Effect of Solvent Quality on the Diffusion of Polystyrene Latex Spheres in Solutions of Poly(methyl methacrylate)

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ABSTRACT: Dynamic light scattering has been used to study the diffusion of polystyrene (PS) latex spheres (≈0.2 μm radius) in poly(methyl methacrylate) (PMMA) solutions at 25 °C. The weight-average molecular weight of the PMMA was 350 000. The sign and magnitude of the deviations from the Stokes−Einstein (SE) equation varied dramatically with solvent quality. Positive deviations from SE behavior ($\eta D_{\text{sphere}}/\eta_0 D_0 > 1$) were observed in good solvents for PMMA, such as dimethylformamide (DMF) and tetrahydrofuran (THF). We argue that these positive deviations are a result of a layer of solution locally surrounding the latex spheres that is rich in solvent and deficient in PMMA. This "depletion layer" is likely caused by a combination of entropic repulsion between the matrix PMMA and the latex spheres, and most importantly the immiscibility of PMMA and PS. A *negative* deviation ($\eta D_{\text{sphere}}/\eta_0 D_0 < 1$) by almost of factor of 3 from the SE equation was observed in a dioxane−water mixed solvent, which is a Θ-solvent for PMMA at 25 °C. PMMA adsorption onto the latex spheres is argued to occur under these unfavorable solvent conditions. At high matrix concentrations, entanglements of the adsorbed PMMA with free PMMA in solution likely occur. A very slow relaxation mode, in addition to the mode associated with sphere diffusion, was present in the CONTIN analyses of the PMMA/PS latex/dioxane−water system. It is possible that this mode is due to PMMA clusters, or less likely, bridged PS latex moieties.

Introduction

The diffusion of spherical particles through polymer solutions has received considerable attention.[1−25] The systems studied have typically been ternary, containing a solvent, a dissolved matrix polymer, and dispersed spherical particles present in trace amounts. The spheres have usually been polystyrene latex or silica, with radii ranging from 200 Å to 1.5 μm. These spherical particles have been referred to as "probes" because their diffusion coefficient may provide information about the microstructure and dynamics of the polymer solution in which they are dispersed.

The diffusion coefficient D of a sphere of radius R dispersed in a medium of viscosity η has ordinarily been described in terms of the Stokes−Einstein (SE) equation

$$D_{\text{sphere}} = kT/6\pi\eta R \qquad (1)$$

Implicit in the derivation of the SE equation is the assumption that the dispersing fluid is a continuous medium. Consequently, the SE equation has typically been applied to systems of noninteracting spheres diffusing through a solvent of small molecules. Spherical probe diffusion through polymer solutions need not follow SE behavior. In these solutions the solvent continuum assumption may not be satisfied, or a host of other possibilities may cause the failure of the SE equation. Indeed, deviations from SE behavior have been reported for numerous matrix polymer/sphere/solvent systems.[2−4,7−9,12−14,18,20,22−24] However, adherence to the SE equation for spherical particles in polymer solutions has been reported in some systems.[6,10,17−19,21]

We have previously reported on the diffusion of highly cross-linked polystyrene (PS) latex spheres of 0.2-μm radius in linear polystyrene/dimethylformamide (DMF) solutions.[19] Two matrix polymer molecular weights (2.15×10^5 and 1.1×10^6) were employed, and matrix concentrations were varied from dilute to far into the semidilute regime. Adherence to the SE equation was observed for both matrix molecular weights at all concentrations studied. The linear PS/PS latex/DMF system is unique in that it is the only system reported where the matrix and probe are chemically similar. In subsequent work, diffusion of the same spheres through solutions of poly(vinyl methyl ether) (PVME) resulted in sphere diffusion coefficients that exceeded those predicted by the SE equation.[20] Deviations were most extreme around $c = c^*$, where c^* is the matrix overlap concentration, followed by a return to SE behavior at higher concentrations. SE behavior was recovered, it was argued, because the matrix concentration was sufficiently high for chain entanglements to be "effective". Under these conditions, the dynamics of the spheres are governed by the relaxation of mesh entanglements, causing the matrix to appear as a continuum to the spheres. Consequently, the return to SE behavior at high concentrations was rationalized. However, these arguments do not explain the behavior observed in the aforementioned linear PS/PS latex/DMF system where the SE equation was followed at all matrix concentrations studied. It is apparent that more research needs to be performed in order to obtain a better understanding of the dynamics within these complex systems.

In this paper, the diffusion of the same latex spheres, studied by quasi-elastic (dynamic) light scattering, through solutions of poly(methyl methacrylate) (PMMA) is reported. The solvent, as opposed to the molecular weight of the matrix polymer, is varied. Three different solvents ranging from thermodynamically good solvents with respect to the matrix PMMA, to a Θ solvent have been employed. It is shown that the solvent quality with respect to the matrix polymer, as well as the probe particle, is a crucial parameter in determining how the spheres behave in the context of the Stokes−Einstein equation.

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Experimental Section

Materials. The three solvents used in this report are tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and a dioxane−water (85:15 vol %) mixed solvent. The THF was spectroscopic grade and obtained from Fisher Scientific. The anhydrous DMF was obtained from Aldrich Chemical Co. The dioxane−water solvent was prepared using distilled, deionized water and spectroscopic grade dioxane obtained from Fisher Scientific.

The preparation of the highly cross-linked polystyrene latex spheres has been described elsewhere.[19,26] These latex spheres were thoroughly dried and dispersed in the three solvents by brief sonication.

The PMMA matrix polymer was obtained from Polysciences, Inc. It had a vendor-advertised molecular weight (M_w) of 350 000 and a polydispersity index of 1.06. The PMMA sample was reprecipitated several times from THF with absolute ethanol and then dried in a vacuum oven at 60−110 °C.

All solutions for dynamic light scattering (DLS) studies were prepared by weight. The appropriate amount of reprecipitated, dry matrix polymer was weighed out into dust-free vials. The solvent, filtered through a 0.22-μm poly(tetrafluoroethylene) filter, was then added by mass to give the desired polymer concentration. The matrix polymer was allowed to dissolve, which in most cases required 1 or 2 days. Since the dioxane−water solvent is a Θ-solvent for PMMA at 25 °C,[27] it was necessary to mechanically agitate this PMMA/solvent mixture with a magnetic stir bar at about 30 °C to afford dissolution. After dissolving the matrix polymer, solutions were filtered through 0.22- or 0.45-μm PTFE filters into dust-free cylindrical sample cells. A few drops of a stock dispersion of dilute polystyrene latex spheres in the appropriate filtered solvent was added to the sample cell followed by brief sonication. The final concentration of the latex spheres was on the order of 10^{-5} g/mL. The PMMA solutions used in viscosity measurements were also prepared by weight with the appropriate filtered solvent.

