Notes

Tracer Diffusion of Flexible Probe Macromolecules at the Sol−Gel Transition

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Introduction

The diffusion of macromolecules in swollen gels is an important component of many different industrial and biological problems such as transport across membranes, gel electrophoresis, flow through porous media, and intracellular protein diffusion. Quasielastic light scattering has been applied to study probe diffusion in swollen gels as a function of the probe polymer's molecular weight and concentration.[1−8] In our previous studies[5,6,8] of the diffusion of linear polystyrene (PS)[5,8] and poly(methyl methacrylate) (PMMA)[6,8] probes in swollen methyl methacrylate (MMA) gels cross-linked with ethylene dimethacrylate (EDMA), we have found that the diffusion constant D_t obeys the reptation prediction $D_t \sim M_p^{-1.8}$ provided the molecular weight M_p is higher than some critical molecular weight M_c. The critical molecular weight depends on the mesh size of the gel, and for $M_p < M_c$ the probe polymer diffuses as a Stokes−Einstein particle of hydrodynamic radius $R_h \sim M_p^{0.6}$. In the corresponding semidilute solutions of linear PMMA prepared by polymerizing MMA under conditions identical to those used for making the gels, we observed Stokes−Einstein scaling even when $M_p > M_e$, the molecular weight between entanglements. In an earlier study of probe diffusion in semidilute solutions of PMMA Numasawa et al.[9] found that the crossover from Stokes−Einstein to reptation scaling occurred when $M_p \approx 4M_e$. Thus, by comparing the results for the gel with the semidilute solution of the same concentration, we suggest that the crossover from Stokes−Einstein to reptation occurs at lower molecular weights in gels as compared to semidilute solutions due to the presence of permanent cross-links in gels.

In this paper the effect of varying the cross-link content on the probe dynamics is studied in semidilute solutions of branched PMMA polymers below the gel point and in gels in the vicinity of the gel point using dynamic light scattering (DLS). To simplify the analysis of DLS data, toluene was chosen as a solvent for this study because it is isorefractive with the PMMA matrices. Although PS and PMMA are incompatible polymers, both are highly soluble in toluene and phase separation does not occur at the low concentrations of PS used in these samples. This point has been discussed extensively in our previous papers.[5,8]

The goal of this study is to understand the role of the permanent cross-links on the probe polymer dynamics, particularly at the sol−gel transition.

Experimental Section

The samples used in these experiments are PMMA solutions and gels obtained by copolymerizing methyl methacrylate monomer (MMA) with small amounts of ethylene dimethacrylate as the cross-linking agent in the presence of toluene. The probe polymer, linear polystyrene (Polysciences, $M_w/M_n < 1.06$), was added to the pregel monomer mixture. The concentration of PS in different samples, c_{PS}, was increased with decreasing molecular weight to compensate for the decrease in the intensity of scattered light with decreasing molecular weight. For all the samples $c_{PS} \ll c^*$, where c^* is the crossover concentration from the dilute to semidilute regime. A set of samples was polymerized with a total monomer concentration of 12% (v/v) and with different degrees of cross-linking: f_c = [EDMA]/[MMA] varying between 0% (the linear polymer) and 4% (gel) containing probe PS of molecular weight from 58 000 to 410 000. The free-radical polymerization 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 polymerization reaction was complete with a conversion better than 95% as determined by precipitation methods. The samples with $f_c < 1.6$ were branched polymer solutions, and those above this value were gels. The sample with $f_c = 0$ was a linear polymer of molecular weight ≈100 000. To remove dust, all monomer solutions were first filtered using 0.22-μm filters (Millipore).

Dynamic light scattering measurements were performed using a standard multiangle Brookhaven Instruments spectrometer with an argon ion laser and a 264-channel BI 2030 (Brookhaven Instruments), multibit, multi-τ autocorrelator operating with four simultaneous sampling times covering 4.5 decades in delay time. The sample were thermostated in a refractive-index-matching liquid (toluene) at 25 °C.

The multisampling time autocorrelation functions were analyzed by inverse Laplace transform using the CONTIN[10] method of constrained regularization to obtain the distribution, $A(\tau)$, of decay times.

