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Tracer Diffusion of Linear Polystyrenes in Poly(vinyl methyl ether) Gels

N. A. Rotstein and T. P. Lodge*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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ABSTRACT: The tracer diffusivity, D_t, has been determined for linear polystyrenes (PS) in poly(vinyl methyl ether) (PVME) gels, by dynamic light scattering (DLS). The tracer molecular weight, M, ranged from 3.2×10^4 to 1.05×10^6. Gel concentrations, c, of 0.200 and 0.235 g/mL in toluene, and monomer-to-cross-linker ratios of 100:1, 50:1, and 25:1, were employed. The gels were synthesized cationically in toluene with the PS tracers incorporated in the reaction mixture and with the gel concentration identical to that used during the DLS measurements. Each gel was dried to constant weight and cut into three pieces. The central piece was reswollen with toluene for the DLS measurements, while the outer two pieces were swollen to equilibrium, to provide an estimate of the molecular weight between cross-links, M_x. The diffusivity scaled approximately as $D_t \sim M_x$, consistent with the reptation model incorporating a Rouse-like friction for the subchains. A series of measurements for gels prepared at $c = 0.235$ g/mL, and subsequently swollen or deswollen, yielded $D_t \sim c^{-0.8\pm0.2}$, consistent with an affine deformation of the cross-links. Comparison with extensive data for PS in PVME solutions indicated that D_t in the gels was consistently less than or equal to D_t in solutions with the same c values, with equality found for the solution data acquired with a high molecular weight matrix polymer. The most important observation, however, was that in the gels $D_t \sim M^{-2.7\pm0.1}$ and $M^{-2.8\pm0.1}$ for $c = 0.200$ and 0.235 g/mL, respectively, in contrast to the reptation model prediction. Possible reasons for this discrepancy are identified, but the results as a whole are apparently not consistent with any currently available theory.

Introduction

The diffusion of polymers through gels is of great interest for at least two reasons. A molecular level understanding of polymer transport through random media would have direct impact on diverse areas of technology, including gel electrophoresis, size-exclusion chromatography, drug delivery, and tertiary oil recovery. At the same time, comparison of tracer mobility in gels with that in un-cross-linked polymer solutions can provide important insight into the dominant diffusion mechanisms in both situations. Despite a large body of solution diffusion data, a consensus of opinion has yet to be attained. In the gel case, data are comparatively sparse.

The main point of discussion is the applicability of the reptation hypothesis[1] to solutions. This approach has been rather successful in reconciling a wide variety of experimental observations on polymer dynamics in melts; this topic has recently been critically reviewed.[2] In many cases the phenomenology of concentrated solutions resembles that of melts (e.g., large-scale elastic recovery, a clear plateau in the elastic shear modulus, the molecular weight (M) dependence of the viscosity), and it is natural to consider the extension of reptation models to entangled solutions. However, the crucial assumption in applying reptation to polymer liquids is that the mobility of the matrix chains is not significant relative to the longitudinal motion of a probe chain; a necessary condition for this assumption to be satisfied is that the probe diffusivity, D_t, is independent of the matrix molecular weight, P. For melts, D_t is indeed independent of P when $P > M$, but in solutions the enhanced mobility of all the chains brings the time scales for lateral and longitudinal motion closer together. The solution case is further complicated by intra- and intermolecular hydrodynamic interactions transmitted through the solvent, by changes in the local friction with concentration, and by changes in coil dimensions.

There have been extensive studies of diffusion in nondilute solutions; the results have been summarized and compared recently.[2-4] Although in general the data may be interpreted in terms of a broad crossover from a "Stokes-Einstein" mechanism in dilute solution to a reptation regime at higher concentration, the existence of a reptation regime in solution has not been established. Specifically, no study has reported concurrent scaling of the diffusivity with M^{-2} and P^0, as reptation requires, in thoroughly entangled solutions. The observation of M exponents near -2 is not sufficient to establish a reptation regime. Nemoto and co-workers have recently reported measurements for the highest concentration solutions examined to date, 40%; the exponent was -2.5 over almost 2 orders of magnitude in M.[4] A similar exponent was reported in the same system for a concentration of 18%.[4] As these solutions represent the highest degree of entanglement examined to date, lack of agreement with the reptation prediction is very significant. At the same time, attempts to interpret the data in terms of alternative models have not met with any greater success. For example, the so-called "hydrodynamic scaling model"[5] is unable to describe the data of Nemoto et al., nor is it able to explain adequately the retardation of star polymers relative to linear polymers of identical molecular weight,[6,7] despite claims to the contrary.[8] Thus, the correct description of diffusion in nondilute solutions remains elusive. As much of the discussion can be cast in terms of a comparison between diffusion in solution and diffusion in gels, examination of the latter is particularly desirable. Application of the reptation model to solutions essentially assumes that the matrix polymer acts to retard the probe just as a gel would; conversely, the hydrodynamic scaling model and similar approaches stress the fundamental dissimilarity of solutions and gels.

The measurement of D_t for linear polymers in chemical gels is not a trivial undertaking. A variety of approaches have been pursued, with varying degrees of success.[9-14] For the purpose of addressing the issues discussed above, there are several criteria for the experimental protocol that one would like to satisfy under ideal conditions. Among these criteria are (i) a reproducible method of gel synthesis, (ii) a means of characterizing the gel concen-

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* Author to whom all correspondence should be addressed.

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Table I
Molecular Weights between Cross-Links for Gel Samples

	$c = 0.235$ g/mL			$c = 0.200$ g/mL		
M	$r = 100{:}1$	$r = 50{:}1$	$r = 25{:}1$	$r = 100{:}1$	$r = 50{:}1$	$r = 25{:}1$
3.2×10^4		6.2×10^3	4.6×10^3		8.7×10^3	2.4×10^3
6.5×10^4	7.0×10^3	7.7×10^3	4.0×10^3	1.6×10^4	1.4×10^4	1.9×10^3
1.00×10^5		7.6×10^3	3.6×10^3		1.2×10^4	
1.79×10^5	1.4×10^4	7.4×10^3		1.1×10^4	7.3×10^3	
3.50×10^5	1.1×10^4				1.9×10^4	
4.22×10^5	1.6×10^4	1.7×10^4		1.4×10^4	6.5×10^3	
1.05×10^6	1.0×10^4			1.5×10^4	5.8×10^3	

tration and cross-link density, (iii) a nonperturbative diffusion measuring technique, (iv) minimal specific interactions between gel and probe, and (v) a body of D_t results in solution for the same chemical system. Point iii effectively rules out techniques involving the imbibing of the probe by the gel. Point iv is important because, in some studies, including those reported here, the probe and the gel are chemically different; in several other studies, polyelectrolytes are involved. Of the results reported previously, the most pertinent are the studies of Bansil and co-workers.[13,14] In particular, an M dependence of −1.8 was reported for the diffusion of polystyrene (PS) in gels of poly(methyl methacrylate) (PMMA), at a gel fraction of 12% and a monomer-to-cross-linker ratio of 25:1.[13] The measurement technique was dynamic light scattering (DLS), and the solvent was chosen to match the refractive index of the gel. These results were interpreted as evidence for reptation (the difference between the observed exponent of −1.8 and the canonical −2 associated with strict reptation was ascribed to tracer chain expansion). One potential problem with this chemical system is the proximity to the phase boundary; ternary PS/PMMA solutions are known to demix at comparable concentration and molecular weight conditions. More recently, DLS has been used to examine PMMA gels containing unattached PMMA chains, thus circumventing this difficulty.[14] In this case, however, the index matching possibility is lost, and the experimental correlation function contains contributions from the gel, the tracer, and cross-terms, thus complicating the extraction of the tracer diffusivity.

