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Diffusion of Polystyrene Latex Spheres in Linear Polystyrene Nonaqueous Solutions

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ABSTRACT: The diffusion of highly cross-linked, nearly monodisperse polystyrene latex spheres of 0.2-μm radius in the presence of linear polystyrene as the matrix polymer in the moderately good solvent *N,N*-dimethylformamide at 25 °C was determined by quasi-elastic light scattering as a function of matrix concentration and molecular weight. This is the first report of a latex probe in trace amounts diffusing in an organic solvent, and with a matrix polymer chemically similar to the probe. The latex diffusion diminished monotonically with matrix concentration, which varied from moderately dilute solutions into the semidilute regime up to a matrix concentration of 8 times c^*. Stokes–Einstein behavior was observed at all matrix concentrations and for both matrix molecular weights (2.15×10^5 and 1.1×10^6), within experimental error. In the semidilute region the entanglement relaxation was always much faster than probe motion. The diffusion data fit the scaling law $D/D_0 = \exp(-ac^{\nu}M^{\gamma})$, with ν equal to 0.99 and γ equal to 0.49. Comparison is made to diffusion of latex probes in aqueous dispersants, and of silica probes in organic dispersants.

Introduction

The diffusion of a spherical particle (probe) in a solution of linear polymer (matrix) has been of both experimental and theoretical interest.[1-18] The spheres have typically been polystyrene latex or silica with radii as small as 200 Å and as large as 1.5 μm. All latex studies have used water as the dispersing fluid and charge-stabilized spheres. Organic solvents have been employed as the dispersing fluid with sterically stabilized silica particles.[6,10,12] The dissolved matrix polymers providing resistance to sphere diffusion have typically been hydrophilic, inasmuch as the dispersing fluid is generally water, and include poly(ethylene oxide),[1,5,14] poly(acrylic acid),[3-4,7-9] polylysine,[11] poly(styrene sulfonate),[2] and carbohydrates[8,13,17,18] with molecular weights from 3600 to one million and concentrations ranging from very dilute to considerably into the semidilute overlap regime. One of the major questions has been the effect of the linear polymer on sphere diffusion at concentrations where a transient network (chain entanglement) of linear polymer is known to exist. Data concerning sphere diffusion have generally been compared to the Stokes–Einstein equation, and to various universal "stretched exponential" scaling laws involving the matrix polymer molecular weight and concentration. With most systems the Stokes–Einstein relationship fails under some conditions; however, in many of these studies complications arose, e.g., adsorption of the linear polymer onto the sphere, compounding interpretation. In some instances[5,8] the spherical probe was reported to diffuse much faster than that predicted by the Stokes–Einstein equation as the concentration of matrix polymer was increased, in other cases slower.

In all previous studies the probe and the matrix have been dissimilar chemically. In this article the probe and the matrix are chemically the same, dispersed in a moderately good solvent for the matrix polymer while the probe has been restricted from dissolving in the solvent through cross-linking. The diffusion of uniform size, cross-linked polystyrene latex in the presence of linear polystyrene using dimethylformamide as the dispersing fluid is determined by quasi-elastic (dynamic) light scattering as a function of the matrix polystyrene molecular weight and concentration. The Stokes–Einstein equation is closely obeyed over all conditions studied. Exponential scaling laws are also observed.

Experimental Section

Materials. Polystyrene latex spheres were prepared using 10 mol % divinyl benzene and 90 mol % styrene in an emulsifier-free emulsion polymerization.[19] These latex spheres, after thorough drying, were redispersed in dry *N,N*-dimethylformamide (DMF), aided by brief sonication.

The source of linear, matrix polystyrene of narrow polydispersity was IBM calibration standards for GPC columns. Two molecular weights were used for diffusion studies, one (PS215K) with M_w of 215 000 and a polydispersity index of 1.05, and the second (PS1100K) with a M_w of 1.1×10^6 and a polydispersity of 1.07. Solutions were prepared by weight in anhydrous DMF (Aldrich Chemical Co.) and filtered through 0.22-μm poly(tetrafluoroethylene) filters into dust-free cylindrical sample cells. The latex dispersion in DMF was filtered through 1.2-μm nylon filters (Microns Separation, Inc.). Solutions for viscosity studies employed several molecular weights and were prepared by weight in anhydrous DMF.

