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Diffusion of Linear Polymer Chains in Methyl Methacrylate Gels

Siniša Pajević,[†] Rama Bansil,[*,†] and Čestmír Koňák[‡]

Department of Physics, Boston University, Boston, Massachusetts 02215, and Institute of Macromolecular Chemistry, Czechoslovak Academy of Science, Prague, Czechoslovakia

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ABSTRACT: We have used dynamic light scattering (DLS) to investigate the probe diffusion of linear polymer chains of varying molecular weight (M_p) in swollen methyl methacrylate (MMA) gels. Two different systems were studied: (i) with polystyrene (PS) as the probe and toluene as solvent and (ii) with poly(methyl methacrylate) (PMMA) as the probe and dioxane as solvent. For system i we found Stokes–Einstein type scaling of the diffusion constant D_t vs M_p at low molecular weights, and a crossover to reptation behavior above a critical molecular weight M_c. The crossover occurs when the radius of gyration of the probe becomes comparable to the correlation length of the gel. For comparison, we also measured probe diffusion of PS in linear PMMA solutions polymerized under conditions identical to that for the gel. A comparison of the effective viscosity of the matrix and D_t for the same probe suggests that the permanent cross-links of the gel help stabilize the transient entanglements in this system. Laplace inversion analysis of the correlation functions shows a broadening of the probe diffusion peak with increasing M_p. Although the average value of D_t is $\sim M_p^{-1.8\pm0.2}$, the width implies that faster and slower diffusional mechanisms also occur, with the D_t vs M_p exponent ranging from −0.5 to −2.7. Our measurements in system ii establish that DLS can be used to study probe diffusion in gels *even without using an isorefractive solvent*. Laplace inversion analysis of composite correlation functions covering 4 decades shows that it is possible to separate the fast collective diffusion of the gel from the slower diffusion of the probe polymer. The average value of this broad mode scales with molecular weight according to the reptation prediction.

Introduction

In recent years there has been an extensive interest in the diffusion of probe polymers in semidilute polymer solutions and melts.[1–6] From a fundamental viewpoint, an understanding of probe diffusion in gels is of relevance to the general question of diffusion in random porous media[7–10] and has applications in problems such as electrophoresis,[11] diffusion of polymers in porous media, and enhanced oil recovery. In addition, this topic is also of importance to many biological problems such as the mobility of organelles and supramolecular assemblies through the cytoplasmic network and controlled drug delivery.

A central issue in much of this work has been whether or not the tracer chains move by reptation[12,13] in such matrices. While this approach has been rather successful in interpretation of experimental observations on polymer diffusion in melts,[2] the existence of a reptation regime in semidilute solutions is still a matter of debate. In solutions, the scaling of the tracer diffusion constant, D_t, vs the molecular weight of the probe polymer, M_p, depends on both the concentration and the molecular weight of the matrix polymer. Numasawa et al.[14] observed a crossover from Stokes–Einstein (S–E) to reptation and determined the crossover curve separating these two regions for polystyrene (PS) probes in poly(methyl methacrylate) (PMMA) solutions in benzene (isorefractive with PMMA matrix).

Many of the difficulties of applying the reptation concept to semidilute solutions and melts come from the fact that the obstacles in such systems are not really fixed.[3] In contrast, fixed obstacles may be encountered in chemically cross-linked gels. However, because of difficulties in making a gel sample with unattached polymer chains, there have been only a few studies of the tracer diffusion of probe polymers in swollen gels[15–21] and cross-linked bulk networks.[22] Recently we have used dynamic light scattering (DLS) to study the diffusion of linear PS and PMMA in methyl methacrylate (MMA) and ethylene dimethacrylate (EDMA) gels.[19,20] We found that for low molecular weight PS probes, $D_t \sim M_p^{-0.6}$, characteristic of S–E behavior, whereas for M_p higher than some critical molecular weight, $D_t \sim M_p^{-1.8}$, characteristic of reptation.

Lodge et al.[21] have investigated the tracer diffusivity of linear PS in poly(vinyl methyl ether) gels with an isorefractive solvent. In contrast to our results, they obtained exponents higher than 2 (i.e., $D_t \sim M_p^{-2.7}$ and $M_p^{-2.8}$ for $c = 0.20$ and 0.235 g/mL, respectively). Such high exponents have been seen in computer simulations[23,24] of the diffusion of a flexible chain through an array of nonuniformly distributed obstacles.

The question of probe diffusion in gels is very complex and depends on several factors such as the size of the probe compared to the characteristic mesh size of the network and the nature of the interaction with the boundary walls. Topological constraints are likely to play a more important role in a gel than in a semidilute solution, and hydrodynamic effects may be of lesser importance. However, the presence of both permanent cross-links and entanglements raises the question of which one of these provides more constraint. De Gennes[25] has suggested that there may be several different regimes for the diffusion of a labeled chain in a swollen gel. In addition, heterogeneities in gel structure cause complications which are not likely to occur in solutions.

All the previous work in this area using DLS has employed an isorefractive solvent. Although such a system is ideally suited for establishing the basic results, this places a severe restriction on the general applicability of DLS to investigate diffusion of polymers in gels. Hence we have extended our study to the case where a nonisorefractive solvent is used by considering the diffusion of PMMA in MMA gels. This case is particularly interesting because the gel and probe polymer are chemically identical.