Methods. (A) Dynamic Light Scattering. A 2-W argon ion laser (Spectra Physics 164) operating at a wavelength of 5145 Å was used in determining diffusion coefficients of the polystyrene latex spheres. The cylindrical sample cells were immersed in a refractive index matching fluid thermostated at 25.0 ± 0.2 °C. No attempt was made to match the refractive indices of the matrix polymer with any of the solvents. Rather, the large difference in size between the PS latex spheres (radius $\approx$ 0.2 μm) and the linear PMMA ($R_g \sim 0.02$ μm), as well as the relatively small refractive index increments at 25 °C for PMMA in the three solvents (0.055−0.087 mL/g) allowed the diffusion of the latex spheres to be studied. The detector was a Pacific 126 photometer. After detection, the scattered light was analyzed by a Langley-Ford Model 1096 correlator. The normalized, base-line-corrected homodyne correlation function, $C(\tau)$, was analyzed by two methods. Data from all systems, which were collected at a minimum of four angles ranging from 45° to 120°, were analyzed by the Laplace inversion computer program CONTIN.[28] The program typically yielded a narrow unimodal distribution, using the data from the THF and DMF solvent systems, from which an average decay rate Γ was extracted. These data were also analyzed by the cumulant method where Γ was computed from a second-order fit. The dioxane−water system was not analyzed by the cumulant method because of the bimodal nature of the CONTIN decay rate distributions associated with this system. In all cases, diffusion coefficients were computed from the Γ vs q^2 plots, which were quite linear with intercepts close to zero. Standard errors in the slope were typically between 1 and 10%. In a few cases, the errors approached 15%.

(B) Viscosity. All viscosity measurements were made at 25.0 ± 0.02 °C using a Cannon-Ubbelohde dilution viscometer.

Results

No sphere aggregation at the latex concentrations encountered in this investigation was observed in the ternary THF and DMF solvent systems. This was evidenced by angle-independent diffusion coefficients and by the quality of the correlation function at all scattering angles, even after allowing samples to stand for weeks. A limited amount of sphere bridging may have occurred in the PMMA/PS latex/dioxane−water system, which will be discussed later in the report. No appreciable swelling of these latex spheres in DMF, THF, or dioxane occurs as evidenced from electron spin resonance experiments.[29]

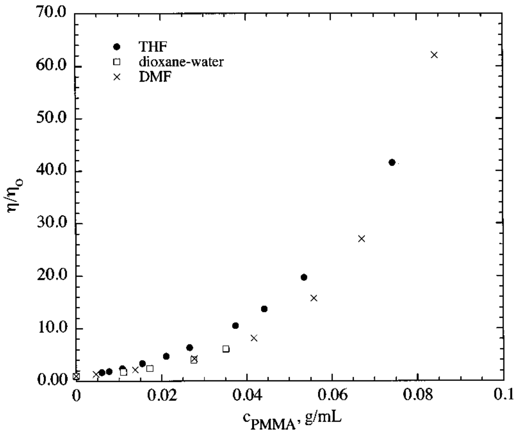

Figure 1. Concentration dependence of the zero-shear relative viscosity for PMMA of molecular weight 350 000 in THF, dioxane−water, and DMF solvents at 25 °C.

Table 1. Intrinsic Viscosity [η], Overlap Concentration c^* ($\approx 1/[\eta]$), and Latex Sphere Scaling Parameter v for Solutions of PMMA of Molecular Weight 350 000 at 25 °C[a]

solvent	[η] (mL/g)	c^* (g/mL)	v
THF	83 ± 1	0.012	0.88 ± 0.05
DMF	57 ± 3	0.018	1.28 ± 0.04
dioxane−water	47 ± 4	0.021	0.97 ± 0.05

[a] Scaling parameter v computed from a nonlinear least-squares fit to eq 4.

Relative viscosity vs matrix polymer concentration plots appear in Figure 1 for the PMMA/solvent systems. Since diffusion measurements were typically performed at different concentrations than the viscosity measurements, least-squares polynomial fits were made on the viscosity data for interpolation.

The intrinsic viscosity [η] of the matrix polymer at 25 °C in each solvent was determined by double extrapolation to infinite dilution of the reduced and inherent viscosities. The values of [η] appear in Table 1. The uncertainties associated with [η] are the standard errors in the y-intercept of the reduced viscosity plots, which are about an order of magnitude larger than the standard errors associated with the inherent viscosity plots. The intrinsic viscosity can be taken as a measure of solvent quality, with large intrinsic viscosities corresponding to good solvents. Consequently, in this report THF is the most favorable solvent for the PMMA, while the dioxane−water Θ-solvent is the least favorable. c^* was computed from the intrinsic viscosity as $1/[\eta]$. The values appear in Table 1.

DLS data from the ternary systems were gathered at least at four of the following angles: 45°, 50°, 60°, 70°, 90°, and 120°. No dependence of the diffusion coefficient on angle was present. Diffusion coefficients from the PMMA/latex sphere/THF system calculated by the cumulant and CONTIN methods agreed well. In the ternary DMF system, the CONTIN values tended to exceed those calculated by the cumulant method by

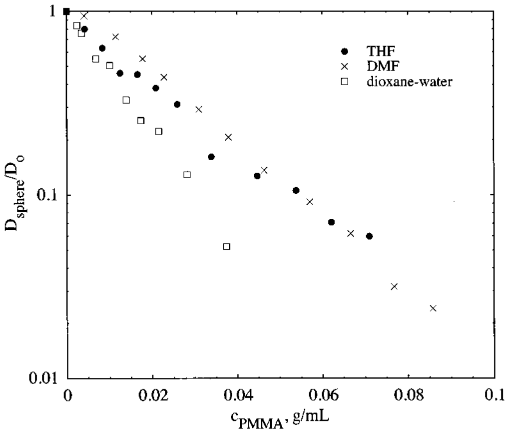

Figure 2. Plot of reduced latex sphere diffusion coefficient as a function of PMMA matrix concentration for the THF, DMF, and dioxane–water solvent systems at 25 °C.

about 20%. In the binary sphere/DMF system, the sphere tracer diffusion coefficient D_0 calculated by CONTIN also exceeded that calculated by cumulant analysis, although the difference was smaller, about 12%. A similar observation was reported by Won et al.[20] in relation to the same spheres diffusing through PVME/toluene solutions. The systematic difference in the values of the diffusion coefficient in DMF calculated by the two methods is not significant in the interpretation of the data.