In this paper, we report measurements of D_t for linear polystyrenes in poly(vinyl methyl ether) (PVME) gels, by DLS. The solvent is toluene, which is almost isorefractive with PVME. PS and PVME form a miscible pair, and thus the onset of phase separation is not a concern. Finally, we have previously reported an extensive series of measurements of D_t for PS in PVME solutions, with probe molecular weight, architecture (linear, 3-arm, and 12-arm stars), matrix molecular weight, and matrix concentration as variables.[3,6,15-17] Thus, point v above is satisfied, and its importance will be underscored by the results to be presented.

Experimental Section

Sample Preparation. The preparation of each sample comprised three steps, which combined required about 3 months per sample. In the first stage, the gel was synthesized cationically in toluene solution, with the polystyrene (PS) tracer incorporated in the reaction medium. In step two, the gels were quenched with methanol and dried to constant weight under vacuum. In step three, the dried samples were cut into three pieces, two of which were used for characterization by swelling and the third reswollen with toluene for the dynamic light scattering (DLS) measurements. The PS tracers were all narrow distribution samples ($M_w/M_n < 1.1$), with weight-average molecular weights of 1.05×10^6 (NBS 1479), 4.22×10^5 (Toyo-Soda), 3.50×10^5 (Pressure Chemicals), 1.79×10^5 (NBS 705), 1.00×10^5 (Pressure Chemicals), 6.5×10^4 (Polysciences), and 3.2×10^4 (Pressure Chemicals).

The gel synthesis was conducted at −78 °C, both because the vinyl methyl ether (VME) monomer (Aldrich) is a gas at room temperature and in order to minimize extraneous side reactions. The reactions were carried out in 12-mm-o.d. scattering cells, equipped with ground-glass stoppers. The reaction mixture was prepared by combining appropriate quantities of separate toluene solutions, containing respectively the PS tracer, the VME, the divinyloxybutane (DVOB) cross-linker (Dajac Laboratories), and BF_3 etherate (Aldrich) as initiator. The final concentrations were such that the PS was well below its coil overlap concentration ($c_{PS} \approx 0.1c^*_{PS}$). The spectrograde toluene (Aldrich) was distilled over CaH_2 and under N_2; the solvent and the PS and DVOB solutions were filtered extensively prior to use. The VME was condensed after passing through KOH and CaH_2 columns to remove impurities and H_2O. The various reagent solutions were added sequentially to the cell under flowing N_2 to minimize uptake of H_2O. Each sample cell contained a small stir bar to permit stirring during the early stages of the reaction, and the reaction was then allowed to proceed for 2–3 days.

After the gelation reaction was deemed sufficiently complete, the scattering cell was cut just above the sample and the sample immersed in methanol at room temperature to quench the carbocations. After a period of approximately 1 week, the sample was uniformly opaque to the eye, as neither PS nor PVME is soluble in methanol. At this point the sample was removed completely from the remainder of the cell. The sample was then dried to constant weight under vacuum over the course of at least 2 months to remove both methanol and residual toluene. The resulting cylindrical plug was sliced into three sections. The upper and lower sections were swollen with toluene for at least 24 h to attain swelling equilibrium. The volumes in the dry, swollen, and initial (i.e., immediately after synthesis) states were calculated and employed in a modified Flory–Rehner equation[18,19] to estimate the average molecular weight between cross-links, M_x, as

$$M_x = \hat{V}_s c_0 (V_0/V_d)^{1/3} \{-\phi_e{}^{1/3}/[\ln(1-\phi_e) + \phi_e + \chi\phi_e{}^2]\} \quad (1)$$

where $\hat{V}_s = 0.107$ L/mol is the solvent molar volume, c_0 is the polymer concentration when the gel synthesis is carried out, V_0 is the volume of the same sample in the relaxed state (i.e., the volume occupied by the polymer and solvent when the cross-links were introduced into the system), V_d is the volume occupied by the dry network, ϕ_e is the volume fraction of polymer in the gel at swelling equilibrium, and $\chi = 0.368$ is the Flory interaction parameter, which was determined from osmotic pressure experiments performed by Dr. K. Goebel at 3M Corp. The results are given in Table I.

The central portion of the dried sample was weighed and placed upright in a new, carefully dedusted scattering cell. Filtered toluene was then added to bring the gel to the same concentration it had in the original reaction mixture (assuming complete reaction). In this way the sample swelled uniformly and touched all the walls of the scattering cell, and presumably the individual strands were in a state of stress comparable to that during the synthesis itself. Each gel was completely clear and homogeneous to the eye.

Completeness of reaction has been assumed for all gels. As a test, the weight of one gel, prepared at 0.235 g/mL, was compared to the expected weight assuming the incorporation of all starting materials; the two weights were found to differ by less than 2%.

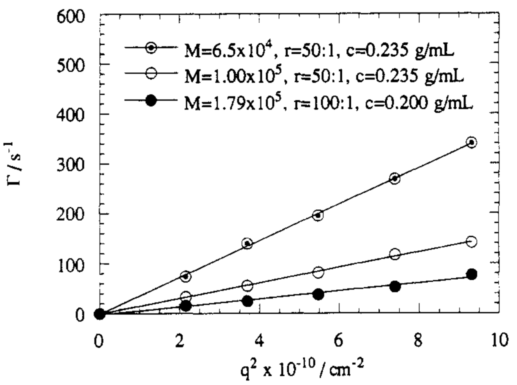

Figure 1. Decay rate versus the squared wave vector for three representative samples.

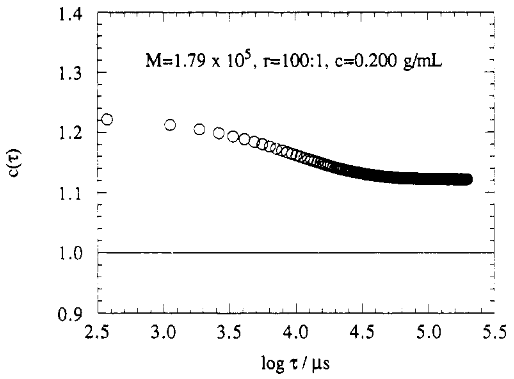

Figure 2. Normalized correlation function versus delay time for a representative sample, illustrating the diffusive decay at short times and the quasi plateau at long times.

