Notes

Diffusion of Polystyrene in Gels

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Introduction

The reptation model[1,2] has been applied successfully to describe the diffusion of a labeled (probe) polymer chain in a concentrated polymer solution or melt.[3,4] One reason for deviations from the reptation predictions is that the model was originally intended to describe the motion of a polymer chain in the presence of fixed obstacles such as might be encountered in a gel and this condition is not really valid for polymer solutions and melts. However, because of difficulties in making a gel sample with unattached polymer chains, there has been no direct study of reptation in a swollen gel + polymer system.[5]

In this paper we present a dynamic light-scattering (DLS) study of the diffusion of polystyrene (PS) linear polymers in methyl methacrylate (MMA) + ethylene dimethacrylate (EDMA) gels made in toluene, which is an isorefractive solvent for the methyl methacrylate gel and thus the measured intensity correlation functions reflect the diffusion constant of the PS probe molecules in the MMA gel matrix. Moreover, toluene is a good solvent for both PS and the MMA gels and thus prevents polymer–gel phase separation. Although the PS + MMA gel in toluene has never before been studied by DLS, the linear PMMA + PS + toluene system has been investigated by DLS[6] as well as by static light scattering.[7] Some information is available on the phase diagram of the linear ternary system of PS + PMMA + toluene.[8]

Theory

de Gennes[1] originally proposed the idea of reptation to describe the motion of a polymer chain around fixed obstacles and predicted that the diffusion constant $D \sim M^{-2}$ where M denotes the molecular weight of the chain. This result, based on the premise that the effect of the obstacles is to confine the polymer to move along a tube that is fixed in space, should hold much better for gels than for melts. The exponent of -2 arises because it is assumed that the chain is doing a random walk inside the tube. Slightly different predictions for the exponent are obtained if one considers self-avoiding walks (good solvent) versus regular random walk (Θ solvent) and chemically identical or dissimilar probe and matrix polymers. Martin[9] has summarized these results for the different cases of relevance to probe diffusion in a semidilute solution. For the case where the labeled chain is not chemically identical with the gel matrix and the solvent is good for both the gel and the linear polymer, one obtains

$$D \sim \xi^2 N^{-1.8} \sim \xi^2 M^{-1.8} \qquad (1)$$

Table I

no.	M, Da	c_{PS}, mg/mL	D, 10^{-8} cm^2/s 12 °C	22 °C	46 °C
1	22 000	20	[a]	8.1	[a]
2	34 500	15	4.8	7.8	13.0
3	50 000	10	2.7	7.0	15.5
4	63 000	7.5	2.9	5.8	10.1
5	80 000	6	1.9	5.1	9.8
6	113 000	5	2.4	2.8	7.2
7	160 000	4	1.3	1.5	3.55
8	207 000	3	0.72	0.89	2.9
9	233 000	2	0.9	0.92	1.8
10	293 000	1	1.2	0.67	1.25
11	410 000	1	[a]	0.54	0.72
12	591 000	0.7	0.72	0.35	0.53
13	771 000	0.5	0.71	0.23	0.3

[a] Data on these samples were not obtained at all temperatures because these gels were used for swelling measurements.

Here M is the molecular weight of the probe polymer, N is the number of monomers in the polymer chain, and ξ is the "mesh size of the gel". It should be pointed out that similar scaling laws can be obtained in melts by a less restrictive model than reptation.[10] However, in the case of gels the reptation assumption of fixed obstacles is better than the alternative mechanisms suggested for melts, which involve mobility of entanglements and the dragging of one chain by another.[10]

Experimental Section

The gels were made by free-radical polymerization of MMA + EDMA in toluene with the catalyst ABIN (azobis(isobutyronitrile)). The probe polymer, linear polystyrene (Polysciences, polydispersity index <1.06) dissolved in toluene was added to the pregel monomer mixture (4% (by volume) of EDMA in MMA). In order to prevent phase separation of PS from the gel, we maintained the total monomer content at 12% and varied M, the molecular weight of polystyrene from 22 000 to 771 000 giving us 13 samples. The concentration of PS in the 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. As shown in Table I $c_{PS}M$ was approximately constant. We note that for all the samples $c_{PS} \ll c^*$, the crossover concentration from the dilute to semidilute regime. Gelation was obtained by adding 20 mg of ABIN/mL of MMA and incubating the sealed pregel mixtures at a temperature of 52.5 °C for approximately 80 h. By the end of this period the gelation reaction was complete and no signs of phase separation were observed. All monomer solutions were filtered with 0.22-μm Millipore filters to remove dust.