CONTIN analysis of the DLS data gave distributions that were dominated by a single relaxation mode at all matrix concentrations in the PMMA/PS latex/THF and PMMA/PS latex/DMF systems. With respect to the ternary dioxane–water Θ-solvent system, an additional very slow mode, other than that associated with sphere diffusion, was often present in the CONTIN inversions of the autocorrelation functions. The occurrence of this slow mode was most persistent at low angle but also sometimes appeared at 90° and 120°. In some cases, the slow mode had small amplitude, while in others, the amplitude approached that of the mode assigned to latex sphere diffusion. The decay rate of the slow mode and the mode associated with sphere diffusion were typically over an order of magnitude apart so the CONTIN program was able to routinely separate them. The diffusivity extracted from the slow mode generally decreased with PMMA concentration. This slow relaxation mode was present in independent experimental runs at all scattering angles and absent in the CONTIN analyses of the data from the other solvent systems. Moreover, the slow mode was usually not present in newly prepared PMMA/PS latex/dioxane–water samples. After 3–12 h, as the sample was allowed to equilibrate, the slow component started to appear. These observations suggest the slow mode is not a result of an experimental artifact like the presence of dust. Rather, it appears to be a real phenomenon unique among the solvent systems studied. Unless otherwise stated, the diffusion coefficients for the dioxane–water system represented in subsequent plots in this paper are those resulting from the fast relaxation mode we associate with latex sphere diffusion. Speculation as to the origin of the slow mode appears later in this report.

Reduced latex sphere diffusion coefficients (D_{sphere}/D_0) as a function of PMMA concentration appear in Figure 2. In this plot, as well as in all subsequent plots involving the sphere diffusion coefficient, the values of D_{sphere} and D_0 extracted from CONTIN are employed.

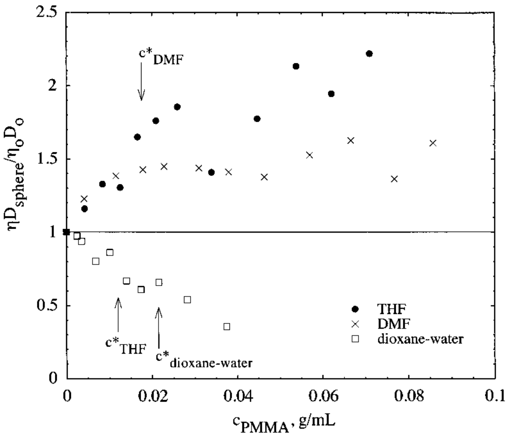

Figure 3. Test of the Stokes–Einstein equation as a function of PMMA matrix concentration for the THF, DMF, and dioxane–water solvent systems.

It is evident that the diffusion coefficients at low matrix concentration approach the values in the binary sphere/solvent systems.

In order for the SE equation (eq 1) to be obeyed, the product ηD_{sphere} should be independent of PMMA matrix concentration. Equivalently, SE behavior requires that the ratio $\eta D_{\text{sphere}}/\eta_0 D_0$ equal unity at all matrix concentrations, where η_0 is the viscosity of the pure solvent and D_0 is the tracer diffusion coefficient of the spheres in the pure solvent. Positive and negative deviations from the SE equation correspond to $\eta D_{\text{sphere}}/\eta_0 D_0 > 1$ and $\eta D_{\text{sphere}}/\eta_0 D_0 < 1$, respectively. Alternatively, one may define a local or "microviscosity" η_μ experienced by the spheres, or an effective hydrodynamic radius of the spheres r_{H} through the SE equation:

$$\eta_\mu = kT/6\pi R D_{\text{sphere}} \tag{2}$$

$$r_{\text{H}} = kT/6\pi\eta D_{\text{sphere}} \tag{3}$$

If $\eta_\mu/\eta < 1$, a positive deviation is indicated, while $\eta_\mu/\eta > 1$ indicates a negative deviation from the SE equation. $r_{\text{H}}/R < 1$ and $r_{\text{H}}/R > 1$ correspond to positive and negative deviations, respectively.

As shown in Figure 3, the PMMA/latex sphere/solvent systems show a variety of behavior in $\eta D_{\text{sphere}}/\eta_0 D_0$ as a function of concentration. For the THF system, $\eta D_{\text{sphere}}/\eta_0 D_0 > 1$ at all matrix concentrations, indicating that the spheres are diffusing at a higher rate than would be expected from the SE equation. At low concentration, deviations from unity are small but generally increase at higher concentrations. At around 0.07 g/mL, $\eta D_{\text{sphere}}/\eta_0 D_0 > 2$, meaning that the diffusion coefficient of the spheres is over twice as large as the value predicted from the SE equation. In the DMF system, $\eta D_{\text{sphere}}/\eta_0 D_0 > 1$ at all matrix concentrations, but deviations from unity are generally lesser in magnitude than the THF system. The dioxane–water Θ-solvent system dramatically differs from the other two systems. Small *negative* deviations from the SE equation are observed in dilute solution which become larger in magnitude with concentration. At the highest concentration studied, $\eta D_{\text{sphere}}/\eta_0 D_0 \approx 1/3$. Such behavior indicates that the latex spheres are diffusing at a much slower rate than would be predicted from the SE equation.

As has been previously reported,[9,16] sphere diffusion D in the presence of matrix polymer often follows a "stretched exponential" scaling law:

$$D/D_0 = \exp(-\alpha c^{v}) \qquad (4)$$

where D_0 is the sphere diffusion coefficient in the absence of matrix polymer, c is the concentration of the matrix polymer, v is a constant, and α is a constant for a given sphere radius and matrix polymer molecular weight. Values of v for each system computed from a nonlinear least-squares fit of the diffusion coefficient data appear in Table 1. Another scaling expression that may be employed is

$$D/D_0 = \exp(-\alpha'(c/c^*)^{v}) \qquad (5)$$

When plotted according to eq 5, the data do not fall on a common curve as is illustrated in Figure 4. This observation suggests that sphere−polymer interactions are different in the three solvent systems. Moreover, Figure 4 indicates that interactions in the dioxane−water solvent system are substantially different from those present in THF or DMF. These differences will become more evident later when the data are discussed in the context of the Stokes−Einstein equation.

Discussion

Latex Sphere Diffusion. Similar arguments as those reported previously indicate that the diffusion coefficients displayed in Figures 2−4 represent diffusion of the latex spheres at effectively infinite latex dilution, i.e., tracer diffusion of the latex spheres.[19] Briefly, the latex concentration is very low (~10^{-5} g/mL), ensuring that no multiple scattering occurs and that tracer diffusion of the spheres is being measured. The size of the latex spheres is much larger than that of the matrix polymer, thus favoring scattering by the spheres, especially at low angle. Sphere diffusion coefficients in all systems are angle-independent and extrapolate well to the diffusion coefficient of the spheres in the absence of matrix polymer. Finally, decay rates due to the matrix polymer were complete before appreciable attenuation of the correlation function had occurred.