In this paper we compare dynamic light scattering results for two types of probe polymers: (i) linear polystyrene, which is chemically distinct from the gel, and (ii) linear

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[†] Boston University.

[‡] Czechoslovak Academy of Science.

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poly(methyl methacrylate), which is chemically identical to the gel.

For the experiments with PS probes (system i), as described in our earlier paper,[19] the gels were made by copolymerizing MMA monomers with the cross-linker EDMA in toluene. The main advantage of this system is the fact that toluene is isorefractive with the gel matrix and thus suppresses the light scattering from the gel network. Moreover, toluene is a good solvent for both PS and the MMA gels and thus prevents polymer–solvent phase separation.[26,27] To further reduce effects of phase separation, all measurements on this system were done at 46 °C.[19]

In an effort to examine the differences between the permanent entanglements in the gel and the temporary entanglements in solutions, we also compare D_t for PS probes in MMA gels with those in linear PMMA solutions at the same concentration.

For system ii, since the gel and probe are chemically identical and have essentially the same refractive index, it is not possible to use an isorefractive solvent. Thus, in this case the gels were made in dioxane and the measured correlation functions contain contributions from both the diffusive motion of the probe and the collective diffusion of the gel. Since the probe and the gel matrix are chemically compatible, problems due to phase separation are avoided. On the other hand, since the index matching possibility is lost the extraction of the probe diffusion from the complex gel dynamic is more complicated.

Experimental Methods

Sample Preparation. System i: PS Probe Polymer. The samples used in these experiments are PMMA solutions and gels obtained by copolymerizing MMA with small amounts of EDMA as the cross-linking agent in toluene with the PS probe polymer added prior to polymerization. A set of samples with total monomer concentration $\Phi = 12.5\%$ (v/v) was prepared with different degrees of cross-linking: $f_c = [\mathrm{EDMA}]/[\mathrm{MMA}]$ varying between 0 (the linear polymer) and 4% (gel). The reaction was initiated with azobis(isobutyronitrile) (20 mg/mL of MMA) and allowed to proceed for 7 days at 52.5 °C in cylindrical light scattering cells. By the end of this period the gelation reaction was complete, with a monomer conversion of ~90%. All monomer and polymer solutions were first filtered using 0.22-μm filters (Millipore).

The concentration, c_p, of the PS probe polymers was selected to be well below the overlap concentration c_p^*. In order to obtain comparable scattering intensity from different probe polymers, the concentrations were modified so as to keep M_pc_p approximately constant. Most of the DLS measurements of the tracer diffusion were performed on gel samples with $f_c = 4\%$. For measurements of probe diffusion in linear polymer solution as a matrix we used two approaches. A set of PMMA samples with PS probes was made by polymerizing MMA in toluene under conditions identical to that for the gels at $\Phi = 12.5\%$ and $f_c = 4\%$ (i.e., without the cross-linker EDMA). A few samples were also made by dissolving PS and linear PMMA (monodisperse standards from Pressure Chemical) of varying molecular weights in toluene.

System ii: PMMA Probe Polymer. PMMA gels containing unattached linear PMMA chains were prepared in 1,4-dioxane using the same method as in the previous case. Total monomer concentration was 10% (v/v). The concentrations of the PMMA probe polymers were selected to be below the overlap concentration for the given polymer. Since for f_c values greater than 4% the gels develop heterogeneities of cf. Figure 1), only samples with $f_c \leq 4\%$ were used for light scattering experiments. The results presented in this paper were obtained on the samples with $f_c = 2$ and 3%.

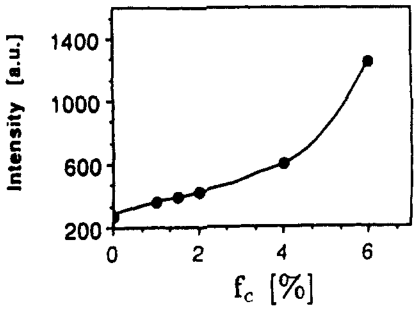

Figure 1. Scattered intensity in arbitrary units at 90° as a function of the EDMA cross-link content for MMA gels in 1,4-dioxane.

Table I
Characteristics of the Gel Matrices

gel system	Φ (v/v)	f_c (v/v)	ξ_h (nm)	ξ_x (nm)	M_x	χ
MMA/toluene	0.125	0.04	10.4	28.7	193 000	0.43
MMA/dioxane	0.10	0.02	5.3	23	122 000	0.46
	0.10	0.03	5.9	21	105 500	0.46

To characterize the gel network, we have made identical gels without probe polymer. Since static light scattering is a sensitive probe of heterogeneities and microphase separation, we measured the intensity of the scattered light at 90° from PMMA gels in dioxane. As shown in Figure 1, the intensity of scattered light increases significantly for samples with $f_c > 4\%$. This implies that at high-cross-link content there may be problems with heterogeneities in the gel. For this reason, with the dioxane/MMA gels we investigated tracer diffusion in gels with $f_c < 4\%$.