Methods. (A) Dynamic Light Scattering. Diffusion coefficients were determined by using a 2-W argon ion laser (Spectra Physics 164) at a wavelength of 5145 Å. The cylindrical sample cells were immersed in a bath of refractive index matching fluid and temperature controlled at 25.0 ± 0.2 °C. The scattered light was received[20] by a Pacific 126 photometer and analyzed by a Langley-Ford Model 1096 correlator. The normalized, base-line-corrected homodyne correlation function, $C(\tau)$, was analyzed by three methods. By the cumulant method the quantity $\ln[C(\tau)]$ was fitted as a quadratic function of delay time τ:

$$\ln[C(\tau)] = (1/2)\ln[g(q,\tau) - B] = -K_1\tau + K_2\tau^2/2 \qquad (1)$$

Here, K_1 and K_2 are the first and second cumulants, respectively. Assuming that scattered light is due to concentration fluctuations, the *z*-average translational diffusion coefficient (D) of the scattering objects is obtained from

$$D = K_1/2q^2 \qquad (2)$$

where q is the scattering wave vector, i.e., $(4\pi n/\lambda)\sin(\theta/2)$, n being the refractive index of the solvent, λ the wavelength of the laser light, and θ the scattering angle. The second cumulant characterizes the deviation from a single exponential decay due, for example, to mild polydispersity. The data were sometimes fitted to a biexponential decay when contributions to the

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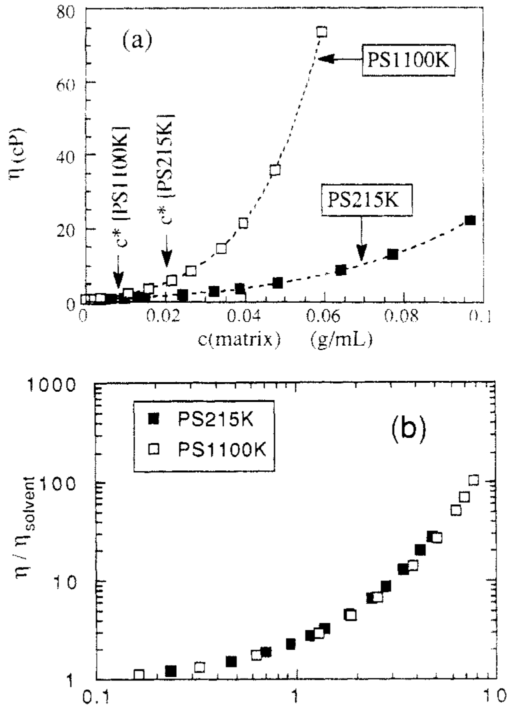

Figure 1. The concentration dependence of the zero shear viscosity of PS215K and PS1100K in dry DMF at 25 °C. In (a) the dashed lines are the least-squares lines through the data points, whereas in (b) the solution viscosity divided by the solvent viscosity is plotted against the matrix polymer concentration divided by the overlap concentration c^*. Overlap concentrations were taken as the inverse of the intrinsic viscosity.

correlation function from both probe and matrix polymers were expected. Finally the data were anlayzed by the use of CONTIN.[21]

(B) Viscosity measurements were made at 25.0 ± 0.02 °C using a Cannon-Ubbelohde dilution viscometer. The effect of shear rate was determined using a RFS II Rheometrics rheometer.