Results and Discussion

Figure 1 shows a typical series of decay time distributions, $A(\tau)$, as obtained by the inverse Laplace transform of multisampling time autocorrelation functions for several MMA samples (matrices) differing in cross-link content, f_c, and containing the same small amount of a linear PS probe (c_{PS} = 5 mg/mL, $M_p = 1.13 \times 10^5$). The distribution functions can be separated into two main bands centered at the fast decay time, τ_f, and the slow decay time, τ_s. A weak intermediate band is also observed for gel samples with probe polymers of higher molecular weights.[8] Both the dynamic processes (fast and slow) are diffusive because the corresponding diffusion constants D_c and D_t, respectively, are independent of the scattering vector.

According to our previous studies,[5,6,8] the fast mode is attributed to the cooperative diffusion of the semidilute solution or gel matrix and the slow mode to the tracer diffusion of the PS probe. The weak intermediate mode observed in gel samples comes from the interdiffusion of the sol inside the gel matrix. The cooperative

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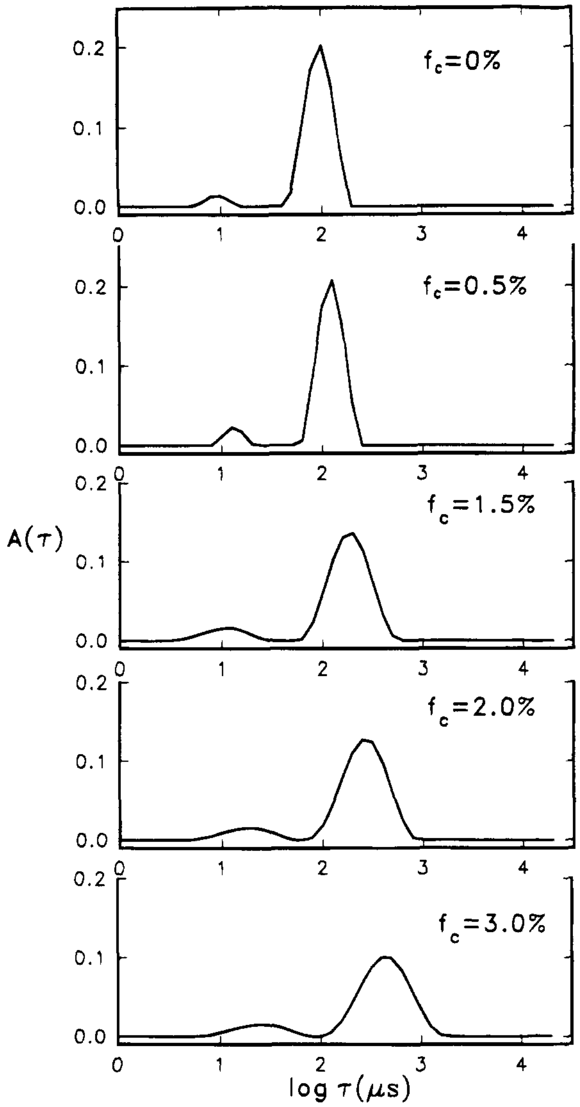

Figure 1. Relaxation time distribution, $A(\tau)$, for MMA gels and pregel solutions in toluene with different cross-linking contents (f_c = 0, 0.5, 1.5, 2, and 3 as indicated). All samples contained the same PS probe polymer of molecular weight M_p = 113 000.

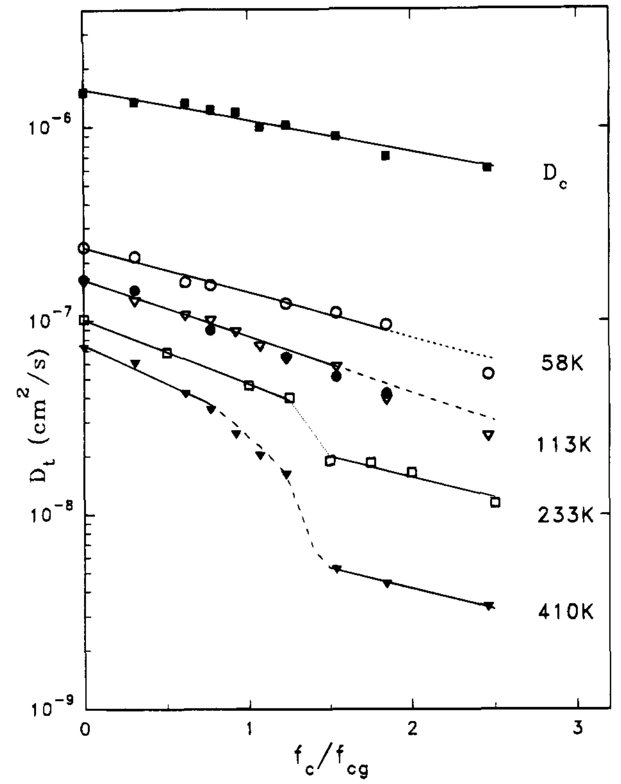

Figure 2. Dependence of the cooperative diffusion coefficient (D_c) of MMA gels and pregel solutions and the tracer diffusion constant (D_t) of PS probes on the normalized cross-linking content (f_c/f_{cg}).