Dynamic light-scattering measurements were done at three different temperatures with a 72-channel Langley–Ford 1096 autocorrelator at a scattering angle of 70° using an argon ion laser (power at the sample ~200 mW).

Results and Discussion

For the PS + MMA gel in toluene the solvent is isorefractive with the gel and the measured intensity correlation functions (Figure 1) are single exponential, reflect-

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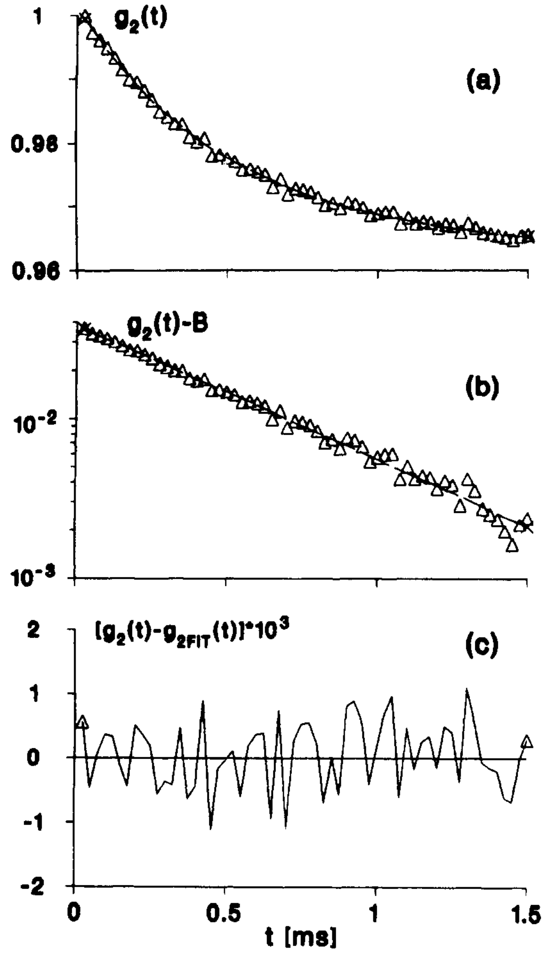

Figure 1. (a) Intensity autocorrelation function $g_2(t)$, from sample number 8, at 46 °C. (b) Semilog plot of $g_2(t) - B$. In (a) and (b) the solid lines indicate the fitted correlation function $g_{2FIT}(t)$. (c) Residuals $[g_2 - g_{2FIT}] \times 10^3$ of the fit.