Swelling equilibrium measurements on these gels were interpreted in terms of the Flory–Rehner equation to determine the molecular weight between cross-links, M_x.[28] The Flory interaction parameter, χ, was estimated from values of the second virial coefficient published for PMMA/toluene[29] solutions. The resulting value of M_x is given in Table I. This M_x value should only be considered as a rough estimate because of the approximations made in this approach and the poor estimate of χ to which the calculation is very sensitive. A 1% change in χ causes a 5% change in M_x. It is also important to note that the small amount of linear PS chains in an MMA gel can also influence the swelling ratio. Moreover, the value of M_x is larger than the value expected on the basis of stoichiometry because not all of the EDMA polymerize as cross-links in a dilute system. The low efficiency of cross-linking compared to the stoichiometric ratio of EDMA to MMA implies that there are many dangling chains in these networks. The end to end distance between cross-links, ξ_x, was estimated by $\xi_x = 6.53 \times 10^{-2} M_x^{0.5}$ nm. This is based on the unperturbed dimensions of PMMA polymers in toluene,[27] assuming that polymer chains between two permanent cross-links are branched chains in a good solvent.[30] It is interesting to note that the exponent of 0.5 in the ξ vs M equation could also arise if the chains between cross-links are thought of as being in a Θ-solvent.

A better way to characterize semidilute solutions and gels is to determine the hydrodynamic correlation length, ξ_h, by using $\xi_h = k_BT/6\pi\eta_sD_{\mathrm{coop}}$, where $D_{\mathrm{coop}} = D_c/(1 - \Phi_p)$. Here D_c is the diffusion coefficient observed in DLS experiments and $1 - \Phi_p$ is a correction factor[31] which takes into account the motion of the solvent relative to the polymer segmental motion (Φ_p is the polymer volume fraction). As shown in Table I, ξ_h for PMMA/toluene gels is ~2 times longer than that of PMMA/dioxane samples. Since the correlation length in weak gels is related to the spacing between entanglements, the number of entanglements in PMMA/dioxane gels should be higher than in those prepared in toluene. This difference is probably due to differences in polymerization kinetics in the different solvents and also due to the small difference in total concentration. This is also reflected in the different values of the critical cross-link concentration corresponding to the gel threshold (~2% in PMMA/toluene gels and less than 1% in the PMMA/dioxane system).

The probe polymers used in this study were monodisperse polymer standards ($M_p/M_n \leq 1.1$) purchased from Polysciences (PS) and Pressure Chemical (PMMA).

Apparatus. Dynamic light scattering measurements were made with an argon ion laser (power at the sample ≤200 mW) and a variable-angle goniometer using either a 72-channel Langley-Ford 1096 autocorrelator or a 264-channel BI 2030 autocorrelator. The samples were thermostated in a refractive index matching liquid (toluene).

On the 72-channel Langley-Ford correlator, we measured single-sampling-time correlation functions covering less than 2 decades of time.

Extended correlation functions were measured in two different ways: (i) composite, on a Langley-Ford 72 channel correlator, by measuring several correlation functions with increasing sample times and then forming out of them a composite one which covered more than 5 orders in time; (ii) multisampling time, on a Brookhaven Instruments correlator, which involved splitting the available 264 real-time channels into four separate groups of channels (64, 64, 64, 72), each with different sampling times, covering more than 4 orders.

Data Analysis. Two different methods were used to analyze the autocorrelation functions: (1) The single-sampling-time autocorrelation functions were analyzed by using single-exponential fitting and the method of cumulants using both the measured and floating baseline options and assuming homodyne detection.[32] (2) Composite and multisampling time autocorrelation functions were analyzed by inverse Laplace transform using two methods of constrained regularization CONTIN[33] and REPES[34] in order to obtain a distribution $A(\tau)$ of decay times.

The REPES method has the advantage over CONTIN in that the probability to reject can be fixed a priori to any desired value. This allows one to have numerical solutions with the same degree of smoothness as well as to systematically examine the effects of varying the probability to reject on the solution. In general, both CONTIN and REPES reproduce major features and peak positions quite accurately. However, since these methods have difficulty in resolving closely spaced peaks we do not attach any significance to such features; instead we consider them as part of a broad band. The average value of the broad band in an oversmoothed solution coincides with the average value of the closely spaced peaks in an undersmoothed Laplace inversion. To overcome some of these problems, we usually measured the correlation function on each sample two to three times and analyzed each measurement separately. This gives more reliable results.

Results and Discussion

Predictions of the Reptation Model. Recently, the reptation hypothesis has been applied to the problem of the transport of a melt through a gel.[25] The diffusion of one labeled chain inside a swollen network has been treated as a limiting case. Three dominant dynamic regimes are predicted, depending on the relative magnitudes of the molecular weight of the probe (M_p), the molecular weight of the chain between cross-links (M_x), and the molecular weight between entanglements if the system were not cross-linked: (1) free-draining regime at $M_p < M_e$ and $M_p < M_x$, with a diffusion coefficient of the form

$$D_t = D_0 M_p^{-1} \tag{1}$$

where D_0 is a microscopic diffusion constant and M_e would be the entanglement molecular weight if the system were not cross-linked; (2) simple reptation at $M_p > M_e$ and $M_x > M_e$ with

$$D_t = D_0 M_e M_p^{-2} \tag{2}$$

(3) strangulation regime at $M_e > M_x$ and $M_p > M_x$ with

$$D_t = D_0 M_x M_p^{-2} \tag{3}$$

In applying these results to the case of the gel matrix used in this study, we assume that we are in either the free-draining or simple reptation regime, depending on M_p. A solution of linear polymers of molecular weight M_x at the concentrations corresponding to the gels used here would be entangled because of the high M_x value (cf. Table I). In other words, for the samples studied here $M_x \geq M_e$.