Also, all samples were swollen to the same concentration they had during synthesis and were always observed to reach the walls of the scattering cell, which would not occur if the reaction fell significantly short of completion. The (number-average) values expected for M_x on the basis of stoichiometry are 2900, 1450, and 725, corresponding to monomer-to-cross-linker ratios, r, of 100:1, 50:1, and 25:1, respectively. These values are typically a factor of 4–5 lower than those determined experimentally. This discrepancy could be due to several factors. First, the Flory–Rehner analysis constitutes a significant source of uncertainty because it is based on the application of an approximate theoretical expression. Moreover, the χ value used was determined in the infinite dilution limit, whereas in general χ is known to be concentration-dependent. Second, it is possible that the cross-linker did not react completely, either because a small percentage of material was not incorporated during synthesis or because some portion of the cross-linker reacted only once. Third, clustering of cross-linker into small spatial regions and acting as one effective cross-link cannot be ruled out. Finally, it is not unusual to find discrepancies of factors of 2–3 in M_x when comparing results obtained by swelling versus other characterization methods.[20] Therefore, while the M_x values reported are very useful as relative values when comparing one gel to another, the absolute values should be viewed with some caution.

Diffusion Measurements. DLS measurements were made in a home-built apparatus described elsewhere.[16] An argon ion laser (λ_0 = 488 nm) was employed as the light source, and a BI2030 multi-τ autocorrelator (Brookhaven Instruments) computed the intensity autocorrelation functions. For each sample, measurements were made at three or more scattering angles between 30° and 135°, and at different positions within the gel, to ensure homogeneity. All measurements were made at 30.0 ± 0.1 °C. The resulting correlation functions were routinely analyzed by the method of cumulants, using both the measured and floated base-line options and assuming homodyne detection.[21] A subset of the correlation functions was also analyzed via the Laplace inversion algorithm CONTIN.

All samples exhibited two relaxation modes. The faster mode had a mean decay rate, Γ, proportional to q^2, where q is the scattering vector, and was attributed to the PS diffusion. Typical examples are shown in Figure 1. The slower mode had a mean decay rate in the hertz to millihertz range, at the long time limit of detectability, and the correlation functions never decayed completely to the calculated base line on the experimental time scale. This mode was assigned to the gel itself, presumably due to some small amount of impurities incorporated during sample preparation and/or to scattering from the cross-link sites which may not be exactly isorefractive with the solvent. It should be noted that this mode was still visible even when no PS was added to the gel. An example of a correlation function is shown in Figure 2. By τ = 100 ms, the correlation function has attained a well-defined plateau, which is substantially higher than the calculated base line indicated by the solid line in the figure.

Care was taken to account for contamination by the (ultraslow) gel mode in the signal of interest. The extent of the contribution of the gel mode was estimated by comparing the measured base line (from the correlator delay channels) and the calculated base line. Base-line differences of up to 15% were often observed, due to the development of this long time mode. In general, the occurrence of such a high base-line difference is attributed to dust contamination and is accompanied by apparent decay rates that decrease as the magnitude of the percent base-line difference increases. However, in the present case the measured decay rates for the fast mode were apparently insensitive to the magnitude of these base-line differences. It should be noted that, for most of the samples examined, the autocorrelation function was seen to decay to the measured base line, as determined by comparing the difference (less than 1%) between the value of the autocorrelation function for the last few channels of the autocorrelator and the measured base line (i.e., delay channels). In other words, the delay channels represented the value of the correlation function prior to the decay due to the gel mode. In most cases agreement between values of Γ for the fast mode obtained by cumulants, with both base-line options, and by CONTIN was quite reasonable (typically within 20%); however, in some cases the results from cumulants (floated base line) and CONTIN were in agreement but the cumulant results (measured base line) differed by up to 75%.

For the slowest decay rates measured (i.e., samples with M = 1.05 × 10^6), the autocorrelation function did not even decay to the measured base line, because the delay channels coincided with the region of decay of the ultraslow gel mode (here the difference between the correlation function for the last few channels and for the delay channels was greater than 1%). For such slow diffusivities separation of the two decay processes could become difficult since the two modes would exhibit some overlap; also, the decay rate of the PS mode alone approached the long time limit measurable by the instrument, and the autocorrelation functions had a very small preexponential factor. Nevertheless, extraction of the PS diffusive mode was attempted whenever possible and was aided by examination of the data using a $C(\tau)$ versus log τ format, where $C(\tau)$ is the normalized autocorrelation function. If the diffusion of the PS probe was sufficiently separated from the gel mode, then this faster mode would terminate in a plateau (such as shown in Figure 2) which would be immediately followed by the ultraslow decay. Measurements were repeated several times, and autocorrelation functions which did not exhibit this plateau were rejected. In general, examination of these high M data by CONTIN revealed two peaks in the distribution of decay rates which were separated by at least 1 order of magnitude. The faster decay rate was typically within a factor of 2 of the decay rate determined by cumulants using the floated base-line feature but was much larger than the decay rate calculated using the measured base-line value. However, since agreement between CONTIN and the floated base-line cumulant analysis was generally found to be very reasonable and because the delay channels could not always provide a stable measured base line (due to delay channel overlap with the gel mode decay), the accepted autocorrelation functions were fitted to a cumulant function using the floated base-line feature and, in effect, taking the plateau as a base line. For consistency all decay rates reported here were obtained via cumulants using the floated base-line feature.

For selected samples, the gels were swollen with THF, which is not isorefractive with PVME. In this way it was possible to use dynamic light scattering to determine the time scale for the cooperative diffusion of the gel itself, which was typically around 10^4 Hz. This established that the PS diffusive mode lay consistently between, and could be separated from, the (invisible) cooperative mode of the gel and the very slow (visible) gel mode; the resulting uncertainty in the diffusion coefficients is estimated to be less than 20%, except for the highest molecular weight PS samples ($M = 1.05 \times 10^6$) where the uncertainty could be as high as 100%. Furthermore, measurement of the cooperative diffusion coefficient of a gel swollen with THF provides an estimate of a dynamic correlation length, ξ, in the gel.[22] For gels with $c = 0.235$ g/mL, $\xi \approx 2$ nm. In comparison, the M value for a PS chain in a good solvent having a radius of gyration of 2 nm would be approximately 5000.

Results and Discussion

Reptation Predictions for D_t. Prior to presenting the tracer diffusion results, it is appropriate to review some of the predictions of the reptation model. The reptation hypothesis has been applied to both melts and solutions, and there are some subtle differences between the two situations that are potentially relevant to the gel case. Consider a diffusing chain of molecular weight M in an unspecified matrix; it could be a melt, a network, a solution, or a gel. We assume that the matrix has a particular topological length scale, d, over which the motion of the probe monomers becomes constrained. This length scale also defines a characteristic subchain of molecular weight M_d, with friction coefficient ζ_d. We will assume that the long-time diffusion process is exclusively reptation. The general result is

$$D_t \sim (kT/M^2)(M_d^{\,2}/\zeta_d) \tag{2}$$

if intramolecular excluded-volume interactions for the probe chain are screened over length scales longer than d, although this need not be the case for all the situations of interest. The effect of excluded-volume interactions on length scales greater than d would be to change the characteristic M^{-2} dependence slightly, as well as the M_d dependence.