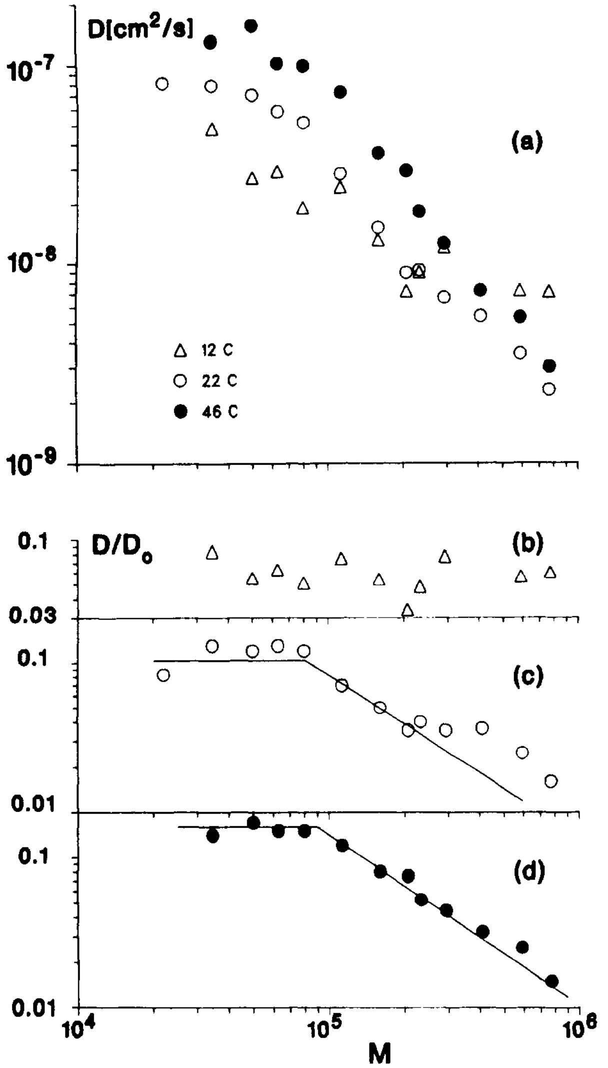

Figure 2. (a) log–log plot of the diffusion constant, D, versus the molecular weight, M, of polystyrene. Data are for three temperatures as indicated. (b–d) Diffusion coefficient of PS in the gel (D) normalized by the diffusion coefficient of PS in toluene (D_0) versus M for (b) 12 °C, (c) 22 °C, and (d) 46 °C. The lines in (c) and (d) indicate the different scaling predictions as discussed in the text.

ing the diffusion of the polystyrene polymer in the gel. The results of a force fit to a single exponential $g_2(t) = B + A \exp(-2Dk^2t)$ and the residuals of the fit are also shown in parts b and c of Figure 1. Here k denotes the scattering vector. The base line B determined from the force fit agreed with the theoretical base line obtained from the run duration and the total number of counts as well as the estimate from the delayed last 8 channels to within 0.6%. The validity of the single-exponential character of the correlation function was confirmed by measuring a composite correlation function extending over 3.5 decades of sampling time from the same sample. We also checked the room-temperature measurements at several different angles and found that the values of D obtained from measurements at different angles agreed within 10%.

Figure 2a and Table I show the diffusion constant D as a function of M, at three different temperatures for all the PS + MMA samples investigated. As seen from Figure 2a the diffusion constant decreases by 2 orders of magnitude over the range of molecular weights used in these experiments. To interpret these results, we examine the plots of D/D_0 versus M at each of the three temperatures separately (parts b–d of Figure 2). Here D_0 is the measured value of the diffusion coefficient of the linear PS in pure toluene at the same temperature and the same concentration as used in the gel samples.

From Figure 2d we can see two distinct scaling regimes for D/D_0 versus M at 46 °C. For $M < M_c \simeq 80\,000$, we find that D/D_0 is very nearly independent of molecular weight, and thus in the low molecular weight region ($M < M_c$), $D \sim D_0 \sim M^{-0.6}$. This is in agreement with the known behavior of polystyrene in dilute solution in a good solvent.[11] The dynamics here is consistent with the probe polymer diffusing as a Stokes–Einstein particle of hydrodynamic radius $R_H \sim M^{-0.6}$ in a medium of effective viscosity η. It is clear that $\eta > \eta_0$, the viscosity of pure toluene and the data suggest $(\eta R_H)_{gel} \sim 10\eta_0 R_{H_0}$ where R_{H_0} is the hydrodynamic radius of the polymer in pure toluene.

For $M > M_c$ at 46 °C the diffusion constant decreases very rapidly with increasing molecular weight and $D/D_0 \sim M^{-(1.2\pm0.2)}$, which implies that $D \sim M^{-(1.8\pm0.2)}$. Thus in this region of molecular weights the dynamical behavior of the probe polymer is consistent with the reptation prediction (eq 1).