Results of Tracer Diffusion Measurements. (i) Diffusion of PS in MMA Gels. Figure 2 shows a typical series of decay time distributions, $A(\tau)$, as obtained by the inverse Laplace transform of autocorrelation functions measured at 46 °C for several MMA gels swollen in toluene with different molecular weight linear PS probes as indicated. The distribution functions may be adequately separated into two bands centered at the fast, τ_f, and the slow decay time, τ_s. A weak intermediate band at τ_m is also observed for samples with probe polymers of higher

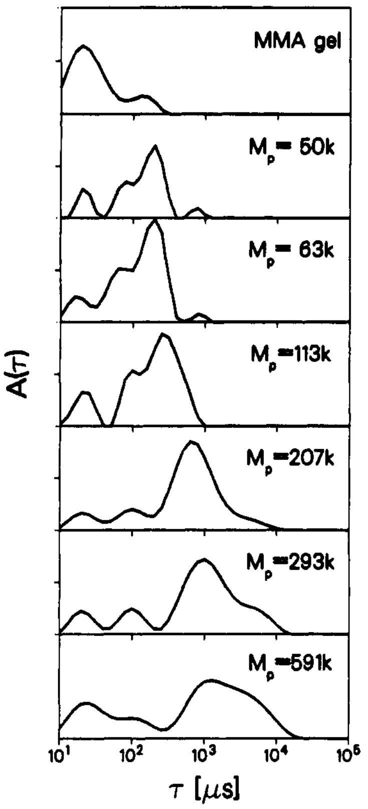

Figure 2. Relaxation time distribution, $A(\tau)$, for MMA gels in toluene ($\Phi = 0.125, f_c = 4\%$), with different PS probes as indicated. The measurements were done at 46 °C and a scattering angle of 90°.

molecular weights. While τ_f and τ_m are independent of M_p, τ_s depends strongly on M_p. We confirmed that all three dynamic processes are diffusive because τ_i^{-1} (i = f, m, s) are linearly dependent on the square of the scattering vector and accordingly we can introduce three diffusion coefficients D_c, D_m, and D_t. Since τ_s is the only mode which depends on M_p, we identify D_t as the tracer diffusion coefficient. The fast diffusion coefficient, D_c, is attributed to the cooperative diffusion of the gel, and this is supported by the observation that τ_f is practically independent of M_p and coincides with the fast dynamic mode in MMA gel (cf. Figure 2). Since the gel is almost isorefractive with the solvent, the measurement of the gel autocorrelation function required very long signal averaging time (>10 h). The position of the gel mode is reproduced for different samples within 10%. This serves as an indication of the reproducibility of both gel preparation and CONTIN analysis.

The remaining diffusion coefficient assigned to an intermediate band, D_m, comes from the interdiffusion of the sol inside the gel matrix. It is observed only for the samples with higher M_p, since for the lower molecular weights D_t and D_m overlap. Such a dynamic mode can also be seen in MMA gels (cf. Figure 2) without any PS probe polymers. Moreover, this mode is more pronounced in samples which are in the vicinity of the gel point.[35]

The fact that we can observe gel and sol dynamic modes for the index-matched system can be attributed to two factors: (1) The index matching conditions for PMMA polymer in toluene are not ideal at 46 °C. In fact, dn/dc is temperature dependent and it is small but nonzero at 46 °C. The matching temperature is around 17 °C.[36] (2) Gel and sol modes can give a contribution to an autocorrelation function through its coupling to the tracer diffusion of a probe polymer. This effect was theoretically predicted and discussed recently.[37,38] Some implications of this theory were experimentally tested by DLS experiments using ternary mixtures of two polymers and solvent isorefractive with one of them.[29,39–43] However, for this system, most of the dynamically scattered light comes from the PS probe, and therefore, distribution of the diffusion coefficient shows a pronounced peak corresponding to the tracer diffusion. This enables us to use a single-exponential fitting to the measured autocorrelation functions in order to evaluate D_t. Figure 3a compares the values of D_t obtained by using both single-exponential fitting and CONTIN analysis of autocorrelation functions for this system at a temperature of 46 °C. As seen from Figure 3a, the diffusion constant decreases by 2 orders of magnitude over the range of molecular weights used in this experiment. To interpret these results we plot D_t/D_o vs M_p (Figure 3b), where D_o is the diffusion constant of PS in pure toluene at the same temperature and concentration as used in the gel samples. From these figures we can see two distinct scaling regimes for D_t/D_o vs M_p at 46 °C. For $M_p < M_c \simeq 80\,000$, we find that D_t/D_o is very nearly independent of molecular weight, and thus, in the low molecular weight region $D_t \sim D_o \sim M_p^{-0.6}$ ($M_p < M_c$). This is in agreement with the well-known behavior of polystyrene in dilute solution in a good solvent.[44] Thus, the dynamics here is consistent with the probe polymer diffusing as a Stokes–Einstein particle of hydrodynamic radius $R_H \sim M_p^{0.6}$.

For $M_p > M_c$ at 46 °C the diffusion constant decreases very rapidly with increasing molecular weight and $D_t/D_o \sim M_p^{-(1.2\pm0.2)}$, which implies that $D_t \sim M_p^{-(1.8\pm0.2)}$. Thus in this region of molecular weights the dynamical behavior of the probe polymer is close to the reptation prediction, eq 2.