In the case of homopolymer melts, it has been customary to assume that the friction coefficient ζ_d is Rouse-like, such that

$$(\zeta_d)_{\text{Rouse}} \sim M_d \zeta_0 \tag{3}$$

where ζ_0 is the monomeric friction coefficient. Taking $M_d = M_e$, the entanglement molecular weight, the familiar expression[23,24]

$$D_t \sim (kT/M^2)(M_e/\zeta_0) \tag{4}$$

is recovered. A Rouse-like friction assumption for ζ_d seems reasonable in this case, given that short chains in the melt follow this relation, but it is not the only possibility. For example, one might assume that ζ_d follows a Stokes-like form

$$(\zeta_d)_{\text{Stokes}} \sim d \sim M_d^{\,\nu} \tag{5}$$

where ν, the standard excluded-volume exponent, allows for the possibility of excluded-volume interactions on length scales shorter than d. In this case

$$D_t \sim (kT/M^2)(M_d^{\,2-\nu}) \tag{6}$$

In the application of reptation to semidilute solutions, it is the Stokes-like assumption that is made.[25,26] In solutions, the concentration dependence enters through d (or M_d), and here another choice is required. If one associates d with the screening length or "blob" size, ξ, then

$$d \sim c^{\nu/(1-3\nu)} \tag{7}$$

which leads to the familiar $c^{-1.75}$ (good solvent) and c^{-3} (Θ solvent) scaling laws for D_t. On the other hand, if one takes the relevant length scale to be determined by $M_e(c)$, i.e., from the c dependence of the plateau modulus G_N, one finds

$$d \sim c^{-1 \text{ to } -1.2} \tag{8}$$

from the empirical result that $G_N \sim c^{2 \text{ to } 2.4}$.[27] Thus, for solutions one can obtain four different sets of concentration scaling laws, according to whether ζ_d is taken as Rouse-like or Stokes-like and according to whether the topological length scale is taken from the screening length or the entanglement length:

$$D_t \sim c^{(2-\nu)/(1-3\nu)} \quad \text{(Stokes friction, blob size)} \tag{9a}$$

$$D_t \sim c^{1/(1-3\nu)} \quad \text{(Rouse friction, blob size)} \tag{9b}$$

$$D_t \sim c^{-3 \text{ to } -3.6} \quad \text{(Stokes friction, entanglement length)} \tag{9c}$$

$$D_t \sim c^{-2 \text{ to } -2.4} \quad \text{(Rouse friction, entanglement length)} \tag{9d}$$

Thus, the "standard" reptation-plus-scaling results for semidilute solutions are embodied in eq 9a, whereas the melt predictions are consistent with eq 9d. Presumably in the high-concentration regime ($10\% < c < 100\%$) one expects a crossover to occur, both in the identification of the appropriate length scale and in the form of the associated friction coefficient. However, it has been well established in melts that reptation predictions are not recovered (if they are recovered at all) until at least $M/M_e > 5$.[2,27] If one applies the same criterion to solutions, it is unlikely that reptation would ever be observed in semidilute solutions, and possibly eq 9d is the only one of the four that may be followed.

In applying these results to the case where the matrix is cross-linked, with an average molecular weight between cross-links M_x, we will assume that the screening of excluded-volume interactions is unaffected, although this may not be the case.[28] Furthermore, we will assume that we are in the so-called "strangulation" regime, where $M_d = M_x \le M_e$.[29] In other words, the cross-linked matrix provides topological constraints that are more closely spaced than the entanglements would be if the system were not cross-linked. This is the regime in which our data fall. In this case, the result is simply

$$D_t \sim (kT/M^2)M_x \tag{10}$$

with the Rouse-like assumption for ζ_d and

$$D_t \sim (kT/M^2)M_x^{\,2-\nu} \tag{11}$$

for the Stokes-like assumption. Concentration is no longer an explicit variable in the gel case, because it is the same during synthesis as during the measurement. However, it will undoubtedly have an effect in the prefactor for ζ_d. Concurrently, the difference between using a "blob" argument or an entanglement length argument disappears because the length scale is imposed through $d \sim M_x^{\,\nu}$.

If a gel synthesized at concentration c_0 is subsequently swollen or deswollen to a concentration c, an affine

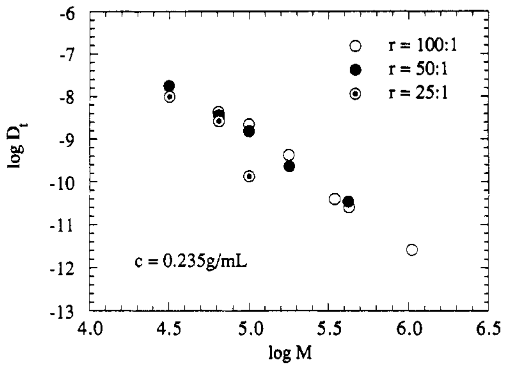

Figure 3. Tracer diffusion coefficient versus molecular weight for gels with c = 0.235 g/mL.

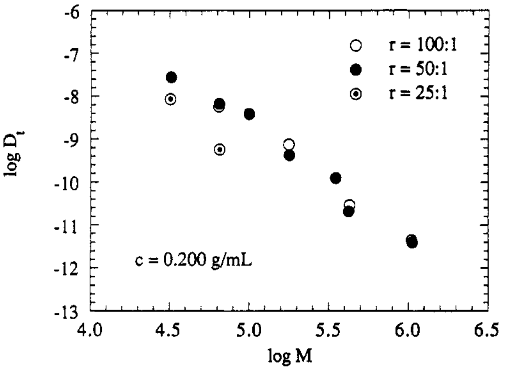

Figure 4. Tracer diffusion coefficient versus molecular weight for gels with c = 0.200 g/mL.

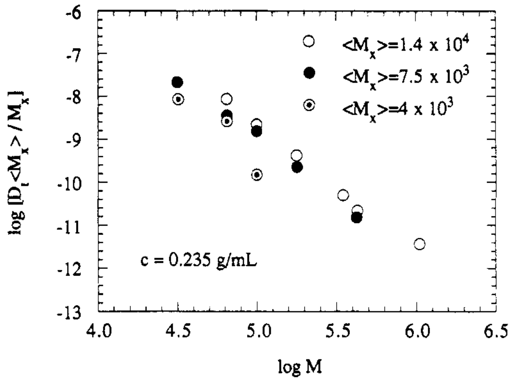

Figure 5. Data from Figure 3, normalized by the ratio of the average molecular weight between cross-links for a given monomer-to-cross-linker ratio to the instantaneous molecular weight between cross-links.

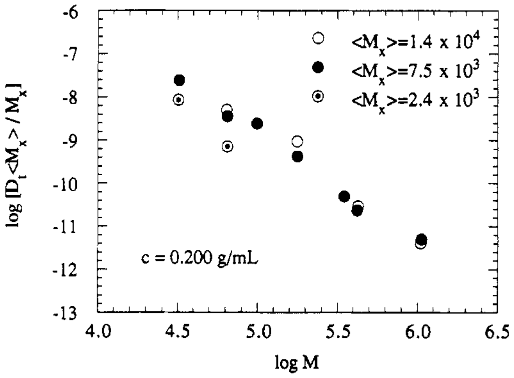

Figure 6. Data from Figure 4, normalized by the ratio of the average molecular weight between cross-links for a given monomer-to-cross-linker ratio to the instantaneous molecular weight between cross-links.

