Diffusion of Linear Deuterated Polystyrene Chains in Cross-Linked Polystyrene Networks

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ABSTRACT: The diffusion of linear deuterated polystyrene (DPS) chains into a cross-linked polystyrene matrix has been studied by secondary ion mass spectrometry (SIMS). The cross-linked matrices were prepared by radiation cross-linking with γ-rays from a ^{60}Co source. The doses used were 40, 75, and 156 Mrad, which resulted in an approximate network density, N_c (number of monomer units between cross-linking points), of 9300, 4900, and 2400. The homopolymer DPS chains were of molecular weight M_w = 85 000, 104 000, 303 000, and 550 000 (corresponding to degrees of polymerization of N_b = 759, 929, 2705, and 4910). Diffusion of the linear chains into the cross-linked matrix was observed at all molecular weights and cross-linking densities studied. Diffusion was significantly slower into the cross-linked systems than into the matrix chains before cross-linking (M_w = 1 030 000). A free energy expression for the system calculated by assuming additivity of Gaussian rubber elasticity and the Flory–Huggins energy of mixing was used in combination with the Hartley–Crank equation to calculate concentration profiles for linear chains diffusing into the matrix. The predictions were then compared with the data obtained by SIMS. The only free parameter used in fitting the data was the relaxed or reference state network volume fraction. Good fits to the data were obtained when the relaxed state of the network accounted for the free sol chains still present after cross-linking. The diffusion of the linear chains became very slow when $N_b \approx N_c$, but no distinct halt to the diffusion was observed at this linear chain length. The tracer diffusion coefficients for the linear chains, which were measured separately, were found to be independent of the cross-linking density and to scale with $M_w^{-2.0}$, in agreement with the reptation model prediction.

Introduction

The diffusion of polymer chains in the melt is important in determining practical processes such as adhesion, interface formation, and phase separation. Recent research has centered on understanding mutual diffusing in polymer melts and its dependence on the relative molecular weights of the components[1,2] or the phase equilibrium properties of the system.[3] Few experiments,[4] however, have explored the diffusion of homopolymer in cross-linked polymer melts. Cross-linked melts have the additional complication that the matrix can swell without any center of mass motion. This complication could not be probed by the experiments of Sillescu and co-workers described in ref 4 since their matrices consisted of tightly cross-linked microgels where the homopolymer diffused between the individual particles rather than through them. The swelling of the micronetworks was therefore minimal, and no deformation energy was considered in their analysis. The first theoretical treatment of this problem was developed by Brochard[5] where she included an elastic deformation energy term in the free energy as well as the usual entropic and enthalpic contributions. A more explicit calculation incorporating the Ferry elastic tensor was later performed by Binder and Frisch[12] and further refined by Briber and co-workers[6] to include concentration fluctuation effects near the critical point. In order to probe this potential in greater detail we studied the diffusion of linear deuterated polystyrene (DPS) into cross-linked polystyrene (PS) matrices using the high resolution profiling technique of secondary ion mass spectroscopy. This system was chosen since the phase diagram for various homopolymer molecular weights and cross-linking densities has been carefully mapped by Briber and co-workers using small angle neutron scattering (SANS).[6] Beginning with the free energy expression obtained in their work, we derive here an expression for the diffusion coefficient for homopolymer chains diffusing into cross-linked polymer networks and compare it with our experimental results. Good fits with only one free fitting parameter were obtained for the diffusion profile at various annealing times and for different DPS molecular weights. The molecular weight dependence of the tracer diffusion coefficient is discussed in the last section where we compare our results with de Gennes's theoretical predictions based on the reptation model.

Experimental Section

The cross-linked networks were prepared by spin coating approximately 5000-Å-thick films of monodisperse (M_w/M_n < 1.1) polystyrene (PS) of M_w = 1 030 000 (Polymer Laboratories) on 2-mm-thick Si wafers. The wafers, together with a few pellets of PS, were then sealed under vacuum in glass ampules and irradiated with 1-MeV γ radiation from a ^{60}Co soure for a total dose of either 40, 75, or 156 Mrads. The sol fraction from the

