Polystyrene diffusion in semidilute solutions and in swollen networks of polydimethylsiloxane*

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We present a comparison of the diffusion coefficient of tracer polystyrene molecules in semidilute solutions and in gels of polydimethylsiloxane in tetrahydrofuran. We show that, in the regime where the size of the probe molecule is comparable to the correlation length of the host medium, the diffusion coefficient of the probe polystyrene is independent of the presence of crosslinks in the network and is well correlated with the polydimethylsiloxane concentration.

(Keywords: diffusion; dynamic light scattering; semidilute solutions; gels; polystyrene; polydimethylsiloxane)

INTRODUCTION

Semidilute polymer solutions have often been regarded as pseudo-networks when the observation timescale is short compared to the macromolecular translational diffusion timescale. This analogy between semidilute solutions and gels should hold when one compares the diffusion of a probe macromolecule through such systems as long as the size of the probe molecule is comparable to or smaller than the correlation length (mesh size or distance between crosslinks) of the host semidilute solution or network.

We have recently presented dynamic light scattering (DLS) results for the diffusion of 'probe' polystyrene (PS) in semidilute isorefractive mixtures of linear 'host' polydimethylsiloxane (PDMS) and tetrahydrofuran (THF)[1]. The scattered intensity correlation from such 'optically matched' ternary mixtures normally consists of two diffusion relaxation modes[2,3]. However, by working at a probe concentration c_2 much smaller than the host concentration c_3, an extrapolation of the results of the probe relaxation mode to $c_2=0$ yields the tracer diffusion coefficient $D_{22}(0)$ of the probe[1,2]. We have extended our experiments to the case where the PDMS is crosslinked by an end-linking procedure and report here that indeed crosslinks have no noticeable effect on the tracer diffusion of the probe molecules when the probe size is of the same order as the correlation length of the host medium.

EXPERIMENTAL

The materials and solution preparation procedures for the mixtures of THF, PS and linear PDMS were described previously[1]. The gels consisted of 'model' PDMS networks[4], synthesized by end-linking α,ω-divinylpolydimethylsiloxane (B_2, $M_n=26\,500$ g mol^{-1}, $M_w/M_n=2.0$) with either phenyltris(dimethylsiloxy)silane (A_3) or tetrakis(dimethylsiloxy)silane (A_4) in the presence of a platinum catalyst (Petrarch Systems Inc., PC072). As the networks were used to investigate whether light detection for a probe diffusing in a clean 'isorefractive' polymer gel would occur in the homodyne mode, we followed a synthesis procedure[5] that minimizes network defects or dust, which could act as local oscillators in DLS experiments. We proceeded by first making a solution of 18 vol% B_2, A_n ($n=3$ or 4) and toluene. After sufficient mixing to form a homogeneous solution, 0.4–1.0 ppm (wt Pt/wt B_2) of catalyst was added. The solution was remixed, filtered through a 0.45 μm pore-size filter into a flamed, dust-free vial, and placed into a vacuum oven. After removal of the toluene at 20°C under vacuum, the temperature was increased to 70°C. After 4 days, the now-crosslinked polymer was removed from the vial and all outside surfaces were cut off. The network was first swollen in pure THF to determine the volume fraction of PDMS in the gel at equilibrium swelling, ϕ_3, and to remove any PDMS that was not incorporated into the network structure. The THF was then removed by immersion of the swollen gels in baths of THF and methanol and subsequent drying in a vacuum oven. Three network samples were chosen for the DLS experiments, having $\phi_3=0.104$ (with crosslinker A_3 and a catalyst concentration [Pt] = 0.4 ppm), $\phi_3=0.131$ (with A_3 and [Pt] = 1.0 ppm) and $\phi_3=0.144$ (with A_4 and [Pt] = 0.4 ppm). These samples were cut into several pieces, with each piece being reswollen in a mixture of THF and a different molecular weight of PS at a PS concentration c_2 of 0.005 g cm^{-3}. The length of time allowed for the gels to equilibrate with the PS solution was one week for the samples containing PS with a weight-average molecular weight $M_{w,2}=4140$ g mol^{-1}, and four months for the gels containing PS with $M_{w,2}=7620$, 14 100 and higher. Because of the very small concentrations of PS used, no difference in ϕ_3 between samples swollen in pure THF and in the PS/THF mixtures was detected. The experimental set-up, data acquisition and autocorrelation function analysis were all as previously described[1].