Results

Angle-dependent dynamic light scattering (DLS) showed no evidence of sphere aggregation at latex concentrations of approximately 1×10^{-4} g/mL and no evidence of swelling in DMF when the hydrodynamic radius was compared with measurement in water. The sphere radius was determined to be 0.209 ± 0.005 μm by DLS and 0.17 ± 0.01 μm by scanning electron microscopy.[19] No aggregation upon standing for weeks was observed, evidenced by a lack of an angle-dependent diffusion coefficient and by the quality of the correlation function at any angle.

The concentration dependence of the viscosity of the linear polystyrene is shown in Figure 1a. The concentration separating the dilute from the semidilute region, c^*, is indicated. Values for c^* were calculated from $1/[\eta]$ and from $3M/[N_A 4\pi R_g{}^3]$, giving 0.0205 and 0.0228 g/mL for PS215K, and 0.0075 and 0.0100 g/mL for PS1100K, respectively. There are several ways in the literature to calculate c^*, and we have elected to use $1/[\eta]$ throughout. The viscosity data, scaled by c^* using $1/[\eta]$, are shown in Figure 1b. An adjustment of one c^* by 5% or each by 2.5% brings the viscosity data for the two molecular weights into complete coincidence. The mean shear rate at the wall of the capillary was estimated to be 10–100 s^{-1}, depending on the matrix polymer concentration. Steady shear measurements on the highest concentrations using parallel plate fixtures indicated Newtonian viscosities at the shear rates typically encountered in the dilution viscometer. Consequently, the viscosities may be taken as zero shear rate values. Inasmuch as diffusion measurements were frequently made using linear polystyrene concentrations different from the viscosity data, least-squares polynomial fits were made for ease in interpolation. The data fit best to a fourth-order (PS215K) or fifth-order (PS1100K) polynomial in polymer concentration with residuals being small, typically a fraction of a percent, and randomly positive and negative.

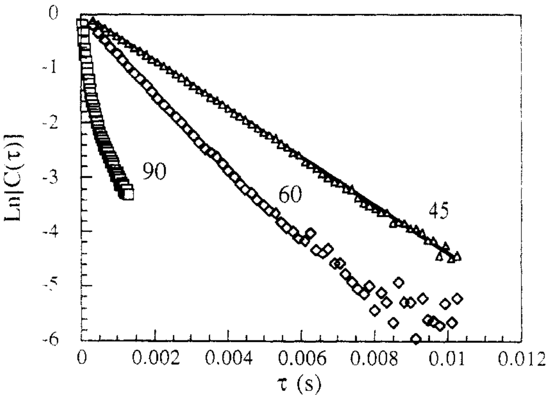

Figure 2. Decay in the autocorrelation function at 45°, 60°, and 90° scattering angle observed with a dry DMF solution containing 0.00117 g/mL PS1100K and about 10^{-5} g/mL latex. The solid line is the least-squares line using the first cumulant only.

For each molecular weight the reduced and the inherent viscosities at low concentration were extrapolated to infinite dilution to determine the intrinsic viscosity, $[\eta]$. The Mark–Houwink exponent was found from the intrinsic viscosity–molecular weight data to be 0.59 ± 0.04 at 25 °C, based on six molecular weights ranging from 1.15×10^5 to 1.1×10^6. DMF is thus a modest solvent for linear polystyrene at 25 °C, and well above the Θ temperature.

Samples for light scattering were prepared by weight by addition of a small volume of dilute latex in DMF to prefiltered linear polystyrene in DMF solutions. The final latex concentration was of the order of 10^{-5} g/mL. Light scattering data were gathered at several angles (45–120°). Typical results using PS1100K as the linear polymer are shown in Figure 2. In preparing the raw data to present as the scaled correlation function for cumulant analysis, the method by which the base-line intensity is deduced may affect the diffusion coefficient extracted from the data. The base-line count B (eq 1) was taken as the last 16 channels in the correlator, and also as a calculated value resulting from an exponential fit to the intensity correlation function–τ data. When the data at 45° in Figure 2 were analyzed by a cumulant fit, they were well represented by a single exponential decay, and the two methods to determine B were generally in good agreement. This is representative of the 45° data at all concentrations and for both molecular weight linear polymers, although occasionally some curvature was observed. The latex diffusion coefficients extracted from cumulant analysis at 45° are shown in Figure 3, where the refractive index of the "solvent" was taken as that of the linear polystyrene/DMF solution. The values extrapolate well to the diffusion coefficient of the very dilute latex in the absence of linear polymer.