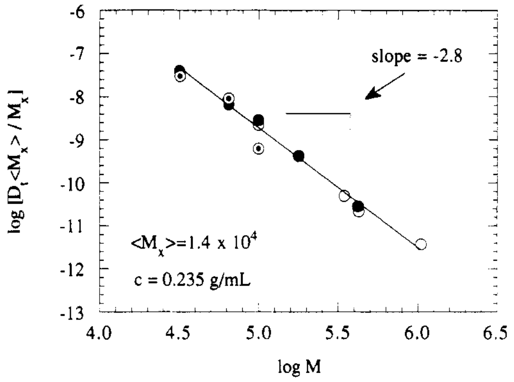

Figure 7. Data from Figure 3, normalized by the ratio of 1.4 × 10^4 to the instantaneous molecular weight between cross-links.

deformation assumption leads to

$$d \sim (c/c_0)^{-1/3} \qquad (12)$$

and thus to

$$D_t \sim c^{-1/3\nu} \qquad (13)$$

in the Rouse-like case and

$$D_t \sim c^{(\nu-2)/3\nu} \qquad (14)$$

for the Stokes-like case. In either eq 13 or eq 14, and for either good (ν = 0.6) or Θ (ν = 0.5) solvents, the effect of isotropic swelling on D_t is predicted to be weak (i.e., concentration exponents of magnitude ≤1). This should be contrasted to solutions, where concentration exponents of −3 or stronger have been reported.[3]

Results for D_t in Gels. The values of D_t for a series of gels with c = 0.235 g/mL are shown in Figure 3, plotted double logarithmically against M. The corresponding data for gels with c = 0.200 g/mL are shown in Figure 4. In both plots, data for gels with nominal monomer-to-cross-linker ratios, r, of 100:1, 50:1, and 25:1 are shown. Four general observations may be made. First, D_t decreases strongly with increasing M; this will be discussed at length subsequently. Second, for r = 25:1 values of D_t were only obtainable for $M \leq 10^5$. Third, for the other two r values, the data appear to be approximately independent of r, within the scatter. Finally, the data for c = 0.200 g/mL generally lie slightly above those at the higher concentration, as expected. The swelling results presented in Table I indicate that M_x fluctuates substantially within a set of gels of constant r. Therefore, the data in these two figures are replotted in Figures 5 and 6, after normalization by the factor $\langle M_x \rangle / M_x$, where M_x is the actual value for each gel and $\langle M_x \rangle$ is a typical value for a given r. Thus, for r = 100:1, $\langle M_x \rangle$ was taken as 1.4 × 10^4, while for 50:1 a value of 7.5 × 10^3 was used. For r = 25:1, $\langle M_x \rangle$ = 4 × 10^3 and 2.5 × 10^3 for c = 0.235 and 0.200 g/mL, respectively. For c = 0.235 g/mL, the data are now clearly separated; i.e., for larger r, D_t is larger, in agreement with expectation. For c = 0.200 g/mL, the separation of the different r sets is not quite as clear, but the difference from the unnormalized data in Figure 4 is distinct and in the expected direction. This scaling of D_t with M_x follows the assumption of a Rouse-like friction, as in eq 10. On the basis of a value for M_e of approximately 7 × 10^3 for PVME melts,[6] we can estimate that M_e would be on the order of 3 × 10^4 for solutions of high molecular weight PVME at the same concentrations as these gels. Therefore, it is reasonable to interpret the data as falling in the strangulation regime.

To assess whether $D_t \sim M_x$ provides a good description of the data, Figures 7 and 8 present the same data as Figures 5 and 6, respectively, but with $\langle M_x \rangle$ held constant at 1.4 × 10^4. In both cases, good reductions to master curves are

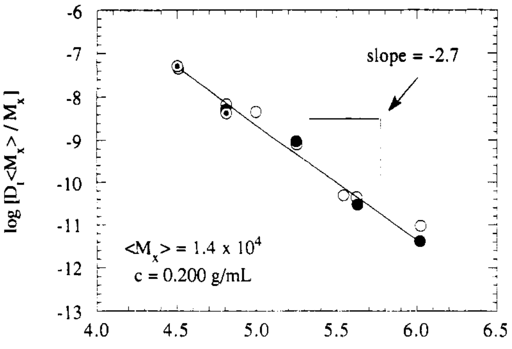

Figure 8. Data from Figure 4, normalized by the ratio of 1.4×10^4 to the instantaneous molecular weight between cross-links.

obtained. However, two individual data points stand out. For $c = 0.235$ g/mL and $r = 25{:}1$, D_t for $M = 1.0 \times 10^5$ lies well below the other values, while for $c = 0.200$ g/mL, the highest M datum for $r = 50{:}1$ is noticeably larger than the value for $r = 100{:}1$. The latter observation we ascribe simply to uncertainty. Of all the values of D_t reported, this one ($M = 1.05 \times 10^6$, $r = 50{:}1$, $c = 0.200$ g/mL) is the only one for which an interpretable correlation function was obtained at only one (high) scattering angle. The former "outlying" point is more interesting, however. We interpret this as reflecting the onset of an effective immobilization of the tracer chains, due presumably to constriction by extremely small pores in the gel. In other words, the distribution of M_x for this value of r is sufficiently broad (at least on the low M_x end) that most of the tracers above a certain length are trapped during synthesis. This is consistent with the fact that no measurable diffusive contributions to the correlation functions were obtained for higher values of M at either concentration for $r = 25{:}1$.

The most important observation to be made from these data, however, is that the M dependence is noticeably stronger than the −2 characteristic of reptation. Best fit straight lines are shown in Figures 7 and 8 (obtained by omitting the two outlying points just discussed), which give slopes of -2.8 ± 0.1 and -2.7 ± 0.1 for $c = 0.235$ and 0.200 g/mL, respectively. Although it is not necessarily the case that these data should be described by a power law, they are reasonably represented in such a manner. Given that the reptation model was designed expressly for the purpose of describing diffusion and relaxation of an unattached chain in a gel or network, these results indicate that the straightforward reptation picture may not apply even to this situation. Possible interpretations and the significance of these results will be discussed subsequently.

Swelling experiments were performed for a series of gels, with $r = 100{:}1$ and $c = 0.235$ g/mL, and with one incorporated probe, with $M = 1.0 \times 10^5$. A series of samples were prepared and either swollen by addition of solvent or deswollen by evaporation. In general, such experiments are rather tedious to perform over a large range of concentrations, as the synthesis needs to be carried out in a smaller diameter cell for each swelling ratio, such that when the gel is swollen to a greater volume, it will just fill the standard 12-mm-o.d. scattering cell. If the swollen gel does not fill the cell, bubbles at the cell walls prohibit scattering measurements from being made, whereas if it is swollen too much, the swelling is not isotropic (which is an interesting topic in itself but beyond the scope of this work). Thus, in this instance only small degrees of swelling were achieved, although for the most swollen sample a new synthesis cell was employed. The results are plotted in a double-logarithmic format in Figure 9. As predicted, D_t has a weak dependence on (c/c_0), where c is the swollen concentration and c_0 the initial concentration. A best fit straight line gives a power law exponent of -0.8 ± 0.2, which is completely consistent with eqs 13 and 14. The uncertainty is such that one cannot distinguish between eqs 13 and 14 or between $\nu = 0.5$ and 0.6. However, it is clearly different from the concentration dependence of D_t obtained for PS tracers in PVME solutions[3] (also indicated in Figure 9), where the data (if forced to a power law dependence) give an exponent of approximately −3. It should also be noted that in this figure the gel data have been corrected for the small changes in local friction with concentration, following the procedure described previously.[3] Furthermore, the close correspondence between the values of D_t for distinct gels prepared under identical conditions lends strong support for the reliability of the experimental protocol.