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* Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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RESULTS AND DISCUSSION

In DLS experiments on ternary mixtures containing an isorefractive host polymer and solvent, and a very dilute probe polymer having a different refractive index, a 'measured' mutual diffusion coefficient $\lambda_2(c_2)$ is obtained. At small c_2, $\lambda_2(c_2)$ can be related to the tracer diffusion coefficient of the infinitely dilute probe, $D_{22}(0)$, by writing[1,6]:

$$\lambda_2(c_2)=D_{22}(0)(1+k_D c_2) \tag{1}$$

where k_D is the concentration coefficient of diffusion. When k_D and c_2 are known, $D_{22}(0)$ may be determined from $\lambda_2(c_2)$ using equation (1). We have previously[1] shown that, to a first approximation, k_D is independent of c_3 for mixtures of THF, PS and semidilute PDMS. Therefore, the k_D values previously determined[1] at $\phi_3=0.150$ can be used for the solutions examined here having other semidilute host polymer concentrations. To provide the best compromise between a moderate c_2, which ensures adequate scattering by PS in DLS experiments, and a small c_2, which minimizes both the amplitude of the decay mode representing cooperative diffusion and the effect of small deviations in k_D on the calculation of $D_{22}(0)$, we used PS concentration where $k_D c_2 \approx -0.1$. The open symbols in *Figure 1* show $D_{22}(0)$ as a function of ϕ_3 for PS in solutions of linear PDMS.

Unlike the homodyne light detection encountered in the solutions, heterodyne light detection typically occurred in the gels. In some cases, however, both homodyne and heterodyne detection occurred from the same gel sample at large and small angles, respectively. Two such cases are shown in *Figures 2* and *3*, representing plots of $\langle\Gamma\rangle/q^2$ vs. q^2, where $\langle\Gamma\rangle$ is the average decay rate of the electric field autocorrelation function[1] $g^{(1)}(q,t)$ and q is the scattering wavevector. The two figures are for PS4.14K (see *Table 1* for sample codes) diffusing in the gel having $\phi_3=0.104$ (*Figure 2*) and $\phi_3=0.131$ (*Figure 3*). It is apparent that two different values of $\langle\Gamma\rangle/q^2$ are observed in these cases, with $\langle\Gamma\rangle/q^2$ at large scattering angles having typically twice the value of $\langle\Gamma\rangle/q^2$ at small angles. A similar behaviour has been reported on poly(acrylic acid) gels[7]. It is believed that, at small angles, detection occurs in the heterodyne mode as the scattering volume contains inhomogeneities that act as local oscillators. The fact that the solvent (THF) is nearly isorefractive with the network (PDMS) does not eliminate the effect of these inhomogeneities, which must have a different refractive index from their environment to act as local oscillators. As the scattering angle is increased, leading to a smaller scattering volume, detection occurs in the homodyne mode. The diffusion coefficient is taken as equal to $2\langle\Gamma\rangle/q^2$ and $\langle\Gamma\rangle/q^2$ for heterodyne and homodyne detection, respectively. Then $\lambda_2(c_2)$ is calculated by averaging the diffusion coefficients from all angles. Owing to the incompatibility of PS and PDMS, it was assumed that very little PS diffused into the gel, as was also demonstrated by the very small increase in