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Table I. Summary of Parameters for the Cross-Linked Matrix

dose (Mrad)	40	75	156
N_c calc	9300	4900	2400
N_c measd		5300	2000
wt % sol	13.1	7.7	3.9
M_w (sol)	316 000	100 000	31 000

pellets was extracted, and the molecular weight distribution was characterized by gel permeation chromatography. The cross-linking density or the number of repeat units between cross-linking points, N_c, was estimated in two ways: from the irradiation dose using the literature[7,8] values of the scission and cross-linking rates at T = 30 °C[7-9] and from swelling measurements of the pellets in toluene. The measured and calculated cross-linking densities are within experimental error for the 75- and 156-Mrad samples. In the case of the 40-Mrad sample, the cross-linking density was low and N_c could not be easily measured by swelling: consequently, only the calculated result was used (Table I). Thin films of monodisperse ($M_w/M_n < 1.1$) deuterated polystyrene (DPS) of molecular weight 85 000, 104 000, 303 000, or 550 000 (Polymer Laboraories, degree of polymerization, N_b = 759, 929, 2705, or 4910, respectively) were spun cast on glass and floated from water onto the silicon wafers covered with the cross-linked PS. The DPS film thicknesses were in the range 100–350 Å for the tracer diffusion experiments and approximately 4000 Å for the mutual diffusion experiments. The samples were annealed in a vacuum of approximately 10^{-5} Torr at 152 °C for times ranging from 0.5 h to 10 days. The interdiffusion of the DPS into the cross-linked networks was measured using secondary ion mass spectrometry (SIMS). The sample preparation required for quantitative analysis of the data has been described[10,11] elsewhere. In the present study, the samples are thicker than those used previously,[10,11] and in order to obtain reasonable data acquisition rates of approximately 2–3 h per sample, a 6-keV sputtering beam of Ar^+ ions was used. At this energy the spatial resolution obtained, corresponding to a Gaussian of FWHM = 140 Å, was worse than the previously quoted[10,11] value of 100 Å for a sputtering energy of 2 keV but was more than adequate for resolving the length scales relevant to this work.

Theory

In order to account for the total free energy of a homopolymer diffusing into a cross-linked network, the energy to elastically deform the network must be added to the enthalpy and entropy of mixing terms present in the melt. Following the formulation of Brochard[5] and Binder and Frisch,[12] Briber and co-workers[6] combined the free energy derived from classical rubber elasticity theory for an isotropic network[13] with the well-known Flory–Huggins free energy for a polymer blend[14,15] to obtain the following expression for the free energy per unit volume of a network swollen with a linear homopolymer:

$$\frac{f}{kT} = \frac{3A}{2V_aN_c}(\phi_s^{2/3}(1-\phi)^{1/3} - (1-\phi)) + B\frac{(1-\phi)}{V_aN_c}\ln\frac{(1-\phi)}{\phi_s} + \frac{\phi}{V_bN_b}\ln\phi + \frac{\chi}{V_0}\phi(1-\phi) \quad (1)$$

In this equation ϕ is the linear chain volume fraction, $1 - \phi_s$ is the initial volume fraction of homopolymer when the network was formed, i.e. the fraction of the original sample not cross-linked during the γ irradiation, which in this case is equivalent to the sol fraction. χ is the Flory interaction parameter,[14] N_c is the number of repeat units between cross-linking points, and N_b is the polymerization index of the homopolymer. V_a, V_b, and V_0 are the volumes of the network monomer units, the homopolymer monomer units, and the lattice reference volume, $V_0 = (V_aV_b)^{1/2}$. The constants A and B depend on the particular model of rubber elasticity chosen and have been given by Flory[13] as A = 1 and B = 0.5 for tetrafunctional cross-linking points. The chemical potential, μ_b, in units of kT, of the homopolymer chains can then be obtained by taking the derivative of the total free energy with respect to the number of homopolymer chains[5,6,12] to obtain

$$\mu_b = V_bN_b\left(\frac{A\phi_s^{2/3}(1-\phi)^{1/3} - B(1-\phi)}{V_aN_c} + \frac{1-\phi+\ln\phi}{V_bN_b} + \frac{\chi}{V_0}(1-\phi)^2\right) \quad (2)$$

The diffusion coefficient for the homopolymer into the network can be calculated in a manner analogous to Sillescu's derivation for the mutual diffusion coefficient of a polymer melt.[16] The Hartley–Crank equation for a polymer blend consisting of two components is given by

$$D = (X_bD_a + X_aD_b)\frac{\phi_a\phi_b}{X_a}\frac{\partial\mu_b}{\partial\phi_b} \quad (3)$$

where ϕ_a and ϕ_b are the volume fraction of the two components, X_a and X_b are the mole fractions of the diffusing species, and D_a and D_b are the corresponding tracer diffusion coefficients. For a cross-linked melt of constant density $D_a = 0$, $\phi_a + \phi_b = 1$, and eq 3 with $\phi = \phi_b$ becomes

$$D = D_b(1-\phi)\phi\frac{\partial\mu_b}{\partial\phi} \quad (4)$$

Substituting μ_b from eq 2 into eq 4 we obtain the following expression for the diffusion coefficient:

$$D = -D_b(1-\phi)\phi N_b\left(\frac{A\phi_s^{2/3}(1-\phi)^{-2/3}}{3N_c} - \frac{B}{N_c} - \frac{(1-\phi)}{N_b\phi} + 2\chi(1-\phi)\right) \quad (5)$$

where we have made the assumption that the homopolymer, network molar volumes, and the reference volume are the same, or $V_a = V_b = V_0$. The expression derived in eq 5 reduces to that obtained by Sillescu[16] for N_a, N_b, when the elastic energy terms, A and B, are omitted. Including the elastic energy terms has the effect of further reducing the diffusion coefficient to reflect slowing down as the new spinodal curve[6,18] (derived from eq 1) is approached. From eq 5, we can calculate numerically the diffusion profile by solving the diffusion equation

$$\frac{\partial}{\partial t}\phi(x,t) = \frac{\partial}{\partial x}\left(D\frac{\partial\phi}{\partial x}\right) \quad (6)$$

subject to the boundary condition[2] that $\phi(x)$ at time zero is a normalized step function.[19,20] The normalization factor is a function of $(1 - \phi_s)$, as discussed in the next section.

Results

(a) Mutual Diffusion. Figure 1 shows the data for DPS films of N_b = 1000, having the same initial thickness, allowed to diffuse for 6 h at T = 150 °C into a PS homopolymer melt of N_b = 9620 (solid line) and into a cross-linked network of N_c = 9300 (dashed line). From the figure it can easily be seen that cross-linking the PS, even with a relatively low density of cross-linking points, significantly decreases the rate of diffusion. Furthermore, since the initial interface positions were the same, the swelling of the network is apparent by the motion of its interface relative to that of the homopolymer sample. Figure 2 shows the SIMS data for the deuterium volume fraction vs depth for DPS film of N_b = 1000 diffused into

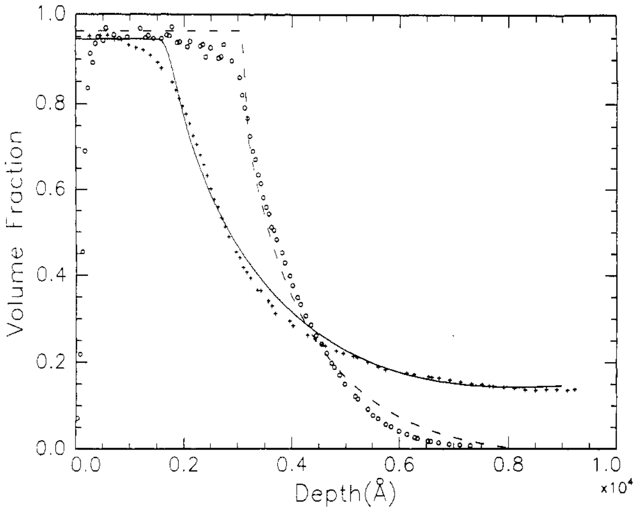

Figure 1. DPS concentration vs depth profile for a DPS film of M_w = 104 000 allowed to diffuse for 6 h at 150 °C into a PS homopolymer matrix of M_w = 1 000 000 (+) and into a cross-linked matrix having N_c = 9300 (○). The solid lines are fits to the profiles derived from eq 6.

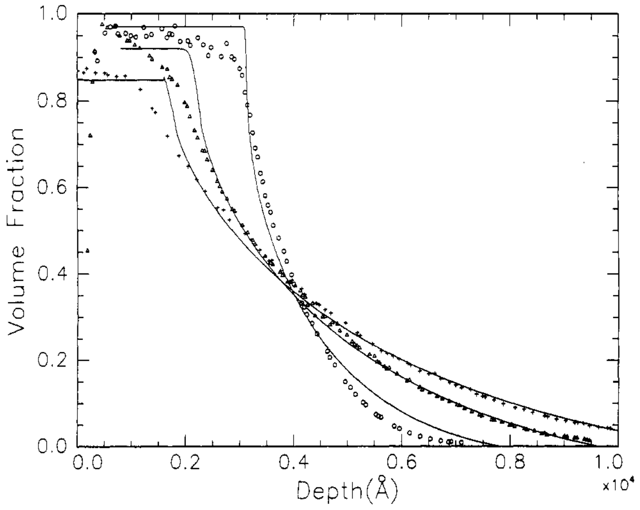

Figure 2. DPS volume fraction vs depth for a DPS film of M_w = 104 000 diffused into a cross-linked PS matrix of N_c = 9300 at 150 °C for 6 (○), 24 (▵), and 36 (+) h. The solid lines are fits to the profiles derived from eq 6.

a cross-linked PS matrix at T = 150 °C of N_c = 9300 for 6, 24, and 36 h. Similarly, Figure 3 shows the data for DPS films of N_b = 759 diffused into a cross-linked PS matrix of N_c = 4900 after annealing times of 6, 13.5, and 24 h.