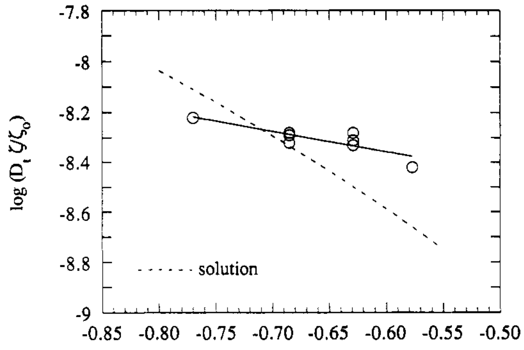

Figure 9. Tracer diffusion coefficient versus concentration for a gel synthesized at $c = 0.235$ g/mL and subsequently swollen or deswollen. The probe had $M = 1.0 \times 10^5$, and the data have been corrected for changes in local friction.

The values of D_t for PS in PVME gels may be compared in more detail with extensive data obtained in solutions and described elsewhere.[3,6,15–17] Indeed, these results provide a unique opportunity to compare diffusion behavior for a given set of probes in cross-linked and un-cross-linked matrices of otherwise identical compositions. (This statement assumes that the cross-link sites introduce no significant new chemical interactions and that the difference between the solvents is irrelevant; the solution data were obtained in *o*-fluorotoluene, because it is more closely indexed matched to PVME than toluene.) Solution data were obtained for three different matrix molecular weights, P, equal to 1.4×10^4, 6.3×10^5, and 1.3×10^6.[3] For the lowest P, data were obtained up to $c = 0.30$ g/mL, while for the higher two P values, the data extended up to $c = 0.200$ g/mL. Therefore, to compare the solution data to the gel data with $c = 0.235$ g/mL, a short extrapolation is necessary. This is accomplished via the stretched exponential function suggested by Phillies,[5] which has been shown to fit the data very well. (The quality of these fits may be assessed by examining Figures 3–5 of ref 3.) However, it should be emphasized that this scaling function will not describe the data up to arbitrarily high concentrations. For example, if these solution data are extrapolated to the melt, the resulting values of D_t scale approximately as M^{-6}, which seems unlikely to be the actual case. Thus, if the extrapolation to $c = 0.235$ g/mL is slightly in error, it at least provides a lower bound for the desired quantity. Finally, the solution data were originally corrected for the concentration dependence of the monomeric friction coefficient via NMR measurements of the solvent diffusivity;[3] this correction has been removed

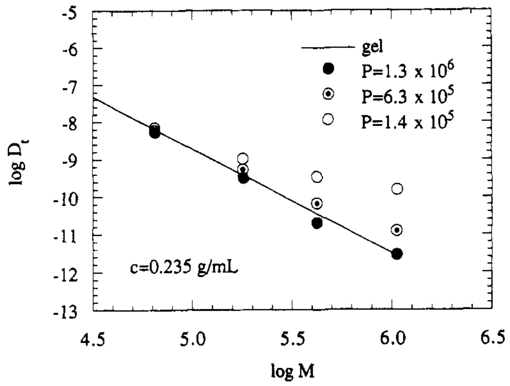

Figure 10. Data from Figure 7, represented by a straight line, compared to tracer diffusion coefficients measured in PVME solutions at the same concentration, reported in ref 3.

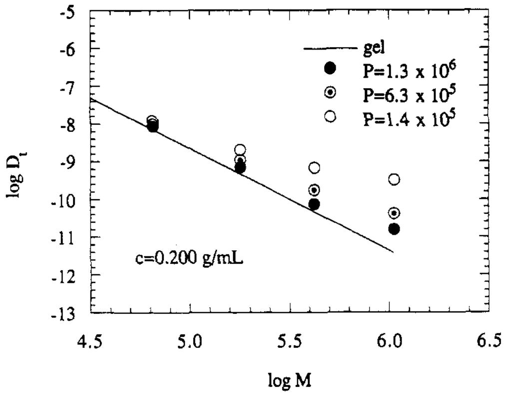

Figure 11. Data from Figure 8, represented by a straight line, compared to tracer diffusion coefficients measured in PVME solutions at the same concentration, reported in ref 3.

in the comparisons to be discussed.

In Figures 10 and 11 the gel data of Figures 7 and 8 are represented by the best fit straight lines and compared to the solution data for the three values of P. At least qualitatively, the results are just what one might expect. First, within the uncertainty, D_t in solution is consistently greater than or equal to D_t in a gel at the same c. Second, as P increases, the solution data approach the gel results, such that, for $P = 1.3 \times 10^6$ and $c = 0.235$ g/mL, D_t in solution is indistinguishable from D_t in the gel. Third, the effect of varying P increases with M, so that for the lowest M examined in solution (6.5×10^4) the results are independent of P for all P examined. The key to understanding these observations is to consider the relative time constants for probe and matrix relaxation. Thus, as P increases for a given M, the matrix relaxation (over length scales greater than M_x or M_e) becomes much slower than that of the probe, leading to D_t independent of P. Similarly, as M increases for a given finite P, D_t will become increasingly P dependent, until the matrix effectively provides only a viscous background for the probe.

A fundamental assumption of the reptation hypothesis is that the matrix relaxation is sufficiently slow; i.e., that P is large enough. At the same time, it is necessary that both probe and matrix be of sufficient length, and the matrix at sufficient concentration, to be well-entangled before the reptation model could apply. For the lowest P examined, the concentrations in Figures 10 and 11 are estimated to correspond to $M/M_e \approx 4$. Thus, the fact that D_t for $M = 6.5 \times 10^4$ is independent of P, including in the gel, is reasonable. The correlation length of the gel, estimated to be approximately 2 nm as discussed in the Experimental Section, is sufficiently small relative to R_g for this probe (estimated to be 8 nm) that the reptation criteria may be satisfied. For this lowest P, as M increases, D_t lies progressively further above the gel results, indicating the transition toward the viscous solvent regime. Indeed, D_t for the two highest M examined suggests an M exponent of approximately -1 or even less, consistent with the constraint release predictions.[30,31] Conversely, the data for the largest P, and particularly for $c = 0.235$ g/mL, demonstrate that over this M range $P = 1.3 \times 10^6$ and $P = \infty$ (i.e., the gel) are indistinguishable and that therefore the reptation model should be applicable. However, the M exponent exceeds the predicted -2, as pointed out before. One other important conclusion may be drawn from these comparisons, namely, that the gels as synthesized do provide a matrix for the probe chains that is equivalent to a solution of high molecular weight PVME. Thus, the assumption that the presence of chemical cross-links has no particular effect on the probe mobility is justified. Furthermore, any explanation for the unexpected M exponents observed in the gel cannot invoke some unspecified artifact unique to the gels, as the results are so consistent with the solution data.