In all systems, latex sphere diffusion was measured in both the dilute and semidilute matrix polymer concentration regimes. In order to understand probe diffusion through semidilute solutions, the probe radius R is often compared to the mesh size of the transient matrix polymer network ξ. ξ is the average distance between chain entanglements in the semidilute concentration regime and is often taken[30] as $R_g(c^*/c)^{3/4}$. If $R \gg \xi$, it is reasonable to expect that probe diffusion may depend on the macroscopic viscosity of the solution, provided that chain entanglements are relaxing rapidly in comparison to probe motion. In this case, probe diffusion will depend on the relaxation of the chain entanglements, and SE behavior would be expected provided no other complicating factors are present. Such behavior is anticipated based on the scaling equation used by Langevin and Rondelez,[1]

$$D/D_0 = \exp[-(R/\xi)^{\epsilon}] + \eta_0/\eta \qquad (6)$$

If $R < \xi$, the probe diffusion should be controlled by the local or microscopic viscosity experienced by the probe particle, which may approach the pure solvent viscosity in extreme situations. For all data acquired in the semidilute concentration regime, R exceeds ξ by more than an order of magnitude. In addition, the disentanglement time of the matrix polymer as estimated by the tube renewal time,[30,31]

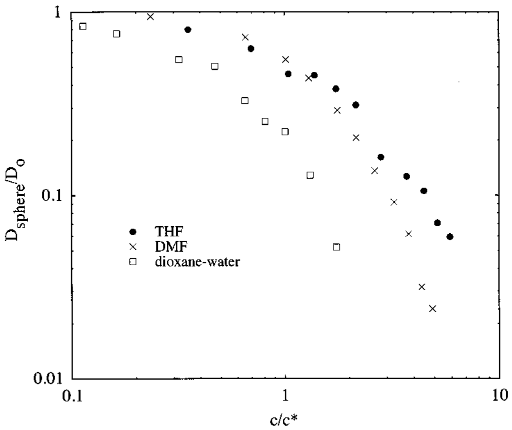

Figure 4. Reduced latex sphere diffusion coefficient versus reduced PMMA matrix concentration for the THF, DMF, and dioxane−water solvent systems.

$$T_R = (6\pi\eta_0/k_BT)R_g^{\,3}(c/c^*)^{1.5} \qquad (7)$$

is much smaller than the decay time of the correlation function reflecting probe motion, given by

$$\tau_{probe} = 1/Dq^2 \qquad (8)$$

Typically, T_R is smaller than τ_{probe} (calculated at 45°) by at least 2 orders of magnitude, and in some cases 3 orders of magnitude. Consequently, in the semidilute regime, the spherical latex probes in all systems are diffusing through a rapidly relaxing matrix of mesh size significantly smaller than the radius of the probe.

Test of the Stokes−Einstein Equation. PMMA/PS Latex/THF and PMMA/PS Latex/DMF Systems. As is evident from Figure 3, a positive deviation from SE behavior is observed for probe diffusion through solutions of both PMMA in THF and DMF. THF is a thermodynamically good solvent for PMMA.[32] Moreover, the intrinsic viscosity data (Table 1) suggest it is the best of the three PMMA solvents used in this report. DMF, on the other hand, is only a modestly good solvent as evidenced in Table 1.

Positive deviations from the SE equation have typically been explained in terms of one of three arguments. One argument is that they are caused by coupling of sphere and matrix dynamics which may lead to cooperative motions in the system. Zhou and Brown argued the existence of such coupling in justifying positive deviations observed for silica spheres diffusing through poly(ethylene oxide)/methanol solutions[12] and polyisobutylene/chloroform[10,33] solutions. When the spherical probe is immersed in a rapidly relaxing matrix of much higher concentration, coupling might be expected, even when sphere−matrix interactions are weak.[10] In addition, coupling is anticipated to increase with sphere−matrix interactions and matrix segment density.[12] Brown and Rymden have studied the diffusion of high molecular weight linear polystyrene through PMMA/toluene solutions.[6] Their study is of interest in that the matrix and probe are the same polymers as those used in this investigation. One significant difference in the work reported by Brown and Rymden is that the PS probe was a linear polymer, not a highly cross-linked latex sphere. Interestingly, the linear PS probe molecules exhibited enhanced diffusion in the context of the SE equation. It was suggested that the increase in ηD_{PS} with matrix concentration was due to coupling of the motions of the PS probe with those of the PMMA matrix.

Another argument is that the positive deviation from the SE equation is a result of shear thinning in the vicinity of the spheres, even though no external shear is present. This argument was suggested by Lin and Phillies in explaining positive deviations from SE behavior for carboxylate-modified PS latex spheres diffusing through poly(acrylic acid)/water solutions.[3,4] A final explanation found in the literature is that if the probe radius R is not significantly larger than the matrix correlation length ξ, a positive deviation from the SE equation is anticipated. Such behavior is predicted by eq 6, and Yang and Jamieson have reported that their data qualitatively follow this equation.[23]

Although the first argument involving coupling of sphere motion with that of the matrix polymer cannot be completely discounted in this investigation, several considerations suggest it is not the dominant mechanism responsible for the enhanced sphere diffusion relative to SE equation observed in the THF and DMF ternary systems. As is evident from Figure 3, $\eta D_{\text{sphere}}/\eta_0 D_0 > 1$ for both systems at concentrations below c^*, albeit the deviations are relatively small. Nevertheless, it is difficult to imagine how dilute PMMA molecules could enhance the diffusion of much larger rigid spheres before a PMMA mesh has even formed. As has been discussed, sphere–matrix coupling is expected to increase with matrix segment density, i.e., with matrix concentration and molecular weight. No evidence of enhanced coupling with PMMA concentration is evident in the DMF ternary system. Figure 3 illustrates that in the semidilute regime the magnitudes of the SE deviations are more or less constant in this system, suggesting the absence of enhanced coupling with increased concentration. Moreover, the linear PS/PS latex/DMF system previously reported,[19] which involves a matrix polymer of much higher molecular weight whose motions should presumably couple more effectively to sphere motions, showed no evidence of enhanced diffusion due to matrix–sphere coupling. Rather, the SE equation was followed at all concentrations and matrix molecular weights studied. Finally, an additional CONTIN relaxation mode might be anticipated if cooperative diffusion was occurring. Bimodal decay rate distributions have been observed in systems involving linear PS, linear PMMA, and single solvent or mixed solvent and suggested to result from the coupling of linear probe motion with matrix motions.[34-36] In the current report, bimodal distributions were not prevalent in the CONTIN analyses of the data from the DMF and THF ternary systems.

The second mechanism involving shear thinning does not appear plausible. Nehme et al. found that the sedimentation coefficient of PS latex spheres in semidilute poly(L-lysine) solutions was independent of rotational speed.[11] This result argues against shear thinning as a reason for enhanced sphere diffusion in polymer solutions, although Nehme et al. did not regard this as conclusive evidence against a shear thinning mechanism. Also, no evidence of shear thinning is present in semidilute polymer solutions involving the same latex spheres, a DMF solvent, and a PS matrix of molecular weight 215K and 1100K.[19] The third mechanism involving R and ξ is certainly not applicable in this investigation since, as has already been discussed, $R \gg \xi$ under all conditions in the semidilute regime.

