutions are consistent with these considerations since $R_G/R_G(0)$ is predicted to be approximately 0.8 for the conditions $\chi = 0$, $C = C^*$ and $N/P = 10$.

We will now discuss the concentration dependence of the polystyrene self-diffusion coefficients shown in Figure 3.

The value of D_0 for polystyrene in toluene at zero PVME concentration can be calculated from the relation between D_0 and M given by Appelt and Meyerhoff[37] for polystyrene in toluene at 20 °C. With a temperature and viscosity temperature correction to 25 °C, D_0 is found to be 1.43×10^{-11} m^2 s^{-1} giving $\log D_0$ the value -10.85. This is consistent with the low concentration data in Figure 3.

The systematic difference between the results of Martin and those of this work almost certainly results from the difference between the molar masses of the polymers used in the two sets of experiments. Both the PVME and the PS used in the work presented here had slightly lower molar masses than the polymers used in Martin's work. These molar mass differences would both tend to increase the values of D_s reported here compared to Martin's results.

If the estimate of C^* given previously is correct, all of the data points in Figure 3 were measured in the semidilute regime for the PVME matrix. (Note that the polydispersity of the PVME introduces additional uncertainty into our determination of C^*). The molar mass of the PS is much higher than the matrix (PVME) molar mass, so reptation is not expected to be the dominant mechanism for the diffusion of the PS tracer molecules. Instead, Martin has suggested that the polystyrene molecules diffuse according to the Stokes–Einstein equation with the macroscopic solution viscosity being the dominant influence on the PS self-diffusion. If the hydrodynamic radius of the polystyrene remains constant as the PVME concentration is increased, the product of the polystyrene self-diffusion coefficient and the macroscopic viscosity of the solution should be independent of concentration, assuming that the polystyrene diffuses by the Stokes–Einstein mechanism. Martin plotted his data in this form and found that ηD_s remains relatively constant up to a volume fraction of 0.14 where it begins to rise steadily. Martin interpreted this upturn as being due to either a crossover of the dominant mechanism for diffusion from Stokes–Einstein diffusion to reptation or a concentration dependent collapse of the hydrodynamic radius of the polystyrene molecules. Our results for R_G determined from the $\mathbf{q}$ dependence of D_{eff} indicate that no dramatic contraction of the polystyrene occurs over the range of concentrations studied here. This gives support to Martin's suggestion that the change in the behavior of ηD_s is due to a crossover of the diffusion mechanism from Stokes–Einstein diffusion to reptation.

DLS Experiments on PS–PVME–Carbon Tetrachloride. An interesting phenomenon was observed when the polystyrene solution was mixed with the PVME solutions during sample preparation. Within an hour of the addition of the polystyrene–carbon tetrachloride solution, "fingers" of polystyrene-rich solution could be seen flowing slowly upward from the bottom of the cell. This was first observed when a cell was placed in the path of the unfocused laser beam to check whether the polystyrene and PVME solutions had mixed thoroughly. At the tips of the fingers, cloudiness due to phase separation could be seen. In the most concentrated solution, the fingers persisted for about 24 h. Once the fingers had dissipated, there were no signs of any cloudiness or nonuniform distribution of polystyrene in the solutions. However, the phase instability of these solutions restricted the range of polymer concentration amenable to measurment. From our observation of phase separation, we can conclude that the equivalent solvent formed from PVME and carbon tetrachloride acted as a poor solvent for polystyrene.

A similar "fingering" effect has been observed before in ternary polymer solutions. Preston et al.[43] observed structured flows in several different multicomponent solutions containing polymers, one of which was the poly(vinylpyrrolidone)–dextran–water system. The structured flows were observed when a dextran solution was layered on top of a similar solution containing a small additional concentration of PVP, even though gravitationally stable initial conditions had been established by placing the more dense solution at the bottom of the cell. McDougall and Turner[44] and Comper, Checkley, and Preston[45] have presented detailed explanations of the effect in terms of convection due to the formation of gravitationally unstable regions near the boundary between the two solutions. Their explanations propose that cross-diffusion effects (i.e., diffusion of one component due to a gradient of another) are responsible for the creation of the instabilities. These structured flows should be distinguished from the "viscous fingers" discussed elsewhere[46] that originate from large pressure gradients.