Interpretation. The principal results from these measurements are (i) D_t scales as M_x, (ii) a limited series of measurements in swollen gels are consistent with an affine deformation of the cross-links, (iii) comparison with D_t in solution indicates that the gel acts to retard probe mobility in the same manner as a solution in the limit of large matrix molecular weight, and (iv) D_t has a significantly stronger M dependence than the reptation model predicts. Result i is in agreement with the reptation model and may be taken as evidence in favor of taking a Rouse-like friction for the subchain rather than the Stokes-like friction commonly employed in applying reptation to semidilute solutions. As far as we are aware, this represents the first time that the dependence of D_t on M_d has been tested directly in gels; Antonietti and Sillescu[32] found a rather complicated dependence on M_x in networks. At the same time, it should be noted that the proportionality to M_x may not be unique to the reptation model. For Gaussian chains, $d^2 \sim M_d$, and thus any model that predicts that D_t is proportional to the cross-sectional area of the average pore in the gel could reach the same result. Result ii is also consistent with the reptation model, but again this result need not be unique to reptation. However, it is important to reemphasize the great difference in concentration dependence obtained by varying c in solution, relative to varying c by swelling a gel.

Result iii is more powerful. It demonstrates that it is possible to satisfy the primary assumption of the reptation model in solution, i.e., that long-range mobility of the matrix chains does not contribute to the diffusion of a probe. Stated in an alternative fashion, these results show that an entangled polymer solution *can* act like a gel in retarding the motion of a linear probe. Probe diffusivities independent of P in solution have been reported previously, generally for $P \geq 3$–$5M$.[4,33,34] Also very important is the corollary that the introduction of chemical cross-links in this system has no ancillary effect on the probe mobility, other than that directly ascribable to the suppression of matrix chain diffusion. This represents the first time, to our knowledge, that it has been possible to make a direct comparison of probe diffusion in entangled solutions and in chemical gels of the same composition. Finally, this result will play an important role in discriminating among possible explanations for the most important and surprising result, listed as iv; the "anomalous" exponents in Figures 7 and 8 are apparently not unique to gels.

One possible explanation for result iv is that it reflects a crossover effect, i.e., that over some range of M mechanisms in addition to reptation contribute to the mobility, thus increasing D_t and leading to a region with a higher exponent than −2 as these extra mechanisms are suppressed as M increases. In favor of this interpretation are the results of Sillescu et al. for PS melt diffusion, where exponents as large as −2.5 were observed in the unentangled-to-entangled crossover.[35,36] Some evidence for this may also be found in the data themselves. One could plausibly draw a line with a slope of −2 through the points for the two highest M in Figures 7 and 8, which when extrapolated would lie below the data for the shorter chains. However, within the uncertainty of the data, such a procedure would have to be viewed as highly speculative; measurements for larger M or c will be required to assess the extent of the anomalous exponent regime. Still further evidence for the crossover explanation could be taken from the computer simulations of Deutsch and Madden, in which loose chains diffusing through a regular network give exponents of approximately −2.5.[37] Their interpretation of these results lies in the tube length fluctuation argument of Doi,[38] which was originally advanced to account for the experimentally observed 3.4 exponent in the viscosity. Previously, it had been thought that these fluctuations would not have a noticeable effect on D_t. The difficulty with Deutsch and Madden's result, however, as they point out, is that experimentally the 3.4 law extends over two or more decades in M, while $D_t \sim M^{-2.5}$ has not been seen *in melts* over any extended range of M. Furthermore, several groups have reported M^{-2}, not $M^{-2.5}$, for computer simulations of chains in regular networks.[39]

In contrast to the melt case, dependences stronger than M^{-2} have been reported in several solution studies, including those for PS in PVME,[3,17] for PS in PS/toluene,[34] and most recently for PS in dibutyl phthalate.[4] These results of Nemoto et al. are potentially very revealing.[4] For concentrations of 18% and 40% PS, they observe exponents of −2.5. The latter data correspond to the highest solution concentration for which an extensive series of D_t versus M results have been reported. The key point is that these data extend to such high molecular weights that M/M_e is greater than for any of the melt systems studied so far. Therefore, it is very difficult to ascribe the exponent of −2.5 solely to a crossover between unentangled and entangled behavior, as the same effect is not seen in melts. Rather, it appears that there is something fundamentally different between diffusion in melts and networks, on the one hand, where $D_t \sim M^{-2}$ is commonly seen,[2,23,39] and solutions and gels, where stronger exponents are the norm for sufficiently high degrees of entanglement. Thus, while the crossover argument could possibly explain these results, it would not reconcile them with the data of Nemoto et al.[4]

In a recent series of computer simulations, Muthukumar and Baumgärtner have followed the diffusion of a flexible chain through an array of obstacles.[40,41] When the obstacles were placed in a spatially regular manner, with a characteristic pore size sufficiently smaller than the chain dimension, reptationlike behavior was observed, i.e., $D_t \sim M^{-2}$. In contrast, if the same overall density of obstacles was distributed randomly, quite different results were found. In particular, the M dependence of D_t was no longer strictly a power law, but regimes with apparent exponents as strong as −3 were seen. This phenomenon was ascribed to "entropic traps", in which chains tended to be localized in larger-than-average pores, where they enjoyed more conformational entropy. The crucial feature, therefore, is a distribution of pore sizes, with the larger pores comparable to the chain dimensions. If the chain molecular weight were increased substantially, then the reptation result would be recovered.

It is certainly plausible that this entropic localization phenomenon could explain the gel data. Undoubtedly, the gels have a distribution of pore sizes, and the r = 25:1 series gave a strong suggestion that this distribution was quite broad. At the same time, it is not clear how closely these computer simulations would correspond to a gel. In the former, there are distinct, finite-sized obstacles which do not move, surrounded by empty space. In the gels, in contrast, the cross-links may sample a considerable region of space on the diffusion time scale, and the space surrounding the cross-links is quite dense in gel strands. This issue notwithstanding, however, there is a more significant and intriguing objection to ascribing the anomalous exponents to a broad distribution of "obstacle" spacings: how can this interpretation be extended to include the solution results?

In the excitement of generating experimental tests of the reptation hypothesis over the past 15 years, relatively little attention has been paid to the older question (which reptation models do not answer) of what constitutes an entanglement. Two extreme views may be posited. In one, which we will call the "site" view, an entanglement is a particular two-chain contact that is long-lived on the time scale of single-chain relaxation. Thus, at any instant, only a small fraction of contacts act as entanglements, and these entanglements are localized at particular sites in the fluid. In the opposite picture, which we will call the "field" view, the entanglement interaction is a cumulative effect of many binary contacts, acting to constrain chain motions over a characteristic entanglement length scale, and all locations within the fluid are essentially equivalent. The predictions for chain diffusion by reptation in eqs 2–14 can be constructed from either picture; all that is required are appropriate topological constraints with a characteristic length scale d. However, when one attempts to modify reptation models to account for some degree of lateral mobility, this is no longer the case. For example, the Doi–Edwards construct of a tube adopts something closer to the field view, with tube "dilation" being the result of enhanced lateral mobility.[42–44] In contrast, treatments of constraint release such as that by Graessley[31] incorporate explicitly the rate at which one chain end passes by another chain, thus releasing an "entanglement"; this approach, at least implicitly, assumes something closer to the site view. The point to be made from this discussion is that if one is to ascribe the anomalous exponents in gels to the spatial randomness of the cross-links, then the same exponents in solution should be attributed to the same mechanism. Thus, one must adopt something close to the site view of entanglements; furthermore, the entanglement spacings must be broadly distributed, and the fluctuations in entanglement spacing must persist over the diffusion time scale. This interpretation is both speculative and provocative, but it has at least one positive feature. It provides a clue to the important difference between concentrated solutions and melts: it suggests that, in the former, the fluctuations in entanglement spacing are much larger and play a crucial role. Thus, whether one observes reptation in a particular system would depend not only on the *number* of entanglements per chain but also on the *breadth* of their spatial distribution.