The scattering data were also analyzed by the CONTIN method.[21] With PS1100K as the matrix polymer the decay in the correlation function at 45° was dominated by relaxation centered around a single frequency, while at higher angles a second, much faster relaxation was present in most samples. If we tentatively make the assumption that the 45° data are dominated by scattering from the latex spheres whereas higher angle data were also picking up scattering from the much more numerous but much

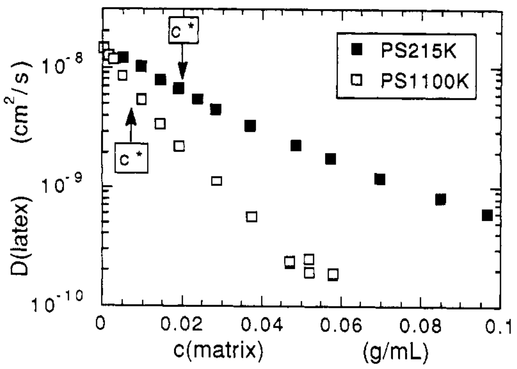

Figure 3. Concentration dependence of latex diffusion coefficient as a function of linear polystyrene concentration and molecular weight, as determined from cumulant fit at 45° scattering angle.

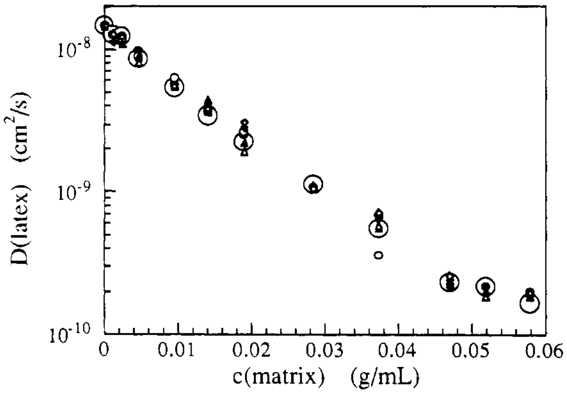

Figure 4. Comparison of latex diffusion coefficients determined from cumulant fit (large open circles) with those deduced from CONTIN analysis (all other symbols) in the presence of PS1100K in dry DMF. At each linear polystyrene concentration there were duplicate runs at 45°, 60°, and 90°.

smaller linear polymer chains, the slow-component CONTIN frequency can be converted to a diffusion coefficient and compared with cumulant analysis at 45°. Such a comparison is shown in Figure 4 for one linear polymer concentration and is representative. There is a good match between the cumulant analysis at 45° and the slow component from CONTIN analysis at all angles.

CONTIN analysis for data using PS215K as the linear polymer gave only a single frequency domain at all angles. This was considered to be a result of less scattering as well as a faster decay from the lower molecular weight linear polymer. In fact, if the same acquisition time and τ are used and the latex is left out, the intensity of the correlation function with only linear polymer present is orders of magnitude lower than when 10^{-5} g/mL of latex is present. When the correlation function as plotted in Figure 2 was highly curved using PS1100K, a bimodal cumulant fit also gave a slow-component diffusion coefficient in agreement with Figure 3.