We offer another interpretation of the data involving the presence of a polymer depletion layer locally surrounding the latex spheres. Won et al. have recently suggested that such a layer should be borne in mind when considering latex spheres as "probes" in solutions of flexible polymers.[20] A polymer depletion layer near a nonadsorbing barrier will exist if the barrier prefers the solvent to the dissolved polymer.[37] One reason why such a situation will exist is that flexible polymer molecules experience an "entropic repulsion" as their centers of mass approach the barrier, a phenomenon first noted by Asakura and Oosawa in 1954.[38] The repulsion is a result of the reduced number of configurations available to the polymer near the barrier that would otherwise be accessible. This excluded volume effect results in a "depletion layer", termed by Joanny et al. in 1979,[39] poor in polymer locally surrounding the barrier.

Polymer depletion layers may also be caused by some specific unfavorable interaction between the polymer and barrier unrelated to configurational entropy, e.g., electrostatic repulsion.[40-43] The presence of such an interaction would likely increase the depletion layer thickness beyond that present when only entropic effects are operative. Another repulsive enthalpic effect that would likely contribute to polymer depletion is polymer/surface incompatibility. In this paper, since PMMA and PS are incompatible (immiscible) polymers, [44,45] it is reasonable to expect a nonentropic contribution to the depletion layer to be present.

We give a brief overview of some of the theoretical and experimental work concerning polymer depletion. For more details, see two review articles and the references within those articles.[46,47] A number of theories and computer simulations predict the presence of a polymer depletion layer near a variety of geometrical barriers.[46,47] Theoretical predictions of concentration profiles have been calculated by Monte Carlo calculations, mean-field theories, scaling theories, and Vincent's "pragmatic" approach.[46,47] For flexible polymers near noninteracting barriers, depletion layer thicknesses are predicted to be of the order of the diameter of the coil in the dilute concentration regime and predicted to decrease in the semidilute regime. In the scaling and mean field theories of de Gennes,[31,39,48] the polymer depletion layer thickness near a wall equals the matrix correlation length ξ in the semidilute regime and is $\approx R_g$ of the polymer in the dilute regime.

Compelling experimental evidence for the presence of polymer depletion layers near solid barriers exists as well. The first direct observation of a polymer depletion layer was reported by Allain, Ausserre, and Rondelez.[46,49] Using an evanescent wave fluorescence technique, they demonstrated the existence of a polymer depletion layer for polystyrene (M_w = 103 000) dissolved in ethyl acetate near a nonadsorbing glass prism surface. The concentration of PS was 1% (w/w) and the depletion layer thickness was found to be 4.5 ± 0.5 nm, which is of the order of the unperturbed radius of gyration (11 nm). The results were in agreement with the entropic repulsion model. A concentration profile could not be calculated. Similar experiments were reported by Ausserre, Hervet, and Rondelez using aqueous xanthan ($M_w = 1.8 \times 10^6$), a stiff polysaccharide, near a nonadsorbing planar silica surface.[46,50,51] In dilute solution, the depletion layer thickness was found to remain constant at about 150 nm, in good agreement with the radius of gyration (159 nm). As expected from theoretical considerations, the depletion layer thickness decreased with increasing bulk concentration in the semidilute regime. Their results agreed best with the expected concentration profile of a semiflexible chain.[52] Evanescent wave ellipsometry has also been used to study polymer depletion layers near surfaces, yielding a thickness of 7.0 nm for PS of molecular weight 100 000 dissolved in ethyl acetate.[53]

Experimental and theoretical evidence for depletion layers in polymer/colloid/solvent complex fluids has been reported as well. Flocculation of particles in colloidal dispersions upon addition of nonadsorbing polymer has been attributed to depletion layers surrounding the colloids.[54−65] In these systems, when two colloidal particles approach one another, polymer molecules are excluded (or partially excluded) from the gap between them due to the depletion layers surrounding both particles. Consequently, the osmotic pressure exerted by the polymer molecules in the region between the particles is less than that exerted in bulk, thus inducing flocculation.[56] Cosgrove, Obey, and Ryan were able to estimate the depletion layer thickness around silica spheres (diameter = 116 ± 9 nm, concentration = 7.8%) in aqueous solutions of nonadsorbing sodium poly(styrenesulfonate) using nuclear magnetic resonance.[40] Molecular weights of the NaPSS ranged from 46 000 to 780 000. For the 780K NaPSS, depletion layer thicknesses of over 85 nm were reported and were found to decrease with NaPSS concentration. Lower molecular weight NaPSS yielded only slightly smaller values for the depletion layer thickness. Since both the PSS and the surface of the silica spheres were negatively charged, the depletion layer resulted from both entropic and electrostatic contributions. Krabi and Donath were able to estimate depletion layer thicknesses around red blood cells and liposomes in aqueous poly(ethylene glycol) and dextran solutions.[66] Electrophoretic mobility measurements on red blood cells yielded depletion layer thicknesses of the order of the radius of gyration of the PEG and dextran. The depletion layer thickness did not strictly decrease with increasing concentration in the majority of the systems studied.

The flocculation due to depletion, the nuclear magnetic resonance, and the electrophoretic mobility experiments are especially interesting in that they demonstrate the existence of depletion layers near colloidal particles in motion. For example, with regard to flocculation due to depletion, [54−65] the colloidal particles are diffusing as the nonadsorbing polymer is added, yet a depletion layer is still formed around the colloids, which subsequently induces flocculation. During the nuclear magnetic resonance experiments of Cosgrove et al.,[40] the depletion layer thickness is measured as the silica spheres diffuse throughout the aqueous solutions of PSS. In addition, the electrophoretic mobility measurements of Krabi and Donath demonstrate depletion around red blood cells and liposomes that are in motion.[66] These experiments suggest that in our systems depletion layers may exist locally around the PS latex spheres as they slowly diffuse throughout the PMMA solutions.

In the current study, if a depletion layer exists locally around the latex spheres, the microviscosity experienced by the spheres will be smaller than the macroscopic viscosity. The PS sphere will be locally diffusing through a rapidly relaxing solvent-rich PMMA solution. The drag force experienced by the spheres will be lower than that in bulk solution, causing $\eta D_{\text{sphere}}/\eta_0 D_0$ to be larger than one. Indeed, this is what was observed for both the THF and DMF solvent systems. Generally, as the concentration increases, the magnitude of departure from the SE equation increases. This is especially evident in the THF solvent system. Initially, this may seem a bit perplexing since the depletion layer thickness is predicted to decrease (as ξ decreases) in the semidilute regime with concentration.[31,39,48] However, as the concentration increases, $\partial\eta/\partial c$ increases. This will tend to make the deviations from unity in $\eta D_{\text{sphere}}/\eta_0 D_0$ larger. Consequently, there exists a competition between the decreasing ξ with concentration and the increasing $\partial\eta/\partial c$ in the semidilute regime. In THF, a good solvent for PMMA where the viscosity rises most rapidly (Figure 1) because of the relatively large dimensions of the PMMA coils, the increase in $\partial\eta/\partial c$ with concentration appears to outweigh the decrease in ξ. In DMF, a less favorable solvent, the two effects appear to somewhat offset each other as $\eta D/\eta_0 D_0$ becomes approximately constant when $c > c^*$.