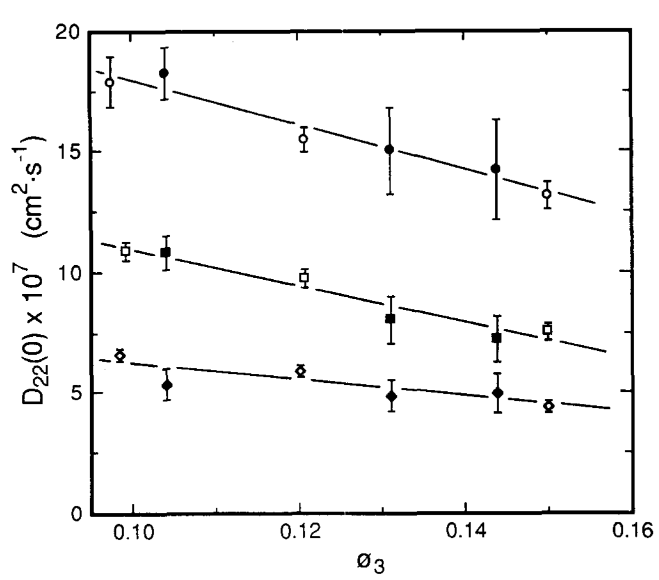

Figure 1 Tracer diffusion coefficients of PS at infinite dilution, $D_{22}(0)$, *versus* volume fraction ϕ_3 of PDMS in solutions or gels at $T=25°C$: (○) PS4.14K, linear PDMS; (●) PS4.14K, crosslinked PDMS; (□), PS7.62K, linear PDMS; (■) PS7.62K, crosslinked PDMS; (◇) PS14.1K, linear PDMS; (◆) PS14.1K, crosslinked PDMS

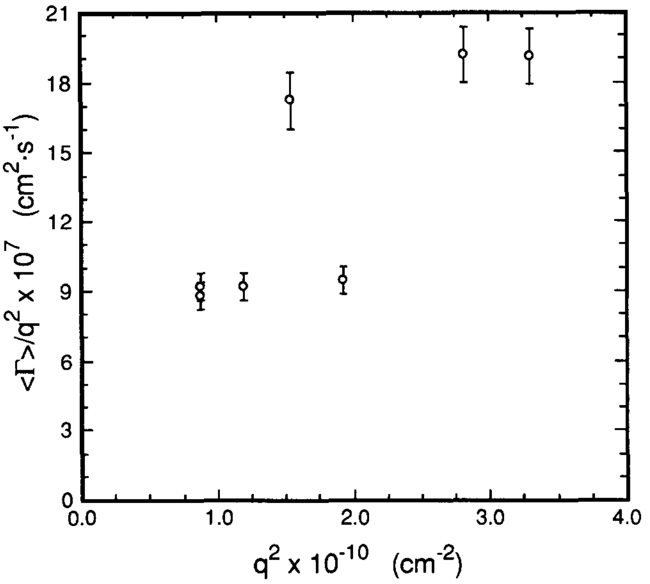

Figure 2 The q^2 dependence of $\langle\Gamma\rangle/q^2$ for PS4.14K in a PDMS gel at $T=25°C$ and $\phi_3=0.104$

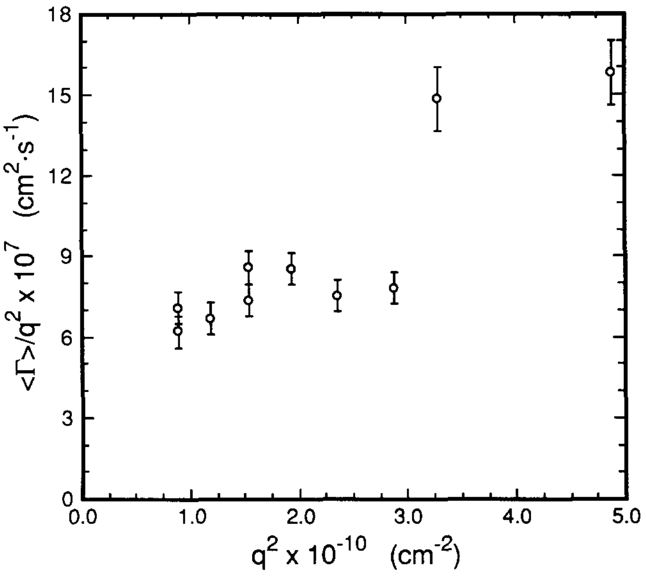

Figure 3 The q^2 dependence of $\langle\Gamma\rangle/q^2$ for PS4.14K in a PDMS gel at $T=25°C$ and $\phi_3=0.131$