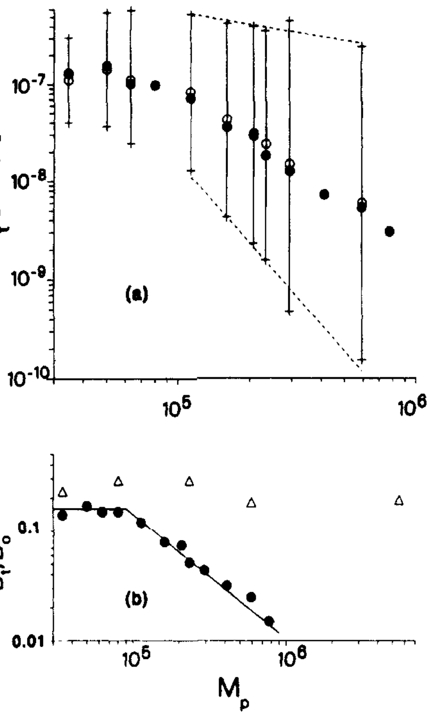

Figure 3. (a) Dependence of the tracer diffusion constant of PS in MMA gel in toluene (D_t) on the molecular weight of PS (M_p) at 46 °C. Filled and open circles represent diffusion constants obtained from single-exponential fitting and CONTIN analysis, respectively. The broadening of the probe diffusion bands is shown by plotting D_+ and D_- above and below the average value D_t (see text). Vertical bars have been drawn connecting D_+ and D_- for visual clarity. These are not to be confused with the usual error bars. The least squares fit through the upper and the lower bounds is represented with dashed lines. (b) The single-exponential data from (a) are plotted as D_t/D_o vs M_p, where D_o is the diffusion constant of PS in toluene solution. Solid lines represent predictions for the Stokes–Einstein and the reptation regime and *are not* the least squares fit to data. Also, D_t/D_o values for different PS probes inside PMMA solutions ($\Phi = 0.125$, f_c = 0%) are shown (triangles).

Similar crossover was also observed in the semidilute solutions.[14,45] It was found that M_c values for matrices formed with high molecular weight polymers are approximately 4 times higher than the molecular weight, yielding the dimension of the correlation length M_ξ. Using the same approach as Numasawa et al.,[14] we calculate a molecular weight M_ξ corresponding to the correlation length ξ_h and find that it is ~100 000 for the gels used in this study. Thus it appears that a crossover to reptation is obtained in the gels when M_c is approximately equal to the mass of the polymer chain between entanglements, M_ξ, or in other words when the radius of gyration of the probe polymer is comparable to the spacing between entanglements. Interestingly, the entanglement spacing in our samples is comparable to ξ_h, which is smaller than the average distance between permanent cross-links ξ_x (see Table I). A comparison of our results for the crossover in gels with those of Numasawa et al. in semidilute solutions implies that crossover to reptation occurs at a smaller ratio of M_c/M_ξ (factor of ~4) in a gel which has both transient entanglements and permanent cross-links as compared to a semidilute solution which only has transient entanglements. Perhaps the presence of permenant cross-links leads to a stabilization of the transient entanglements. Another possibility is that due to the very low cross-linking efficiency of the polymerization reaction in MMA + EDMA there exist many dangling chains in the gel which are clearly

Table II
Comparison of Measurements of PS Probe Diffusion in MMA/EDMA/Toluene Gels with Those in Linear PMMA Matrices

		probe					
		34 500		80 000		233 000	591 000
polymer matrix	ξ_h (nm)	D_t ($\mu m^2/s$)	η_m/η_o	D_t ($\mu m^2/s$)	η_m/η_o	D_t ($\mu m^2/s$)	D_t ($\mu m^2/s$)
gel ($f_c = 0.04$)	10.4	13	6.2	9.8	6.5	1.8	0.53
polymerized MMA ($f_c = 0$)	7.3	21	3.9	19	3.4	10	3.8
PMMA solution (M_m = 74K)	9.2	15	5.4	10	6.4	8	2.5
PMMA solution (M_m = 448K)	9.4	9.6	8.4	a	a	a	0.71
toluene		81	1	64	1	30	22

[a] Due to complications of phase separation at the concentrations of PS needed here, DLS measurements could not be made on these samples.

not present in the linear PMMA polymerized under the same conditions. Although these chains are elastically ineffective, they could influence the diffusion of the probe chain. A more detailed study of the dependence of the crossover from Stokes–Einstein to reptation as a function of the cross-link content is currently underway.[46]

It is intersting to note that for $M_p < M_c$ the effective viscosity of the gel medium is higher than the viscosity of pure toluene, η_o, and the data are consistent with $(\eta R_H)_{gel} \sim 6.5\eta_o R_{H_o}$, where R_{H_o} is the hydrodynamic radius of the polymer in pure toluene. The question arises of how the increase in viscosity observed in the gel compares to that for PS diffusing in a linear PMMA solution in toluene. To address this issue, we measured the diffusion constant of PS probes in solutions obtained by polymerizing MMA ($f_c = 0$) under identical conditions to those used for making the gels. The D_t data for these solutions are plotted for the sake of comparison in Figure 3b. We found that the ratio D_t/D_0 in solutions is higher than in gels and does not show a crossover from the S–E to reptation (cf. Figure 3b and Table II). Since the entanglement spacing in the linear polymer solution obtained by polymerization with $f_c = 0$ should be very similar to that of the gel prepared under identical conditions, comparison of D_t in these two cases bears on the role of temporary vs permanent cross-links in causing reptation. The fact that even high molecular weight probes do not reptate in this particular linear polymer matrix whereas they reptate in the gel implies that the presence of permanent cross-links stabilizes the transient entanglements in the gel.