Correlation functions measured in DLS experiments on the highest and lowest concentration samples are shown in Figure 4a,b. A feature of the data that is immediately apparent is the nonexponentiality of the correlation function measured at the higher concentration. The values of the normalized variance of the distribution of decay rates $\mu_2/\langle\Gamma\rangle^2$, measured at 27° (the most precise values), fell from 0.25 to 0.09 as the PVME concentration decreased. The nonexponentiality of the correlation functions measured at higher concentrations is not attributed to the appearance of the collective mode for the following reasons. Firstly, the polystyrene content represented by x was too small. A value of x of at least 0.5 is required for the amplitude of the collective mode to become measurable.[17] Also, if a collective mode were to appear, it would have a faster decay rate than the interdiffusion mode. The correlation functions measured in these experiments showed a general curvature of the log plots rather than

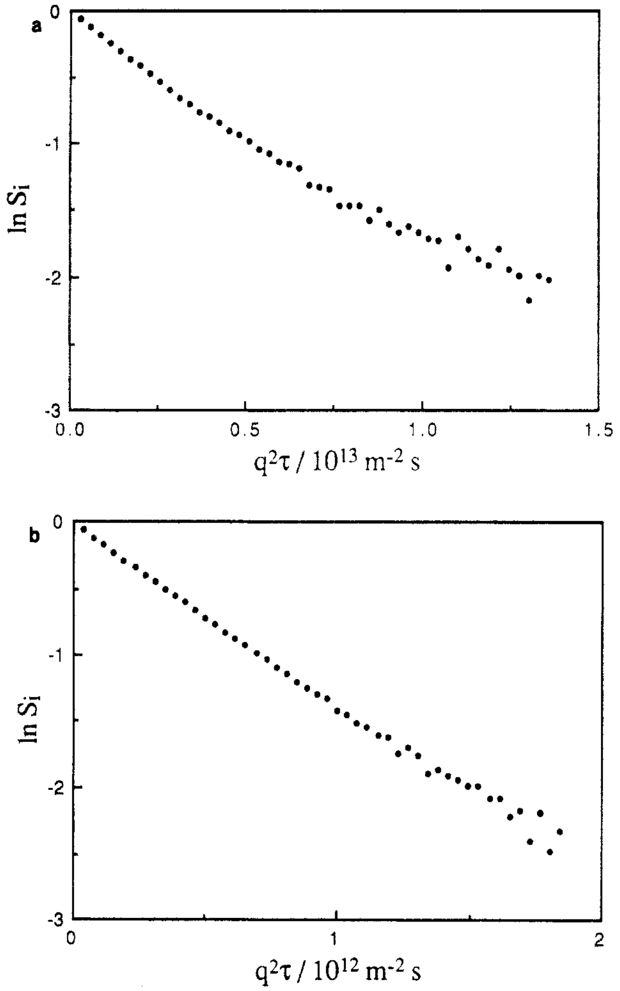

Figure 4. DLS data obtained for the PVME–PS–carbon tetrachloride system. (a) The total polymer volume fraction was 0.092, and the polystyrene mass fraction was 0.000 21. The correlation function shown here is an average of four correlation functions measured at an angle of 90°, each having a base line B for the unnormalized photocount correlation function of about 4.3×10^4. Note that the intercept was adjusted before averaging the correlation functions. (b) The total polymer volume fraction was 0.035. Seven runs measured at an angle of 27°, each having a base line $B = 4 \times 10^5$ were averaged to produce this correlation function.

the onset of a fast mode at short times. The decay rate of the collective mode would be expected to increase while that of the interdiffusion mode would be expected to decrease at higher concentration, increasing the resolution of the two modes. This was not obeserved in our experiments. The most likely cause of the nonexponentiality of the correlation functions is very slow viscoelastic relaxation of the solution. This phenomenon has also been reported by Brown et al.[47] who have demonstrated that viscoelastic relation is more significant in poor solvents. Wang[48] has investigated the effects of viscoelastic relaxation on dynamic light scattering measurements. Alternative, less likely, causes of the nonexponentiality are residual polystyrene aggregation or the effect of slow fluctuations associated with the proximity of the cloud point in the high concentration samples.