Table 1 Estimates of $R_{H,2}/\xi_3$ at 25°C

Sample	$M_{w,2}\times10^{-3}$ (g mol^{-1})	$M_{w,2}/M_{n,2}$	$D_2(0)\times10^{7a}$ (cm^2 s^{-1})	$R_{H,2}$ (nm)	$R_{H,2}/\xi_3$	
					$\phi_3=0.10$	$\phi_3=0.15$
PS4.14K	4.14	1.04	26.6	1.81	0.60	0.77
PS7.62K	7.62	1.10	19.5	2.47	0.82	1.05
PS14.1K	14.1	1.03	14.2	3.40	1.13	1.44

^{a} From equation (3)

intensity of light scattered by a gel containing PS over that of the same gel swollen only in THF. We have therefore taken $\lambda_2(c_2)\approx\lambda_2(0)=D_{22}(0)$ in the gels. The full symbols in *Figure 1* show $D_{22}(0)$ as a function of ϕ_3 for PS in the gels. It is seen that, within the accuracy of the experiments, $D_{22}(0)$ is independent of whether PS diffuses in a gel or in a semidilute solution of linear chains at the same ϕ_3. The lines on *Figure 1* are only guides to the eye. We noted, however, that a least-squares linear fit of the data gave an intercept at $\phi_3=0$ of 27.3×10^{-7} cm^2 s^{-1} for PS 4.14K, 18.7×10^{-7} cm^2 s^{-1} for PS 7.62K and 9.4×10^{-7} cm^2 s^{-1} for PS14.1K. The first two values are in good agreement with the corresponding values of $D_2(0)$ in *Table 1*. The reason for the difference between the third value and $D_2(0)$ of PS14.1K may be due to the fact that in this case $R_{H,2}/\xi_3$ is larger than unity and the linear regime observed between $\phi_3=0.10$ and 0.15 cannot be extrapolated to $\phi_3=0$.

To obtain the dynamic correlation lengths ξ_3 of the semidilute PDMS solutions, we use the scaling relationship:

$$D_{\mathrm{coop,THF}}=k_BT/6\pi\eta_s\xi_3=6.59\times10^{-6}c^{0.61}\ \mathrm{cm^2\,s^{-1}} \quad (2)$$

previously established[1], where η_s is the solvent viscosity, k_B is the Boltzmann constant and T is the absolute temperature. At 25°C, one then gets the values of 2.36, 2.72 and 3.01 nm for ξ_3 at $\phi_3=0.15$, 012 and 0.10, respectively. We have argued previously[1] that the size of the probe macromolecule in the semidilute host solution should not vary appreciably from that in pure THF. Values of the probe size, represented by the hydrodynamic radius in pure THF, $R_{H,2}$, are listed in *Table 1* and are obtained using the previously established relation[1]:

$$D_2(0)=k_BT/6\pi\eta_sR_{H,2}=1.86\times10^{-4}M_{w,2}^{-0.51}\ \mathrm{cm^2\,s^{-1}} \quad (3)$$

for low values of $M_{w,2}$. As can be seen from the last two columns of *Table 1*, the values of $R_{H,2}/\xi_3$ are all of order unity. By examining *Figure 1*, it can be concluded that, in this range of $R_{H,2}/\xi_3$, crosslinks indeed have a negligible effect on $D_{22}(0)$. As $R_{H,2}/\xi_3$ increases appreciably beyond unity, we may expect to see differences between diffusion in semidilute solutions and in gels as the separation in timescales between probe diffusion and macromolecular host diffusion discussed in the 'Introduction' diminishes. In the regime investigated here, our results imply no effect of the molecular weight of the host polymer on the diffusion of the probe. Recently, others[8,9] have shown that for compatible polymers this is not the case when the probe size is larger than the correlation length of the host polymer in the semidilute range, where probe diffusion scales approximately with M_w^{-2} as predicted by reptation. Thus, the analogy between semidilute polymer solutions and gels appears to hold for the diffusion of macromolecular probes that are smaller than or comparable to the correlation length of the host matrix but would break down for larger probes. Higher values of $R_{H,2}/\xi_3$ could not be achieved in our system due primarily to the incompatibility of PS and PDMS. Gels immersed in THF solutions of PS25.5K for four months had an insufficient signal-to-noise ratio for DLS results to be analysed with any confidence. The autocorrelation functions for gels immersed in PS46.1K solutions did not deviate from the baseline, indicating that no PS46.1K was detected.

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