mode of MMA matrices can be observed in the index-matched solvent (toluene) because of its coupling to the tracer diffusion of a PS probe polymer.[11,12]

The effect of varying the cross-link content on the cooperative and tracer diffusion constants is shown in Figure 2 where both D_c and D_t are plotted as a function of f_c/f_{cg}, where f_{cg} is the content of cross-links in the sample at the gel point (f_{cg} = 1.6 ± 0.1), for different molecular weights of linear PS probes. The cooperative diffusion of the gel, D_c, decreases slightly as the number of permanent cross-links increases which is in agreement with published data.[13,14] Since the total concentration of the gel and thus its hydrodynamic correlation length is unchanged with increasing the fraction of cross-links, the decrease could be interpreted as an increase in the effective friction of the gel network with increasing the cross-link content. Since $D_c = kT/6\pi\eta\xi_h$, where ξ_h is the hydrodynamic correlation length of the matrix, the above reasoning suggests that ξ_h is determined by the entanglement spacing among polymer chains and not by the density of permanent cross-links.

The decrease of the tracer diffusion constant, D_t, with increasing the cross-link content depends on the molecular weight of the probe. For the smaller probes (58 and 113 × 10^3) the tracer diffusion shows a linear decrease almost parallel to that of D_c on a semilog plot. According to our previous data, these small probes diffuse as Brownian particles of size equal to their hydrodynamic radius obeying the Stokes–Einstein relation. The decrease in D_t with increasing the cross-links can be interpreted as arising from an increased microscopic viscosity of the solvent due to the presence of the gel network. The data show that both D_c and $D_t \sim \exp(-af_c)$, implying that the microscopic viscosity $\sim\exp(\Delta F/kT)$, with $\Delta F/kT = af_c$ being the excess free energy (in units of kT) due to the presence of cross-links. The slight increase in the slope, i.e., in the constant a, with increasing the size of the probe polymer is consistent with the idea that the microscopic viscosity increases with increasing the length scale, eventually approaching the bulk viscosity at macroscopic length scales.

The tracer diffusion for probes with higher molecular weights (2.33 and 4.1 × 10^5) shows a more complicated dependence on the cross-link content. For $f_c/f_{cg} < 1$ the dependence of D_t on the cross-link content is similar to that of the lower molecular weight probes. However, for samples in the vicinity of the gel point, between f_c/f_{cg} = 1 and 1.5, D_t decreases significantly, reflecting changes in the diffusional mechanism of the probe polymer. According to our previous results,[8] a transition from Stokes–Einstein (S–E) diffusion to reptation should take place in this f_c region. In order to support this interpretation the values of D_t have been plotted logarithmically as a function of M_p in Figure 3 for f_c/f_{cg} = 0, 1, and 1.5. It can be seen in Figure 3 that $D_t \sim M_p^{-0.6}$ for $f_c = 0$ and that D_t approaches M_p^{-2} dependence for probes with higher molecular weights (M_p = 2.33 and 4.1 × 10^5). Thus, the dynamics of probe polymers is consistent with the diffusion as a S–E