The idea of local matrix depletion in these systems is supported by the fact that PS and PMMA are immiscible polymers.[44,45] In addition, both THF and, to a lesser extent, DMF are good solvents for PS.[26,32] Consequently, a depletion layer poor in PMMA matrix polymer and rich in solvent locally surrounding the PS latex spheres is very plausible. The combination of enthalpic (immiscibility) and entropic (configurational) depletion effects probably results in a depletion layer thickness in dilute solution that is somewhat larger than the radius of gyration of the matrix PMMA. Still, the depletion thickness (~20 nm) is perhaps about an order of magnitude smaller than the sphere radius (~200 nm). Since the DLS experiments measure diffusion over distances of about $1/q$ (30−70 nm in our case), one might be potentially concerned that diffusion might actually be retarded as the sphere traverses beyond the depletion layer during the course of the experiment and that D might be q dependent. We propose that since that matrix PMMA has a diffusion coefficient that is 1−3 orders of magnitude larger than the sphere diffusion coefficient, the PMMA can rapidly reorient and relocate as the sphere moves, thus creating a new depletion layer. We suggest that the depletion layer continually relocates as the sphere diffuses so that the sphere is essentially always diffusing through solvent-rich space. Consequently, if one accepts that the matrix PMMA rapidly relocates as the sphere diffuses, then the fact that the diffusion distance is slightly larger than the depletion layer thickness would not be expected to significantly retard sphere diffusion. Moreover, no q dependence of D would necessarily be expected.

The presence of a PMMA depletion zone locally surrounding the PS latex spheres is supported by the work of Lin and Rosen, who determined the radius of gyration of PS coils by static light scattering in a PMMA−toluene "solvent" as a function of PMMA concentration at 20 °C.[67] Toluene is essentially isorefractive with PMMA at 20 °C. They found that at the Θ condition for PS, as indicated by the second virial coefficient equaling zero, the expansion factor $\alpha = \langle R_g\rangle^{0.5}/\langle R_g\rangle_{\Theta}^{0.5}$ significantly exceeded 1. In other words, the PS coils were expanded well beyond Gaussian dimensions under conditions where the second virial coefficient vanished. It was argued that this occurred because the PMMA (a "poor solvent" for PS) was almost completely excluded from the PS coils, while toluene (a good solvent for both PS and PMMA) was preferentially present, increasing coil dimensions. Similar experimental results have been reported for PS coils in PMMA−benzene "solvents".[68] The unfavorable interaction between PMMA and PS, as well as the solvent affinity for both polymers, exists in the current study as well. Therefore, PMMA would likely be preferentially excluded from region locally surrounding the PS latex spheres.

In the dilute regime, the magnitudes of the SE deviations in the THF and DMF systems are about the same, within experimental error. However, in the semidilute regime it is evident from Figure 3 that the magnitudes of the deviations from the SE equation are greater in the THF system than in the DMF system. This is likely due to two factors. First, THF is a better solvent for PMMA than DMF as evidenced by the intrinsic viscosity data in Table 1. Consequently, PMMA will tend to avoid the latex spheres more in THF than in DMF because of the very favorable contacts between PMMA segments and THF molecules. Second, THF is a better solvent for PS than DMF. We have previously reported the Mark−Houwink exponent for PS in DMF at 25 °C to be 0.59 ± 0.04.[19] The Mark−Houwink exponent for PS in THF at 25 °C has been reported by several authors.[32] The values range from 0.700 to 0.725. In addition, data dealing with these latex spheres indicate that they swell more in THF than in DMF.[29] Clearly, based on these data, THF is a thermodynamically more favorable solvent for PS latex than DMF. As a result, THF will better solvate the surface chains of the PS latex spheres as compared to DMF. In the complex fluids, therefore, THF will tend to locally surround the latex spheres more than DMF. Since THF is a better solvent for both PMMA and PS than DMF, the effect of the depletion layer in the THF solvent system should be greater than that in the DMF solvent. Consequently, one might expect deviations from unity in Figure 3 to be greater in the THF system.

Brown and Rymden studied the diffusion of stearic acid coated silica spheres of radius 0.1595 μm though PMMA/chloroform solutions.[6] Chloroform is a good solvent for PMMA. The molecular weight of the matrix PMMA varied from 1.01×10^5 to 4.45×10^5. The SE equation was followed for all molecular weights at all matrix concentrations studied. Several reasons could account for the fact that the data reported by Brown and Rymden are different in the context of the SE equation than our data concerning PMMA/PS latex/good solvent systems. For example, the interactions between solvent, probe, and matrix may be quite different in their systems considering the solvent and, most importantly, the probe are chemically different than those used in the current study. Moreover, the highest matrix concentration studied by Brown and Rymden was about 3%. At such low concentrations, $\partial\eta/\partial c$ might not be large enough to cause measurable positive deviations from the SE equation and to outweigh the decreasing ξ.

The Dioxane−Water Θ-Solvent System. Figure 3 shows a negative deviation by almost a factor of 3 from the SE equation at highest concentration in the dioxane−water Θ-solvent system. At very dilute matrix concentrations, only a slight negative deviation from SE behavior is observed. When the concentration is increased, the negative deviations become more dramatic. At the largest matrix concentration studied, $\eta D_{\text{sphere}}/\eta_0 D_0 \approx 0.36$, corresponding to a negative deviation from the SE equation by a factor of ≈3. Equivalently, the effective hydrodynamic radius of the spheres r_H (eq 3) at the highest matrix concentration studied is almost 3 times larger than the hydrodynamic radius when no matrix PMMA is present.

Negative deviations from the SE equation have been reported previously;[2,4,7,14,18] however, all involve probe diffusion through aqueous polymer solutions. This report is the first example that we are aware of in which such behavior has been observed in polymer solutions where the solvent is primarily organic. In aqueous solution, adsorption of the matrix polymer onto the spherical probes has usually been argued to be the origin of the negative SE deviations. However, Russo et al. have suggested that clusters formed by bridging of spheres through matrix polymers may accompany adsorption in causing negative deviations from the SE equation.[18]

We interpret our data in terms of adsorption alone causing the observed negative deviation from the SE equation in Figure 3. No angular dependence of the diffusion coefficient was observed, which would be expected if bridged moieties of different sizes existed. Furthermore, if significant bridging occurred, larger deviations from the SE equation would be expected at low matrix concentration. Russo et al. observed an increase by approximately a factor of 2 in the hydrodynamic radius of PS latex spheres dispersed in water when only a very small amount of (hydroxypropyl)-cellulose was added (the viscosity of the solution only changed slightly from that of water upon addition of the matrix polymer).[18] This was presumably caused by the presence of clusters of bridged latex spheres. No such large deviations at low matrix concentration appear in Figure 3. Adsorption, which appears to occur at all PMMA concentrations studied, is a more likely explanation.