The Stokes–Einstein expression for the diffusion of dilute spheres of radius R in a medium of viscosity η is given by

$$D_{\text{latex}} = k_B T / 6\pi\eta R \qquad (3)$$

If the data follow this expression, ηD_{latex} should be independent of the matrix polymer concentration or molecular weight. As shown in Figure 5, the Stokes–Einstein equation is followed within the precision of the data. With PS215K as the matrix polymer ηD_{latex} equals an average of 1.26 (±0.05) × 10^{-8} cP cm^2/s, and with PS1100K it equals an average of 1.26 (±0.17) × 10^{-8} cP cm^2/s if all concentrations are included or 1.25 (±0.05) × 10^{-8} cP cm^2/s if data points are excluded when $c/c^* > 5$. At high matrix polymer concentration ($c/c^* > 5$) it was more difficult to extract the latex diffusion coefficient with precision using PS1100K. The imprecision can be traced to the determination of D, and not to viscosity or concentration. Linear regression of the merged data set yields a slight positive increase with matrix polymer concentration, but the slope is within one standard deviation of zero.

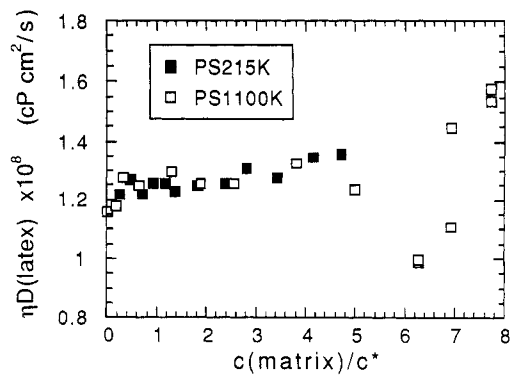

Figure 5. Test of the Stokes–Einstein equation as a function of the reduced concentration.

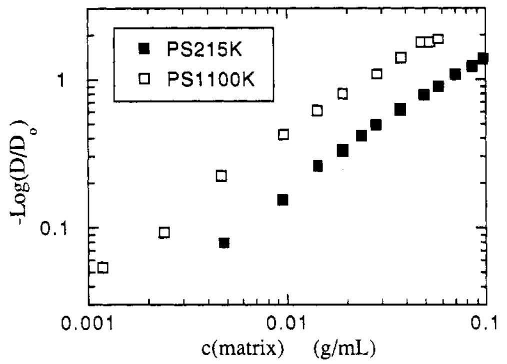

Figure 6. Plot of the reduced latex diffusion coefficient (D/D_0) to test the applicability of the stretched exponential, eq 4.

In previous studies[9,16] on sphere diffusion in the presence of linear polymer the probe diffusion coefficient frequently followed a "stretched exponential" scaling law:

$$D/D_0 = \exp(-ac^{\nu}M^{\gamma}R^{\delta}) \qquad (4)$$

where D_0 is the sphere diffusion coefficient in the absence of matrix polymer, c is the concentration of matrix polymer of molecular weight M, R is the sphere radius, and a, ν, γ, and δ are constants. Our data followed this scaling law reasonably well for c and M, as shown in Figure 6, where a nonlinear least-squares fit yields $\nu = 0.99 \pm 0.04$ and $\gamma = 0.49 \pm 0.03$.

An alternate scaling function sometimes used is

$$D/D_0 = \exp(-a'(c/c^*)^{\nu}] \qquad (5)$$

Figure 7 shows the data plotted in this manner, where it is seen that scaling c by c^* makes the probe diffusion for both matrix molecular weights fall on a common curve. Similar to the viscosity data, Figure 1b, adjusting one c^* by 5% or each by 2.5% brings the two data sets into excellent coincidence.

Discussion

Probe Diffusion Coefficient. The mass concentration of the probe, a cross-linked, essentially unswollen polystyrene latex sphere,[19] is as much as 10^4 times less than the matrix polystyrene retardant. The latex concentration is so low, about 10 μg/mL, that if its diffusion coefficient

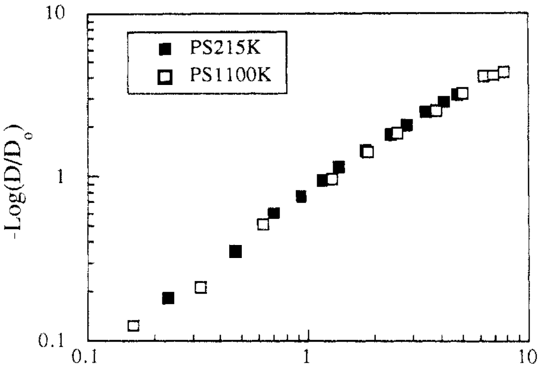

Figure 7. Plot of the reduced latex diffusion coefficient against the reduced matrix concentration according to eq 5.