The **q** dependence of the effective diffusion coefficient ($D_{\rm eff} = \langle\Gamma\rangle/\mathbf{q}^2$) for the highest concentration sample is shown in Figure 5. Similar plots were obtained for the other samples, and the results of linear fits to these plots are given in Table I. Assuming that eq 15 with $K = 0.1$ governs these observations we find the apparent radius of gyration of the polystyrene coils to be approximately 10% smaller than for the toluene solutions. Such a slight reduction is not significant given the uncertainties involved. Nose's theory for the concentration and excluded volume dependence of R_G does not apply to the solutions formed with carbon tetrachloride since solvents of unequal solvent quality for the polymers are excluded. However, if we were to assume that the major effect of the solvent would be to increase χ then the theory predicts the reduction in $R_G/R_G(0)$ to be small for concentrations $\phi/\phi^* < 5$. This is consistent with our results.

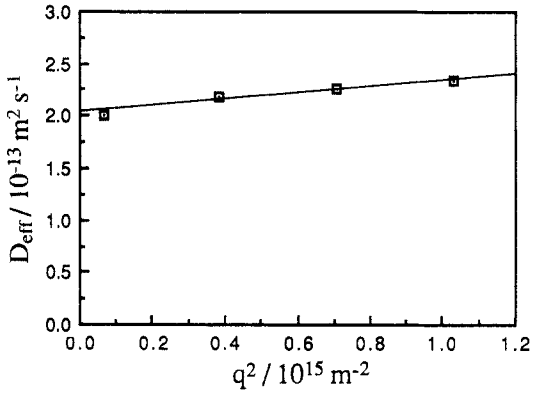

Figure 5. Scattering vector dependence of $D_{\rm eff}$ for a PVME–polystyrene–carbon tetrachloride sample. The polymer volume fraction for this sample was 0.092.

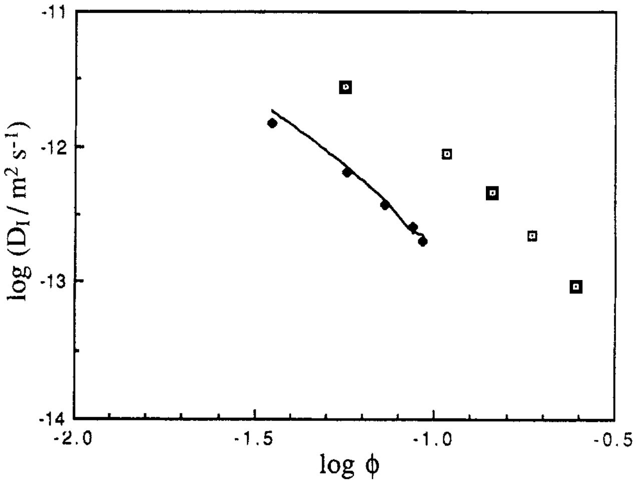

Figure 6. Concentration dependence of D_I (eq 3) for the PVME–PS–carbon tetrachloride system (◆). The curve is an interpolation of points calculated from eq 12 as described in the text. The D_s values obtained for the PVME–PS–toluene system are also shown (▣) for comparison. In both cases, the PS molar mass was 929 000 g mol^{-1}. In the toluene measurements the PVME molar mass was 102 000 g mol^{-1}, and in the carbon tetrachloride measurements the PVME molar mass was 110 000 g mol^{-1}.

Table I. Results of Linear Fits to the Scattering Vector Dependence of the Effective Diffusion Coefficient for PVME–PS–Carbon Tetrachloride

polymer vol fraction, ϕ	intercept $D_I/10^{-13}$ m^2 s^{-1}	slope/10^{-29} m^4 s^{-1}	R_G/nm (estimated)
0.035	14.8	12.4	29
0.057	6.55	5.36	29
0.072	3.80	4.67	35
0.087	2.55	2.79	33
0.092	2.02	3.16	40

The values of $D_{\rm eff}$ extrapolated to zero angle are plotted against concentration in Figure 6. The results of experiments on the PVME–PS–toluene system are also shown for comparison. Also shown is a theoretical curve which will be discussed later.

The value of D_0 for the 929 000 g mol^{-1} polystyrene alone in carbon tetrachloride at 0.2 mg g^{-1} was also measured by DLS. These measurements were performed at low angles (17° and 27°) because the low scattered intensity combined with shorter sample times made measurements at higher angles very difficult. Assuming that this measurement gives a good approximation to the value of the diffusion coefficient at infinite dilution, we found D_0 to be 1.02×10^{-11} m^2 s^{-1} (i.e., log D_0 was −10.99).