The dioxane (85 vol %)/water (15 vol %) solvent is a Θ-solvent for PMMA at 25 °C.[27] This was determined by the second virial coefficient vanishing in static light scattering experiments. As polymer concentration is increased in a Θ-solvent, solvent conditions typically worsen (i.e., the Flory−Huggins polymer−solvent interaction parameter χ becomes larger than 0.5).[32] Complex polymer solutions can become unstable under these conditions, and adsorption of the PMMA matrix chains onto the surface of the PS latex spheres can occur, even though PMMA and PS are not compatible polymers.

Since r_H has increased by almost a factor of 3 at the highest matrix concentration studied, it is apparent that the effective thickness of the adsorbed layer is not simply twice the radius of gyration of the PMMA ($R_g \approx 160$ Å). An interpretation consistent with the data is that the PMMA chains adsorbed onto the latex spheres extend into the surrounding solution. In very dilute PMMA solutions, the increased hydrodynamic drag resulting from such a moiety is not expected to cause a large increase in r_H. For example, increasing the radius of the latex sphere by $\approx 2R_g$ to $3R_g$ results in an increase in the hydrodynamic radius of the sphere by a factor of about 1.2 in dilute matrix solution. This is consistent with the small negative deviations we observed at low matrix concentrations. However, as c^* is approached, it is likely that the adsorbed PMMA chains, which extend into solution, become entangled with the matrix chains. Such a situation would further increase the drag experienced by the sphere−PMMA moieties because of topological constraints. The relaxation of entanglements involving adsorbed PMMA chains and free PMMA chains would be expected to be much slower than entanglement relaxations involving free PMMA polymers in bulk solution. This is anticipated since the dynamics of the adsorbed chains are highly confined.

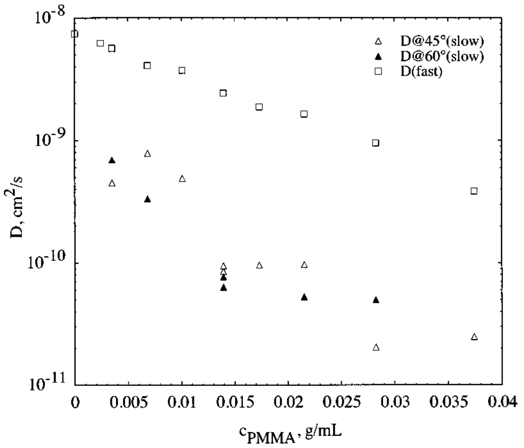

Figure 5. Diffusivities extracted from the slow CONTIN mode at 45° and 60° as a function of matrix concentration for the dioxane−water solvent system. Diffusivities extracted from the fast mode for this system, which are associated with single-sphere diffusion, are shown for comparison.

Consequently, as the occurrence of entanglements between adsorbed chains and free matrix chains becomes more frequent with increasing PMMA concentration, it is quite reasonable to expect that the apparent hydrodynamic radius of the latex spheres should increase, perhaps by as much as a factor of 3, as we have observed. Equivalently, as PMMA concentration increases, the microviscosity η_μ experienced by the latex spheres should exceed the macroscopic viscosity by greater and greater amounts. Cooper, Johnson, and Donald have previously argued how the microviscosity around spheres is expected to exceed the macroscopic viscosity when entanglements of adsorbed chains with free matrix chains occur.[14]

Probe diffusion as a function of solvent quality has been recently reported by Phillies et al.[69,70] The probe was a 67-nm-diameter (non-cross-linked) latex sphere, the matrix polymer was (hydroxypropyl)cellulose (HPC), and the solvent was water. The solvent quality was altered by changing the temperature. Near Θ conditions, positive deviations from the Stokes−Einstein equation were reported, albeit they were smaller in magnitude than the positive deviations reported in good solvents. Evidently, adsorption does not occur in this system at Θ conditions. The HPC/latex sphere/water system is clearly quite different from many other systems that have been reported since positive deviations by a factor of almost 100 from the SE equation are reported in solutions of 4% HPC of molecular weight 300 kDa at 10 °C.

As has been mentioned, an additional very slow relaxation mode was observed in the CONTIN analyses of the DLS data for the dioxane−water solvent system. This mode was most prominent at low angle and generally occurred at a smaller average decay rate with increasing matrix concentration. The slow mode was not present for this solvent system when the matrix PMMA was absent. A plot of the diffusivities extracted from the slow mode at 45° and 60°, along with those extracted from the (fast) mode associated with sphere diffusion, appears in Figure 5. We speculate that the origin of the slow mode is due to large clusters of PMMA molecules. Its frequent occurrence at low angle and its small diffusion coefficient are consistent with this interpretation. The broadness of the mode and its nontrivial dependence of decay rate on scattering angle may suggest the presence of PMMA clusters with a variety of sizes. In addition, the diffusivities associated with the slow mode are about an order of magnitude smaller than those associated with sphere diffusion. This is in agreement with the work reported by Zhou and Brown, who studied the diffusion of poly(ethylene oxide) (PEO) in binary PEO/methanol solutions and the diffusion of stearic acid coated SiO_2 spheres in PEO/methanol solutions.[12] Methanol is a poor solvent for PEO and the SiO_2 spheres. DLS data on the binary PEO/methanol solutions yielded a bimodal distribution, with the slow mode being assigned to the mobility of molecular clusters or ordered domains. The clusters, which were determined to have a similar size as the SiO_2 spheres, had diffusion coefficients about an order of magnitude smaller than the spheres at the same matrix concentration, as is the case in our PMMA/PS latex/Θ-solvent system.

An alternate interpretation of the slow mode is that it is due to latex spheres bridged by PMMA molecules. This explanation is less likely in that the latex spheres are on average about 15 μm apart in our samples. Consequently, if bridged latex spheres exist, they are likely permanent moieties as opposed to transient. In any event, the presence of the slow mode underscores the complexity of the PMMA/PS latex/dioxane−water Θ-solvent system.

Comparison with Other Systems Involving Cross-Linked PS Latex, a Matrix Polymer, and an Organic Solvent. We have reported on the diffusion of PS latex spheres in linear PS/DMF solutions.[19] SE behavior was observed within the precision of the data for both matrix molecular weights (2.15×10^5 and 1.1×10^6) at all concentrations studied, which varied from dilute far into the semidilute regime. The solvent, anhydrous DMF, is a moderately good solvent for PS. This system was unique in the sense that the probe was chemically similar to the matrix polymer. Consequently, there existed no thermodynamic reason for the matrix chains to adsorb onto the probe. In addition, no repulsive enthalpic interaction existed between matrix and probe that would contribute to matrix polymer depletion around the latex spheres. However, entropic repulsion would likely be present.