The diffusion of PS in linear PMMA solutions in benzene was studied extensively by Numasawa et al.[14] Since they investigated only high molecular weight matrices (850 000 and higher) and high molecular weight probes (185 000 and higher) and since the solvent in their work was benzene, we measured the tracer diffusion of PS probes in semidilute solutions of different PMMA polymer matrices in toluene; the concentration of PMMA was kept the same as the total monomer concentration (w/v) in gel. The resulting D_t for the matrix consisting of the linear polymer chains with M_m = 74 000 is comparable with D_t for the gel matrix and is somewhat lower for the high molecular weight matrix (M_m = 400 000). However, the differences among D_t values are minimal. For the probe of 591 000 we observe that D_t in the 448 000 matrix is very close to that seen in the gel; thus perhaps this high M_w probe reptates in the semidilute solutions of 448 000. Our results are in reasonable agreement with the results of Numasawa et al.[14] They found that reptational diffusion takes place only for the high molecular weight probe and matrix polymers, while for the low molecular weights, S–E diffusion was observed. This explains why D_t/D_0 for solutions in the Figure 3b is independent of M_p.

As shown in Figure 2, the width of the probe diffusion band increases with increasing M_p. To quantify this effect we plotted the distribution $A(D) = A(\tau)$ vs log D and measured the values of the diffusion constants D_+ and D_- corresponding to $A(D)$ at half-height for the probe diffusion band. These values of D_+ and D_- are shown above and below the average value of the probe diffusion constant in Figure 3a. For the sake of consistency, we performed Laplace inversions for all the data using the same probability to reject (0.5). This value of 0.5 is suggested for obtaining the most probable solution of the inverse Laplace transform.[34] Dashed lines drawn through D_+ and D_- provide effective limits for the dynamic processes involved in the diffusion of the probe polymer through the gel. Figure 3a shows that the fastest process scales with exponents of −0.5 while the slowest one scales with exponent of −2.7. Such a broadening cannot be due to the polydispersity of probe polymers, and thus, our results imply that the tracer diffusion of polymer probes in gels is a complex dynamic process extending from nearly free diffusion in large pores, to reptation in the average-sized pores of the gel, to still slower diffusional mechanisms with high exponents of M_p. The last process can arise from anomalous diffusion accompanied by temporary trapping of diffusing chains.[8] This interpretation is supported by computer simulation[23,24] of the diffusion of a flexible chain through an array of obstacles. In the case of randomly distributed obstacles, they found that D_t vs M_p was no longer strictly a power law but rather showed regimes with apparent exponents as high as −3. This phenomenon was ascribed to "entropic traps", in which chains tend to be localized in certain pores, where they have more conformational entropy. On the other hand, a temporary trapping of chains can occur in very dense parts of the gel for purely geometrical reasons.[8] It seems that the distribution of mesh sizes is a crucial feature of the gel for description of the tracer diffusion. Also, the possibility of PS chain aggregation cannot be completely excluded.

Recently Rotstein and Lodge[21] published results for the probe diffusion of PS in vinyl methyl ether (VME) gels. They observed the exponents of D_t vs M_p to range from 2 to 2.8. Since the concentration of VME gels was higher (0.200 and 0.235 g/mL) than that of the PMMA gels used in our study (0.118 g/mL) and the correlation length ξ_h substantially shorter (~2.0 nm) than in PMMa gels (10.4 nm), it is possible that fast diffusive processes are suppressed in VME gels. Therefore, the mean value of D_t could be shifted to lower values and the exponent to higher than that in the weaker MMA gels. Unfortunately we are not able to verify this hypothesis experimentally since the incompatibility of PS and PMMA restricts our experiments to lower concentrations of PMMA gels only.

(ii) Diffusion of PMMA in MMA Gels. In order to minimize complications due to polymer incompatibility in PS/MMA/toluene gel, we also investigated the diffusion of linear PMMA chains in MMA gels swollen in 1,4-dioxane. In this case, both the probe polymer and gel are chemically identical; therefore phase separation is not