The values of D_I obtained in these experiments clearly differ from those obtained for the PVME–PS–toluene system. Several factors contribute to differences between the two sets of experiments. The temperature and solvent viscosity have been changed from 25 °C and 5.516×10^{-4} Pa s in the case of the PVME–PS–toluene experiments to 30 °C and 8.43×10^{-4} Pa s in these experiments. In addition, the unfractionated PVME was used in the previous experiments, while those discussed here used PVME fraction B2. The combined effects of these factors are still insufficient to explain the large difference seen in Figure 6. The temperature and viscosity effects can be approximately accounted for by multiplying the values of D_s by the appropriate ratios of temperatures and solvent viscosities. (This assumes that the hydrodynamic radius of PS in carbon tetrachloride is the same as it is in toluene.) The net effect would be an upward shift of log D_I for the carbon tetrachloride data by only 0.18 units. The infinite dilution values of the diffusion coefficients of fraction B2 and the unfractionated PVME in the same solvent were virtually identical, suggesting that their average molar masses were equal. Therefore, the lower diffusion coefficients are unlikely to have been caused by the use of fractionated rather than unfractionated PVME as the matrix polymer.

If the mechanism of the polystyrene diffusion is assumed to be Stokes–Einstein diffusion, as it was for the solutions made with toluene, and it is assumed that D_I is equal to D_s in these measurements, there are two possible explanations for the lower diffusion coefficients in the PVME–PS–carbon tetrachloride system. The first is an increase in the viscosity of the matrix polymer solution, and the second is an increase in the hydrodynamic radius of the polystyrene. A large increase in the viscosity of the PVME–carbon tetrachloride solutions over that of the PVME–toluene solutions could be expected to be accompanied by a decrease in the PVME self-diffusion coefficient. However, D_s values for PVME in two different solvents agreed well after temperature and solvent viscosity corrections.[31] The radius of gyration obtained from the q-dependence of D_{eff} for PS in PS–PVME–carbon tetrachloride solutions was not significantly different from that for PS in PS–PVME–toluene solutions, so a change in the size of the PS must also be ruled out as a possible reason for the low D_I values in carbon tetrachloride. This leads to the conclusion that D_I is not equal to D_s in these experiments.

The significant reduction in the observed value of the effective diffusion coefficient must be due to the use of the solvent carbon tetrachloride. The polystyrene concentration (C_1) was sufficiently small for the Aven and Cohen theory (eq 3) to apply, and these data give $A_{2,\text{app}}$ as approximately -2×10^{-3}. Moreover, this value is only slightly dependent on total polymer concentration. There are no independent data available for the apparent second virial coefficient of polystyrene in the equivalent solvent PVME and carbon tetrachloride. However, Aven and Cohen have used dynamic light scattering to investigate the diffusion of polystyrenes dissolved in 148 000 molar mass polydimethylsiloxane (PDMS) and tetrahydrofuran (THF). They ensured that the total polymer concentration was 5 times overlap and varied the polystyrene concentration up to 3.5×10^{-3} g mL^{-1}. They found that $A_{2,\text{app}}$ for their system was dependent on the polystyrene molar mass over the molar mass range investigated. Extrapolating their results to a polystyrene molar mass of 929 000 we predict $A_{2,\text{app}}$ to be approximately -1.5×10^{-3} for the system PS–PDMS–THF. This value is not remarkably different from that found above for the PS–PVME–carbon tetrachloride system. Also, the insensitivity of $A_{2,\text{app}}$ to polymer concentration at concentrations greater than overlap has been predicted by Stockmayer[49] and independently by Nose[42] and has been experimentally verified for polystyrenes dissolved in PVME and toluene,[2] PMMA, and toluene[50] and in PMMA and benzene.[51]

Equation 11 can be used to fit our data for D_I and provide a value of the parameter χ/v. The curve in Figure 6 was obtained by assuming that the toluene measurements, corrected for temperature and solvent viscosity differences, gave a good estimate of D_s for PS in PVME–carbon tetrachloride solutions. With $\phi^* = 0.044$, we find that the best fit to our data is obtained with $\chi/v = 2.1$. This value may be compared with the result $\chi/v = 0.19$ obtained by Giebel et al.[7] for PMMA–PDMS–THF solutions at concentrations below the cloud point concentration.