is being measured, it should correspond approximately to the self-diffusion coefficient of the latex. The large difference in size between the latex and the retardant, with the radius of the solid latex sphere being one-third the wavelength of the light whereas the radius of gyration of the highly solvent swollen retardant polymer is less than a tenth of the incident radiation, will highly bias the scattering of the latex to low angles. The finding that the lowest angle data follow a single exponential decay yielding a diffusion coefficient which extrapolates into D_0 as the matrix polymer concentration goes to zero is suggestive that latex diffusion is being measured. At higher angles where scattering from the matrix polymer (PS1100K) would be expected, CONTIN analysis gave a second component with typically an order of magnitude faster decay than the slow component. The diffusion coefficient calculated from the slow component at any angle matched the diffusion coefficient at low angle determined from a cumulant fit (Figure 4). Using PS215K as the matrix polymer, with τ values similar to that when PS1100K was the retardant, resulted in a decay from the matrix polymer that was essentially complete before data were accumulated.

In previous light scattering studies on latex probe diffusion in the presence of a matrix polymer the refractive index of the matrix has generally been close enough to that of the solvent compared to the probe with the solvent that the matrix is effectively optically invisible even though the mass concentration of the matrix is much larger than that of the probe. In this study the probe and the matrix have the same refractive index. However, it has been shown that if the probe is very dilute and can be monitored, a single-particle diffusion coefficient of the probe can be obtained even if the matrix polymer is not dilute.[22-24] On the basis of theoretical justification plus the empirical evidence outlined above, we feel that the diffusion coefficients presented in Figures 3–7 indeed represent the latex diffusion at effectively infinite latex dilution.

Stokes–Einstein Diffusion. The data as plotted in Figure 5 indicate that sphere diffusion in the systems studied here follows Stokes–Einstein behavior at linear polymer concentrations ranging from less than one-fifth of the overlap concentration c^* to up to 8 times c^*. The effective hydrodynamic radius of the latex as calculated from eq 3 is independent of the concentration of matrix polymer. At the highest concentrations studied, the matrix polymer is highly entangled and provides a transient network through which the latex must diffuse, yet Stokes–Einstein behavior is observed when the matrix polymer concentration is much larger than the entangelment threshold as well as when it is much less.

One theoretical approach[1] to an understanding of probe diffusion through an entangled polymer matrix is to compare the radius R of the probe with the matrix correlation length, ξ, the average distance between chain entanglements in the semidilute region. If $R > \xi$, the matrix may have a totally different retardation effect on probe diffusion than when $R < \xi$. In the latter case the probe diffusion is not controlled by the macroscopic viscosity of the matrix solution but by a local microviscosity; otherwise the effect of entanglement will depend on the relaxation of the entanglements compared to probe motion. If one takes[25] ξ as $R_g(c^*/c)^{3/4}$, then $R > \xi$ under all conditions in our work in the semidilute region.

We turn next to entanglement relaxation compared to probe motion. Above c^* it is convenient to take the disentanglement time of the matrix polymer as the tube renewal time, T_R, i.e., the time for a complete change in the topological relation of one matrix chain with its neighbors,[25,26] given by

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

This can be compared to the motion of the probe which we take as the decay time of the correlation function reflecting probe motion, given by

$$\tau_{\text{probe}} = 1/Dq^2 \qquad (7)$$

If the entanglements relax much faster than the probe motion, one would expect no special effect on passing the entanglement threshold, and diffusion would be expected to be a simple function of the zero shear viscosity of the matrix. Using PS1100K as matrix at the highest concentration studied, the maximum T_R is about 4×10^{-3} s whereas the τ_{probe} is 0.3 s, calculated at 45°. Even when the matrix polymer concentration is reduced to c^*, T_R is still almost 2 orders of magnitude less than τ_{probe}.