The preceding discussion has emphasized the interpretation of D_t in gels and solutions in the context of the reptation hypothesis. However, it is also possible to try

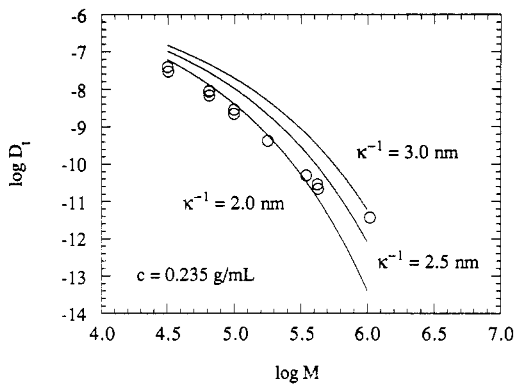

Figure 12. Data from Figure 7 compared to the predictions of eq 15.

to understand the basic features of the data through alternative treatments of transport of Brownian particles in gels and porous media. Several calculations, albeit with different assumptions and different levels of rigor, arrive at the prediction[25,45-49]

$$D_t = D_0 \exp\{-\kappa R\} \qquad (15)$$

where D_0 is the probe diffusion coefficient at infinite dilution, R is the probe radius, and κ^{-1} is a screening length. The concentration dependence of D_t would appear in κ but is not of direct importance here. This equation has been employed for a variety of probes, including both hard spheres and random coils. In the case of flexible chains, therefore, eq 15 could be viewed as the antithesis to reptation in that the mechanism of motion is the same as for a hard sphere. This expression can be compared directly with the data in Figure 7, as shown in Figure 12. To make the comparison, D_0 is taken as $2.54 \times 10^{-4} M^{-0.545}$ cm^2/s from the data for linear polystyrenes reported previously.[3] The radius is taken as the radius of gyration, R_g, and Θ dimensions are assumed: $R_g = 0.03 M^{0.5}$ in nanometers. Direct measurements of R_g for PS in PVME solutions indicate that by a matrix concentration of only 0.05 g/mL the coils have contracted approximately two-thirds of the way to their Θ dimensions,[6] and so this Gaussian approximation is quite reasonable for the gel concentrations of 0.200 and 0.235 g/mL. Finally, the screening length is taken to be comparable to the correlation length, ξ, obtained by DLS on the gels as discussed in the Experimental Section. One could argue about whether R_g is the appropriate radius to take and about numerical prefactors between κ^{-1} and ξ, but it is simpler to compare the data with eq 15 for a range of values of κ^{-1}, as shown in Figure 12. For a particular value of $\kappa^{-1} = 2.0$ nm, which is identical to the estimated $\xi \approx 2$ nm, the curve agrees rather well with the data, particularly for the lower molecular weights. By extension, therefore, the curve would also describe the solution data for $P = 1.3 \times 10^6$. Furthermore, this agreement is obtained without any freely adjustable parameters.

On closer inspection, however, this apparent success of eq 15 should be viewed with some skepticism. First, the observed M dependence of D_t is not really captured by eq 15. The predictions are very sensitive to the choice of κ^{-1}, and in all cases the instantaneous M dependence increases with increasing M; i.e., $\partial^2(\log D_t)/\partial(\log M)^2$ is negative, whereas experimentally this quantity appears to be zero or slightly positive at high M. In other words, for progressively higher values of M the fit would be worse and worse, unless the experimental M dependence were to become much stronger. Second, extensive results for PS stars in PVME solutions,[6] and preliminary results for stars in similar PVME gels,[50] indicate that D_t/D_0 for stars is often much less than the same quantity for linear polymers, even when the radius of the linear polymer is larger than that of the star. These results clearly conflict with the idea that flexible coils move by the same mechanism as hard spheres, as discussed extensively elsewhere.[6,7] Finally, the solution data of Nemoto et al. exhibit a clear power law relation $D_t \sim M^{-2.5}$ over almost 2 orders of magnitude in M,[4] which also cannot possibly be described by eq 15.

Summary

The tracer diffusion of linear polystyrenes in poly(vinyl methyl ether) gels has been followed by dynamic light scattering. Two series of gels, with concentrations, c, of 0.200 and 0.235 g/mL and with monomer-to-cross-linker ratios of 100:1, 50:1, and 25:1 have been examined. For each gel, the molecular weight between cross-links, M_x, has been estimated on the basis of swelling experiments. One major conclusion from these results is that a reliable and reproducible method for the preparation of the gel samples has been demonstrated and that the mobility of the tracer chains can be determined with a precision of better than ±20%. The principal experimental observations are as follows:

1. The diffusivity, D_t, scales with tracer molecular weight as $M^{-2.7}$ and $M^{-2.8}$ in gels with $c = 0.200$ and 0.235 g/mL, respectively.

2. The diffusivity in the gels is always less than or equal to the diffusivity of linear polystyrenes in poly(vinyl methyl ether) solutions.[3] The gel and solution diffusivities are equal for the highest matrix molecular weight employed in solution, over the entire range of M examined, for $c = 0.235$ g/mL.

3. The diffusivity scales as M_x, supporting a Rouse-like friction for the subchains.

4. A restricted set of measurements for swollen and deswollen gels are consistent with affine deformation of the spatial separation of cross-links.

5. For the gels with $r = 25{:}1$, measurements of D_t were not possible except for the lower molecular weights, suggesting that the longer chains are effectively trapped in "tight" regions of the gel.

The results as a whole are not consistent with any available theory. While observations 2–4 are completely consistent with the reptation model, observation 1 is not. It is possible that the data lie in a broad crossover region, but this would be surprising, given the equivalence of the data in gels and in solutions with high molecular weight matrix polymers. The results are also reminiscent of the entropic trapping mechanism suggested by Muthukumar and Baumgärtner on the basis of computer simulations.[40,41] However, it is not clear that these simulations of diffusion through randomly placed, fixed obstacles should be compared directly with diffusion through chemical gels, even though there is evidence that the strand distribution in the gels is quite broad (observation 5). Furthermore, the equivalence of the gel and solution diffusivities would then imply that the entanglements in solution act as distinct but irregularly spaced obstacles. Finally, the data are also not consistent with models of spherical Brownian particles diffusing through gels, as reflected in eq 15. Observation 2 indicates that the cross-links have been introduced into the system without any adverse effect on the diffusivity of the tracer chains. Now that reliable gel preparation, characterization, and diffusion measurement protocols have been developed, further studies of D_t are underway. Of particular interest are measurements for higher c and M and for branched tracers.

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