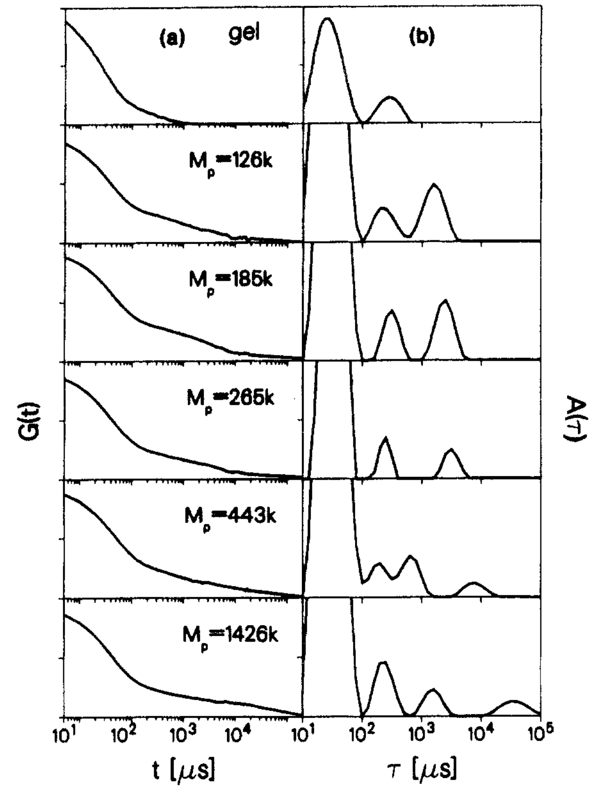

Figure 4. (a) Autocorrelation function for MMA gels in 1,4-dioxane ($\Phi = 0.10, f_c = 2\%$) with different PMMA probe polymers. The measurements were done at 25 °C and a scattering angle of 90°. (b) Relaxation time distribution $A(\tau)$ obtained by Laplace inversion of the functions in (a) using CONTIN analysis.

likely to occur. For this system the solvent can no longer be isorefractive with the gel, and thus we observe the cooperative diffusion mode of the gel in addition to the diffusion of the linear probe polymer. Since the gel mode is faster than the trace diffusion of adequately high molecular weight probes, we were able to separate both dynamic modes by the inverse Laplace transformation of the autocorrelation functions covering proper dynamic range. Figure 4a shows typical results in a measurement of the multisampling time correlation function, $G(t)$, for a set of samples with different PMMA probes as indicated. It can be seen that the long-time tail of $G(t)$ shifts to longer delay times with an increase in the molecular weight of the PMMA probe polymers while the short part of $G(t)$ is insensitive of M_p. These changes becomes more clear in the CONTIN inversion of the correlation functions in Figure 4b. The distribution functions, $A(\tau)$, may be reduced to three main separated bands, similar to the case of PS/MMA/toluene gel. Contrary to the experiments with system i, the contribution of the gel mode is dominant in this case. While the position of the two short-time bands is independent of the molecular weight of the probes, the position of the long-time band is strongly dependent on M_p. By analogy to system i, three diffusion coefficients D_c, D_m, and D_t may be introduced. The fastest diffusion mode (D_c) can be again identified with the cooperative diffusion mode and D_m to the interdiffusion of the residual sol inside the gel matrix. The latter assignment is supported by the observation that when the gel without probe polymer was washed in the solvent to remove the low molecular weight sol the intensity of the second peak in the gel data decreased considerably.

The slowest diffusion mode (D_t), which is strongly M_p dependent, is again identified with the probe polymer's diffusion. Figure 5 shows the molecular weight dependence of the slow mode plotted as D_t vs M_p for MMA gels with $f_c = 2$ and 3% using both the composite and multisampling time autocorrelation functions. The values of D_t given in Figure 5 for high values of M_p are evaluated from measurements at sufficiently long sampling times in order to cover all the slow dyanmic processes seen in these samples. Because of the overlapping of the sol and the probe dynamical processes in the DLS data, it is not possible to accurately determine D_t values for low molecular weight probes. We find that, within experimental error, D_t seems to be independent of f_c. The scaling of D_t with molecular weight M_p is consistent with the reptation prediction and similar to the exponent obtained for the PS probes in Figure 3a. The crossover between the S–E and reptation regime was not observed here, primarily because the contribution of low molecular weight probes and of the gel overlaps. With the increase of molecular weight of the linear PMMA probe polymer, the width of this slow mode again increases, apparently for the same reasons as discussed above for PS probes.

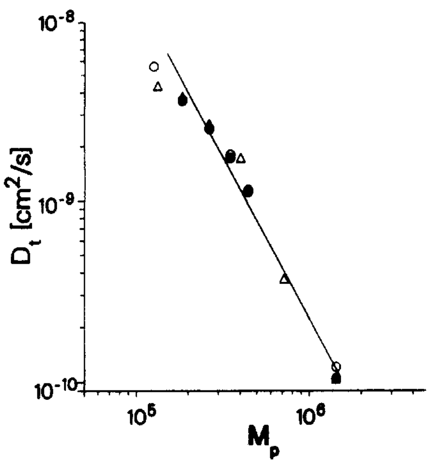

Figure 5. Average value of the tracer diffusion constant D_t vs M_p for the PMMA probe polymer diffusing in a MMA gel in 1,4-dioxane. Values obtained for the $f_c = 2\%$ gels by using CONTIN and REPES analysis are marked with open and filled circles, respectively. Triangles show REPES values for the $f_c = 3\%$ gels. The solid line has a slope of −1.8, represents the prediction for the reptation regime, and *is not* the least squares fit to data.

The experimental result that D_t data are independent of f_c can be understood by adopting eq 2 for the reptation regime in chemically cross-linked gels. Inserting $N_e \sim \xi_h^2$ we obtain

$$D_t \approx \xi_h^2 M_p^{-2} \tag{4}$$

Comparing the values of ξ_h of gels with $f_c = 2$ and 3% in Table I, D_t values for MMA gel with $f_c = 2\%$ should be about 20% lower than those for the 3% gel. Unfortunately this is on the limit of the experimental resolution.

Equation 4 can be successfully used to explain the differences between D_t values for PS and PMMA probes. If we take the difference in the solvent viscosities and ξ_h values in Table I into account, then D_t of PMMA pobes in MMA/dioxane gels should be approximately 8 times smaller than those of PS probes in MMA/toluene gels. This is approximately fulfilled.