This analysis must be treated with caution. Our large value of χ/v and the observed phase separation on addition of PS indicate that our solutions may be near the cloud point. The inadequacy of the random-phase approximation, and consequently Benmouna's theory, near the cloud point has been noted previously.[17] Benmouna et al.[13] have discussed phase separation in ternary polymer solutions in terms of their theory. They concluded that the theory was only approximate since it gave inconsistent predictions regarding the spinodal. According to the Flory–Huggins theory, ternary polymer solutions can suffer phase separation in one of two ways. Both polymers could precipitate, in which case the mutual diffusion coefficient between the polymers and the solvent would approach zero. This would occur if the solvent were "equally poor" for the polymers. Alternatively, the solution could separate into two phases, one rich in the first polymer the other rich in the second, in which case the interdiffusion coefficient would approach zero. This would occur if the polymers were incompatible. Giebel et al.[7,8] have also discussed this effect and have demonstrated that D_I is significantly less than D_s in solutions of PDMS/PMMA and various solvents. Indeed, Giebel et al. were able to verify the dependence of D_I on x in eq 5. For these systems the solvents were equally good for both polymers and the polymer polymer interaction parameter was positive, so D_I was expected to be less than D_s.

According to the Flory–Huggins theory of polymer solutions the compatibility of two polymers in a ternary solution is governed by the effective polymer–polymer interaction parameter χ, irrespective of the polymer–solvent interaction parameters χ_{1s} and χ_{2s}. However, Patterson and his co-workers have shown that polymer compatibility in ternary solutions is also dependent on the difference between the solvent affinities for the two polymers $\Delta\chi$ ($= \chi_{1s} - \chi_{2s}$). Thus, the compatible polymers polystyrene and PVME form single-phase ternary solutions in the solvents benzene, toluene, and tetrachloroethene for which $\Delta\chi$ is less than 0.15 but two-phase solutions in the solvents chloroform, dichloromethane, and trichloroethane for which $\Delta\chi$ is greater than 0.45.[25] Chloroform is a particularly interesting case since it is a good (but not equally good) solvent for the polymers, as was pointed out previously by Al-Saigh and Munk.[52] A brief summary of the data presented by Patterson et al. is given in Table II. Notice that the difference between the carbon tetrachloride affinities for PVME and PS is 0.25, so carbon tetrachloride satisfies neither of Patterson's criteria. Nevertheless, we believe that the most likely reason for the anomalous behavior of ternary solutions

Table II. Solvent–Polymer Interaction Parameters Taken from Ref 25

solvent	solvent–polystyrene interaction param	solvent–PVME interaction param	$\Delta\chi$
benzene	0.26	0.15	0.11
toluene	0.19	0.14	0.05
tetrachloroethene	0.36	0.34	0.02
chloroform	0.13	–0.92	1.05
dichloromethane	0.34	–0.7	0.73
trichloroethene	0.19	–0.26	0.45
carbon tetrachloride	0.29	0.06	0.23

formed with carbon tetrachloride is a decrease in the polymer compatibility caused by the unequal solvent quality.

5. Conclusions

We have investigated PVME–PS–toluene solutions and PVME–PS–carbon tetrachloride solutions using dynamic light scattering experiments conducted under "optical tracer" conditions, in which one solute (PVME) has its refractive index matched by the solvent and the other solute is present only as a dilute tracer.

Three interesting features of the data have been discussed. First, the nonexponential nature of the autocorrelation function of the light scattered from the solutions formed with carbon tetrachloride has been ascribed to the enhanced contribution of the effects of viscoelastic relaxation in poor solvents.

Second, the large discrepancy between the measured diffusion coefficients of the polystyrene obtained from the solutions formed with toluene and those formed with carbon tetrachloride have been accounted for by citing the increased polymer polymer interaction parameter in solvents with unequal polymer affinities. the theories of Benmouna et al.[13] and Cohen et al.[18,19] have been used to interpret the results.

Third, the radius of gyration of polystyrene in the ternary solutions was discussed. The radius of gyration of the polystyrene was obtained from the scattering vector dependence of the effective diffusion coefficient. After compensating for the dependence of the results on the experimental time scale, we found values for R_G that were about 80% of the infinite dilution values, in agreement with the theoretical results of Nose.[42]

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