We next question why Stokes–Einstein behavior is observed at the lowest matrix concentration studied. Consider PS215K, where R_g is about 160 Å. At the lowest concentration the average distance between centers of matrix molecules is less than 500 Å, whereas the probe diameter is about 4000 Å. Dependence on the macroscopic viscosity seems reasonable when one realizes the density of matrix chains. Thus under the conditions of our work one might expect Stokes–Einstein behavior over the entire matrix concentration studied, which we indeed observe.

It is puzzling that in previous studies on latex probe diffusion in a linear polymer matrix Stokes–Einstein behavior of the probe is reported as violated under some condition of study, such as probe size, or the nature of the matrix polymer or its molecular weight or concentration. All latex–matrix studies done previously are different from ours in several ways. In this work the probe and matrix are chemically the same, and there is no experimental observation[19] nor thermodynamic reason for matrix polymer adsorption on the probe. In other studies the probe and matrix are chemically dissimilar. In most cases matrix polymer absorption onto the probe was a possibility, or else was known to occur under some circumstances. This of course would be expected to reduce the probe diffusion more than just a bulk viscosity effect. Although that was observed in some cases, in other cases the probe diffusion was reported to be considerably faster than expected from Stokes–Einstein behavior.

In addition to probe–matrix chemical dissimilarity, all other latex studies are in water as the dispersant for the probe whereas ours is in an organic solvent. Three probe studies in organic solvents have appeared; in all the cases the probes are silica spheres sterically stabilized by stearic acid. In one case the matrix polymer is poly(isobutylene) (PIB) and the solvent chloroform;[10] in the second, the matrix polymer is poly(ethylene oxide) (PEO) in methanol.[12] In both studies self-diffusion of the matrix polymer was monitored by pulsed gradient spin-echo NMR as well as diffusion of the probe by quasi-elastic light scattering. In the third case the matrix polymer is poly(methyl methacrylate) (PMMA)[6] in chloroform. With PIB or PMMA as the matrix polymer there was no evidence of adsorption. Stokes–Einstein behavior was closely followed, with perhaps a slight increase in ηD with concentration at high matrix concentration in the case of PIB. The slight increase in ηD concentration was suggested to be a coupling of the motion of the probe and the matrix polymer. The dependence of ηD on concentration is comparable to the trend seen in our data (Figure 5), though in our data the trend is not statistically significant. In another study by the same authors[12] with PEO as the matrix in methanol there was considerable deviation from Stokes–Einstein behavior at all matrix molecular weights. Matrix diffusion gave evidence of matrix clustering. Thus with spheres as probes the only examples which appear to follow Stokes–Einstein behavior reasonably well are in organic solvents where there is no evidence that the matrix polymer adsorbs on the spherical probe. A final factor to be considered is the concentration range of matrix polymer which has been studied. In the two silica studies where Stokes–Einstein behavior is observed the largest matrix concentration was around 3 times c^*, whereas in several published aqueous latex studies the maximum matrix concentration has been many times c^*. The data do not give a hint that the maximum matrix concentration is of importance. It is not clear why most aqueous latex systems do not follow Stokes–Einstein behavior, and generally have the complication of matrix polymer adsorption.