The critical molecular weight M_c, which separates the Stokes–Einstein and reptation regimes, can be related to the mesh size. We can write D(Stokes–Einstein) = $(kT/\eta b)N^{-0.6}$ and D(reptation) = $(kT/\eta b)(\xi/b)^2N^{-1.8}$ where b is the size of the monomer, N the number of monomers in the polymer (i.e., $N = M/m$, where m is the molecular weight of the monomer (m = 104 for styrene)), and ξ/b is the dimensionless mesh size or the average number of monomers between two cross-links. Here purely geometrical factors such as 6π have been absorbed in the factor η. At the crossover molecular weight $M = M_c \simeq 80\,000$, ($N = N_c$) the two expressions for D can be equated and this gives $N_c^{1.2} = (\xi/b)^2$. We note that this identity could be off by a numerical factor of 2 since the geometrical factor may be different in reptation versus Stokes–Einstein diffusion. Substituting $N_c = M_c/m \simeq 800$, we obtain $\xi/b \sim 55$. This value is in reasonable agreement with the average ratio of 25 MMA monomers between two EDMA monomers, which would be the case for our samples made from 4% EDMA in MMA (by weight).[12] Clearly one does not expect all the EDMAs to polymerize as cross-links nor is it likely that the cross-links are absolutely uniformly distributed. In fact one expects that ξ/b is greater than the ratio of MMA/EDMA in the pregel mixture. In view of these observations the agreement between the predicted mesh size from the location of the crossover in dynamical behaviors and the mesh size obtained by assuming that the cross-link density is the same as the EDMA/MMA ratio prior to selection is reasonable.

For the data at 22 °C as shown in Figure 2c, the crossover to reptation can be seen, but for $M > 300\,000$ D is much higher than predicted by reptation. This unusual *increase* of D with *decreasing* temperature is even more pronounced at 12 °C where D/D_0 appears to be almost independent of molecular weight. A possible explanation for this unusual temperature dependence is related to the incompatibility of PS and PMMA (or MMA gels). As noted earlier, these polymers would not have made a single-phase system were it not for the use of toluene. Their incompatibility increases with increasing molecular weight and decreasing temperature. Thus although there is no optically visible evidence of phase separation in any of the samples, it is plausible that the unfavorable thermodynamic interaction between PS and the MMA gel becomes significant for $M > 300\,000$ at room temperature and below. As a result of this the polystyrene molecules try to minimizetheir interaction with the MMA molecules and this may result in one or both of the following: (i) a collapse of the PS coils (similar to the collapse seen near Θ-solvent condition), causing D to increase or (ii) the PS molecules undergo a microphase separation, preferring to be in regions high in toluene concentration and low in the MMA chain concentration. This would cause the effective viscosity η felt by the PS to decrease, leading to an increase in the diffusion coefficient. Another possibility is that the dynamics changes from reptation to either Rouse or Zimm, leading to higher values of the diffusion coefficient.

This unusual temperature dependence and departure from reptation prediction at the very highest molecular weights clearly needs to be investigated further, not only in gels but also in solution samples at composition close to the phase-separation limits.

In conclusion, we have observed a complex molecular weight and temperature dependence of the linear polymer's probe diffusion constant in a gel. For $M < M_c$ the linear polymer exhibits a Stokes–Einstein behavior with $D \sim M^{-0.6}$ just as in dilute solutions. In this regime the diffusion constant is ~10 times smaller in the gel as compared to the dilute solution, reflecting the retardational effects due to the friction of the network. For $M > M_c$ and temperatures high enough to prevent any polymer–polymer incompatibility, we observe reptation with $D \sim M^{-1.8}$. The molecular weight at which the crossover from Stokes–Einstein to reptation occurs is related to the mesh size of the gel. Finally we observe a departure from the reptation prediction in high molecular weight PS in gels at low temperature, which we attribute to unfavorable thermodynamic interactions due to the increasing incompatibility of the two polymers.

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