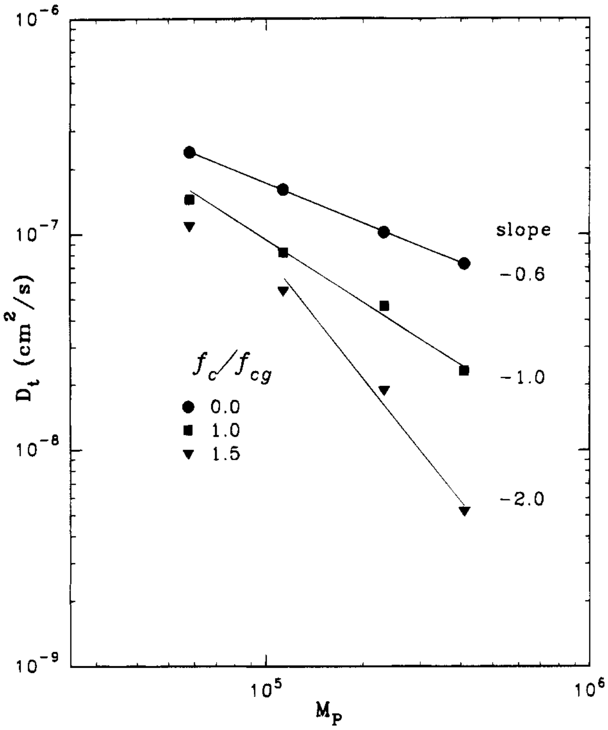

Figure 3. Dependence of tracer diffusion coefficients (D_t) on the molecular weight, M_p, of PS probes ($58\,000 \le M_p \le 410\,000$) within MMA gels and pregel solutions with different cross-linking contents (f_c/f_{cg}) as indicated on the left-hand side. The straight lines have slopes of −0.6, −1, and −2 as indicated on the right-hand side.

particle of hydrodynamic radius $R_h \approx M_p^{0.6}$ in a medium of effective viscosity η in semidilute solutions of the linear PMMA ($f_c = 0$) and for $M_p > 1.13 \times 10^5$ is close to the reptation prediction in MMA gels with $f_c/f_{cg} \ge 1.5$.[15] Reptation has been observed for probe polymers with hydrodynamic diameters ($2R_h$) larger than the mesh sizes, ξ_m, of the cross-linked gels and S−E diffusion for $2R_h < \xi_m$. The effective ξ_m seems to be related to the spacing between permanent cross-links rather than to that between transient entanglements. It is interesting to note that for the high molecular weight probes in the reptation regime, $f_c/f_{cg} \ge 1.5$, the slope of $\log D_t$ versus f_c/f_{cg} is again similar to the values obtained for the low molecular weight probes, implying that the effective microscopic viscosity follows the same exponential dependence on cross-link content, irrespective of the diffusional mechanism of the probe.

The most interesting regime of f_c in the MMA system under study is in the vicinity of the gel point where it is plausible to suppose $\xi_m \sim 2R_h$. For this regime the scaling theories of de Gennes et al.[16,17] describing the passage of flexible chains through pores can be adopted. Assuming that the permanent cross-links are forming channels (pores, tubes) with the pore size of ξ_m, then the ratio of the probe diffusivity in the pore D_p ($=D_t$) to that in the solution, D_0, is given by[16-18]

$$D_p/D_0 \approx (R_h/\xi_m)^{-2/3} \qquad (1)$$

which is equivalent to $D_p = D_t \sim M_p^{-1}$ for a good solvent ($D_p \sim D_0 R_h^{-2/3} \sim M_p^{-6/10} M_p^{-4/10} = M_p^{-1}$). Figure 3 also serves as a comparison of the experimental results to this scaling theory. The molecular weight dependence M_p^{-1} can be observed for D_t data at the gel point ($f_c/f_{cg} = 1$). Thus, our results support the application of the "pore" model to the transport of flexible chains through a gel in the vicinity of the gel point.

In the region from $f_c/f_{cg} = 1$ to 1.5 the exponent of the M_p dependence of D_t varies continuously from the value of −1 to −2. This experimental result cannot be explained, to the best of our knowledge, by existing theories.

In conclusion, we point out that the role of temporal cross-links (entanglements) has been overestimated in the reptation theory of semidilute solutions. The fact that even high molecular weight probes do not reptate in these particular linear polymer matrices whereas they reptate in the corresponding gels implies that the presence of permanent cross-links stabilizes the transient entanglements. Only in semidilute solutions of high molecular weight polymers, where the dynamics of the matrix chains is slowed down by several entanglements[9] (>4), the transient network is stable enough to control the transport of probe polymer chains and causes the probe to reptate. A possible explanation for this difference in probe diffusion between semidilute solution and gel is suggested by a model describing the fluctuations in the dynamics of concentrated polymer solutions.[19] The essential idea is that when a chain reptates in some medium, there is an increase in the local chain concentration in the newly created part of the tube and a concommitant decrease in the local concentration around the part of the tube from which the chain moved out. This creates a potential barrier for diffusion. In the un-cross-linked solution this barrier has a finite lifetime, while increasing the cross-link content increases the lifetime of this barrier, and the retardation of the diffusion due to this barrier is more and more pronounced. We also find that in both the Stokes−Einstein and the reptation regimes increasing the cross-link content leads to an increased microscopic viscosity, which depends exponentially on the cross-link content.

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