Scaling Behavior. A variety of approaches have been used which predict scaling laws for probe diffusion and matrix viscosity for dilute and semidilute solutions of random coil polymers.[1,25–33] The predicted scaling parameters are considerably model dependent. A number of ternary systems involving linear chains as well as spheres experimentally follow scaling laws.[34] In the probe–matrix studies referenced scaling behavior is typically observed irrespective of whether or not Stokes–Einstein behavior is followed by a spherical probe. It would not be surprising that our latex–matrix–solvent system behaves similarly. We have already discussed that the matrix–solvent viscosity scales with c/c^* (Figure 1b). In Figures 6 and 7, D/D_0 was shown to scale with matrix concentration and molecular weight according to either eq 4 or eq 5. The dependence on c with ν equal to 0.99 and on M with γ equal to 0.49 is within the range observed in other systems. However, since D does not follow Stokes–Einstein behavior in most of the other studies, it is unclear if a comparison should be made. A closer look at these scaling parameters will be discussed in a subsequent paper.[35]

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References and Notes

(1) Langevin, D.; Rondelez, F. *Polymer* **1978**, *19*, 875.
(2) Gorti, S.; Ware, B. R. *J. Chem. Phys.* **1985**, *83*, 6449.
(3) Lin, T.-H.; Phillies, G. D. J. *J. Colloid Interface Sci.* **1984**, *100*, 82.
(4) Lin, T.-H.; Phillies, G. D. J. *Macromolecules* **1984**, *17*, 1686.
(5) Ullmann, G. S.; Ullmann, K.; Lindner, R. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 692.
(6) Brown, W.; Rymden, R. *Macromolecules* **1988**, *21*, 840.
(7) Lin, T.-H.; Phillies, G. D. J. *J. Phys. Chem.* **1982**, *86*, 4073.
(8) Brown, W.; Rymden, R. *Macromolecules* **1986**, *19*, 2942.
(9) Phillies, G. D. J.; Malone, C.; Ullmann, K.; Ullmann, G. S.; Rollings, J.; Yu, L.-P. *Macromolecules* **1987**, *20*, 2280.
(10) Zhou, P.; Brown, W. *Macromolecules* **1989**, *22*, 890.
(11) Nahme, O. A.; Johnson, P.; Donald, A. M. *Macromolecules* **1989**, *22*, 4326.
(12) Zhou, P.; Brown, W. *Macromolecules* **1990**, *23*, 1131.
(13) Furukawa, R.; Arauz-Lara, J. L.; Ware, B. R. *Macromolecules* **1991**, *24*, 599.
(14) Couper, E. C.; Johnson, P.; Donald, A. M. *Polymer* **1991**, *32*, 2815.
(15) Phillies, G. D. J.; Brown, W.; Zhou, P. *Macromolecules* **1992**, *25*, 4948.
(16) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K. *J. Chem. Phys.* **1985**, *82*, 5242.
(17) Phillies, G. D. J.; Gong, J.; Li, L.; Rau, A.; Zhang, K.; Yu, L.-P.; Rollins, J. *J. Phys. Chem.* **1989**, *93*, 6219.
(18) Russo, P. S.; Mustafa, M.; Cao, T.; Stephens, L. K. *J. Colloid Interface Sci.* **1988**, *122*, 120.
(19) Onyenemezu, C. N.; Roman, M.; Fedic, R.; Miller, W. G. *J. Appl. Polym. Sci.*, to be submitted.
(20) Russo, P. D. Ph.D. Thesis, University of Minnesota, 1981.
(21) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(22) Phillies, G. D. J. *J. Chem. Phys.* **1974**, *60*, 983.
(23) Kops-Werkhofen, M. M.; Fijnaut, H. M. *J. Chem. Phys.* **1981**, *74*, 1618.
(24) Pusey, P. N.; Fijnaut, H. M.; Virj, A. *J. Chem. Phys.* **1982**, *77*, 4270.
(25) de Gennes, P. G. *Macromolecules* **1976**, *9*, 594.
(26) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(27) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
(28) Cukier, R. I. *J. Chem. Phys.* **1983**, *79*, 3911.
(29) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(30) Altenberger, A. R.; Tirrell, M. *J. Chem. Phys.* **1984**, *80*, 2208.
(31) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122.
(32) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1978**, *68*, 2088.
(33) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367.
(34) Brown, W.; Pu, Z. *Polymer* **1990**, *21*, 772.
(35) Onyenemezu, C. N.; Roman, M.; Miller, W. G. *Macromolecules*, to be submitted.