Adherence to the SE equation within the precision of the data for the linear PS/PS latex/DMF system suggests that no significant depletion (or adsorption) occurs in this system. The absence of significant depletion layers surrounding the spheres in these systems is reasonable. The unfavorable polymer−polymer interactions present in the PMMA/PS latex/solvent systems are not present when the matrix is chemically similar to the probe. Consequently, the propensity for local depletion is diminished. Moreover, the matrix PS chains can mix with the surface chains of the PS latex spheres with little thermodynamic penalty, further diminishing depletion. It should be noted that although SE behavior was observed within the precision of the data, a slight trend toward a positive deviation was present for concentrations where $c(\text{matrix})/c^* < 5$ (Figure 5 in ref 19). If this trend is real, it could be due to entropic repulsion between the matrix PS and the PS latex spheres. Such repulsion, if present, appears to have a minimal effect. Interestingly, unpublished data suggest that adherence to the SE equation occurs in other linear PS/PS latex/good solvent systems.[26] These data suggest that depletion may depend more on enthalpic rather than entropic effects.

The data reported by Won et al.[20] concerning the PVME/PS latex/toluene system indicate an initial positive deviation from SE behavior that is maximum at concentrations slightly greater than c^*, where $\eta D_{\text{sphere}}/\eta_0 D_0 > 3$. At higher concentrations, a return to SE behavior was observed. The initial positive deviation may have been a result of local depletion around the latex spheres. The relatively large radius of gyration (54 nm) and molecular weight ($M_w = 1.3 \times 10^6$) of the matrix PVME would contribute to such depletion. Interestingly, the polymer−polymer interaction parameter for linear PS and linear PVME is slightly negative,[71] implying miscibilty. However, interaction experiments were only performed on relatively low molecular weight linear PS and PVME, and $\chi_{\text{PS-PVME}}$ becomes less negative with molecular weight. For example, χ for PS (M_w = 17 500) and PVME (M_w = 55 000) is −0.018 at 20 °C. When the molecular weight of the PS increases to 110 000 keeping the molecular weight of PVME constant, $\chi_{\text{PS-PVME}}$ increases to −0.006. The interaction parameter for PVME of molecular weight over 10^6 and relatively large, highly cross-linked, minimally swollen PS latex spheres is unknown, but may be positive. Even if $\chi_{\text{PS latex-PVME}}$ is negative at a given temperature, a large difference in the polymer−solvent interaction parameters for linear PVME and the cross-linked latex spheres could still result in polymers which are not "compatible". The quotation marks are necessary because the latex spheres always constitute a separate phase. However, these cross-linked spheres swell about 10% by volume (about 2% in radius),[29] so the matrix chains can mix with swollen PS chains near the surface of the sphere. "Compatibility" is meant to denote extensive mixing of matrix and surface chains due to the absence of repulsive enthalpic interactions between them. This phenomenon, involving the large difference in polymer−solvent interaction parameters, termed the "$|\Delta\chi|$ effect",[72] has been observed for linear PVME and linear PS in some chlorinated organic solvents.[72−77] Moreover, dielectric loss,[74] differential calorimetry, [74] and nuclear magnetic resonance[78] experiments indicate that even macroscopically compatible PVME−PS films cast from toluene can be described as microheterogeneous, in that the PS and PVME chains are not completely mixed on the segmental level. Finally, Bauer et al. have reported that linear PVME (mol wt = 633 000) phase separates from cross-linked deuterated PS when the cross-link density is raised from about 0.25% to 1%.[79] This was determined both visually and by small-angle neutron scattering. The latex spheres employed in the current report have a cross-link density of greater than 7%.[26]

Another important aspect that should be considered in the work of Won et al. is the return to SE behavior observed at sufficiently high matrix concentrations. We observed no recovery of SE behavior at the concentrations studied for our PMMA/PS latex/good solvent systems. However, it should be kept in mind that SE behavior was recovered when $c[\eta] \approx 11$ in the work by Won et al., while we have collected data up to $c[\eta] = c/c^* \approx 6$. Moreover, the return to SE behavior observed by Won et al. is consistent with local polymer depletion in that depletion layer thickness is predicted to be $\approx\xi$ in the semidilute regime[31,39,48] and decreases[30] as $c^{-3/4}$with matrix concentration. Our systems could very well return to SE behavior when the depletion layer has contracted enough, i.e., at larger PMMA concentrations than we have studied. Consequently, the interpretation of our data is not in disagreement with the work reported by Won et al.

The diffusion of highly cross-linked PS latex spheres through a rigid rod polymer matrix has also been studied. The rodlike polymer employed was poly(γ-benzyl α,L-glutamate) (PBLG), and the solvent used was DMF. The results are consistent with a rod monomer depletion layer locally surrounding the latex spheres. The details concerning this system are described in the following paper of this issue.

Conclusion

Dynamic light scattering has been used to study the diffusion of PS latex spheres in PMMA solutions at 25 °C. As the solvent quality with respect to the matrix PMMA and the PS probe was varied, the sign and magnitude of the deviations from the Stokes−Einstein equation varied. Positive deviations occurred in THF and DMF, which are good/modestly good solvents for PMMA. We have argued that these positive deviations are due to the PS latex spheres being locally surrounded by a depletion layer rich in solvent and poor in matrix PMMA. The immiscibility of PMMA and PS appears to be the major cause of the depletion layer, although entropic repulsion between the matrix PMMA and the latex spheres is likely present as well. The magnitudes of the positive deviations are generally greater in the THF system because THF is a better solvent for both PMMA and the latex spheres than DMF, causing the depletion layer to have a larger effect. In previously reported data on the linear PS/PS latex/DMF (good solvent) system,[19] where the probe particle is chemically similar to the matrix, adherence to the Stokes−Einstein equation was observed. In this system only entropic repulsion effects are operative, which are apparently not large enough to alone result in a significant departure from Stokes−Einstein behavior. A negative deviation by almost a factor of 3 from the SE equation was observed in the dioxane−water Θ-solvent system. We have argued that adsorption of the matrix PMMA onto the latex spheres occurs when the solvent quality is reduced to Θ conditions or below. Entanglements of the adsorbed chains with free PMMA chains may occur at high PMMA concentrations. In addition to the mode we associated with sphere diffusion in the PMMA/PS latex/dioxane−water system, a very slow relaxation mode was present that may be due to PMMA clusters, or a less likely possibility, bridged latex moieties.

In the three PMMA/latex sphere/solvent systems investigated, we observed a wide range of behavior depending on the solvent affinity for both the matrix polymer and the latex spheres. We therefore feel that solvent quality is a critical parameter that substantially affects the nature and magnitudes of Stokes−Einstein deviations.

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