The contribution of the probe diffusion to the total autocorrelation function appears to be surprising dependent on the cross-link concentration f_c and monomer volume fraction Φ. Thus, the ratio of the dynamic amplitudes of the tracer diffusion mode for the PS probe with $M_p = 1.85 \times 10^5$ to the amplitude of the gel mode has been found to be 9.7% in 2% gel and only 3.6% in the gel with $f_c = 3\%$. The higher the M_p of the PMMA probe, the more

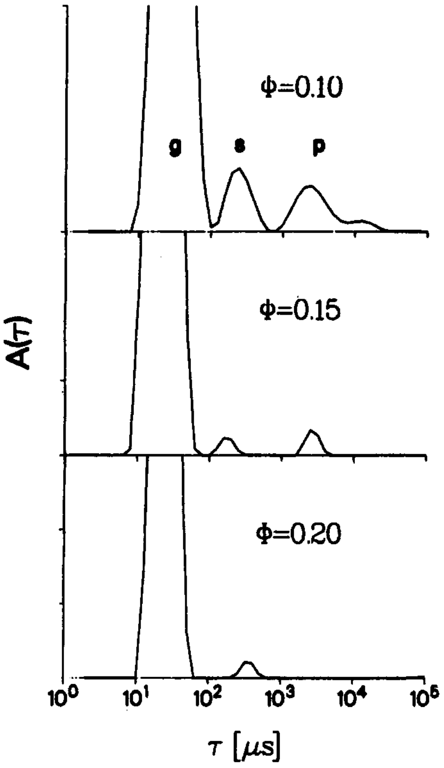

Figure 6. Relaxation time distribution $A(\tau)$ for MMA gels in 1,4-dioxane with different total monomer concentrations (Φ = 0.10, 0.15, and 0.20 as indicated) and with PMMA probe having molecular weight M_p = 350 000. Gel, sol, and probe bands are indicated with g, s, and p, respectively.

pronounced was the decrease of the relative dynamic amplitude in gels. The tracer diffusion contribution to the total correlation function was below the detection limit for 4% gels.

The effect of the monomer volume fraction Φ is demonstrated in Figure 6, where the decay time distributions $A(\tau)$ for Φ = 0.10, 0.15, and 0.20 are plotted. The probe polymer was PMMA with $M_p = 3.5 \times 10^5$. The dynamic amplitude of the probe diffusion decreases with increasing Φ and is below the detection limit for the Φ = 0.20 sample. At the same time, the sol contribution also decreases with increasing Φ. The question arises as to what kind of mechanism is producing such an effect. One plausible explanation is based on the idea that the decrease of the dynamic amplitude is due to a trapping of the probe polymer chains inside dense regions of the gel. This hypothesis is supported by the measurements of the angular dependence of the integral scattered intensity. Although there was no visible evidence of phase separation in these samples, a pronounced downward curvature of the radiation envelopes, typical for the microphase-separated regions, was observed at low scattering angles for samples with Φ = 0.15, 0.20, and 0.25. Evidently the probe molecules are preferably trapped inside the microphase-separated regions because their molecular weights are generally higher than that between chemical cross-links (M_x).

Conclusion

In conclusion, we have observed scaling behavior of the mean probe polymer diffusion constant which is consistent with the reptation prediction, irrespective of whether the probe and the gel are chemically identical or distinct. Evidence for a more complex dynamic behavior of probe polymers inside the gel was seen in the broadening of the decay distributions.

In the case where the probe and the gel are chemically different, we have observed Stokes–Einstein behavior for low molecular weights and reptation scaling for higher molecular weights. We found that the crossover occurs when the molecular weight of the probe is comparable to the molecular weight between entanglements. This result is in contrast to the result of Numasawa et al.,[14] who observed that in semidilute solutions the crossover occurs when M_c is about 4 times the molecular weight between entanglements. By comparing probe diffusion measurements in gels with identical solution samples prepared by leaving out the cross-linker EDMA we confirmed this result. Thus it appears that the presence of permanent cross-links in the gels stabilizes the temporary entanglements. It is also possible that the elastically ineffective, dangling chains and the residual sol influence the probe diffusion in the gel as compared to the diffusion in a linear polymer solution polymerized under identical conditions.

In the case where we had chemically identical probe and gel, the dependence of D_t on M_p was consistent with the reptation prediction. The crossover to Stokes–Einstein behavior could not be studied because the tracer diffusion of low molecular weight PMMA probes was masked by the cooperative diffusion mode of the gel. In this set of samples we have also observed the modes due to the diffusion of the sol and the collective motion of the gel network. This suggests that the technique of DLS can be used quite generally to measure the diffusion of polymers in gels even without using an isorefractive solvent.

Trapping of probe chains inside the microphase-separated regions may occur for gels with higher monomer volume fractions and cross-link concentrations.

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(32) Since the intensity of the light scattered from the gel was relatively high, this raises the possibility of having a heterodyne signal. We have tested this by making measurements of the cooperative gel mode with external heterodyning using a reference beam. We found that the value of the cooperative diffusion constant calculated from the heterodyne measurement was in excellent agreement with that obtained from the regular homodyne measurements. Furthermore, since the error that would be introduced with this assumption would be within a factor of 2 and would be approximately the same for all samples, it does not affect our conclusions regarding scaling.

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