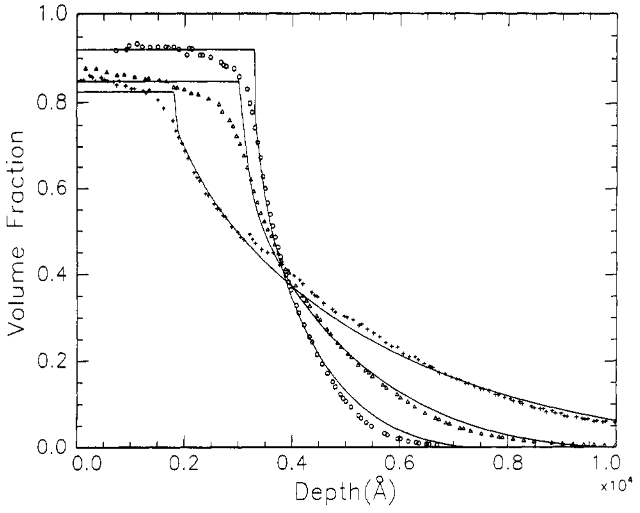

Figure 3. DPS volume fraction vs depth for a DPS film of M_w = 85 000 diffused into a cross-linked PS matrix of N_c = 4900 for 6 (○), 13.5 (▵), and 24 (+) h. The solid lines are fits to the profiles calculated from eq 6.

Table II. Summary of the Tracer Diffusion Coefficients Used in the Calculation

$M_w(k)$	27	50	85	104	188	550	713
$10^{14}D^*$ (cm^2/s)[a]	31.9	9.30	3.22	2.15	0.66	0.077	0.046
$10^{14}D^*$ (cm^2/s), N_c = 9300	26.10		2.475	1.751	0.612	0.069	0.036
$10^{14}D^*$ (cm^2/s), N_c = 2400		6.587	3.154	1.618	0.510	0.061	0.033

[a] Homopolymer M_w = 1 030 000 matrix.

The solid lines in the figures are fits to eq 6 with ϕ_s being the only free fitting parameter, and the normalization constant being approximated from the plateau region as discussed below. The value of $\chi = 1.6 \times 10^{-4}$ at T = 150 °C was calculated from the measured temperature dependence given in ref 17. A and B were set to the usual Flory values of 1 and 0.5, respectively, for Figures 2 and 3, and the mutual diffusion coefficient[16] was used for the homopolymer matrix in Figure 1. The tracer diffusion coefficients at 150 °C in the two cross-linked matrices were measured separately (next section) and are listed in Table II. From the figures it can be seen that the profiles calculated from the diffusion coefficient in eq 5 yield fairly good fits to the experimental data. The best fit values of ϕ_s, which were 0.8 and 0.9 for the N_c = 9300 and N_c = 4900 matrices, respectively, are consistent with the sol fraction listed in Table I. The sol fraction is essentially the concentration of homopolymer chains present when the lattice was cross-linked and hence should be equivalent to $1 - \phi_s$. A careful inspection of Figures 2 and 3 shows that the volume fraction of deuterium in the overlayer film (the plateau region) drops to approximately 0.85 after 36 and 13.5 h for the N_c = 9300 and 4900 matrices, respectively. In addition it can be seen that the calculated profiles in both cases yield somewhat better fits as the annealing times get longer. As evidenced from Table I, the mean molecular weights of the sol fractions are such that the chains can easily diffuse throughout the DPS overlayer within the experimental annealing time. This mutual diffusion is not considered in the $D(\phi)$ used in eq 6 and consequently degrades the χ^2 of the fit at shorter times. For longer times, these chains are uniformly distributed within the DPS overlayer and, since they are hydrogenated, we observe an effective decrease in the DPS concentration. The mean DPS concentration, approximated by a straight line through the plateau region was then used as the normalization constant for the step function in eq 6.

The data for DPS films of N_b = 759, 2705, and 4910 diffused into a cross-linked matrix of N_c = 4900 for 24 h for the first two molecular weights and 10 days for the third are shown in Figure 4. From the figure we can see that significant diffusion occurs only for the N_b = 759 homopolymer. The solid lines again are fits to the data with ϕ_s as the only free parameter, and again $D(\phi)$ derived from eq 5 predicts fairly well the dependence of the diffusion profiles on the homopolymer molecular weight. Figure 5a shows the calculated diffusion coefficient $D(\phi)$ vs ϕ for the ratios of N_b/N_c corresponding to the data in Figure 4. The dashed line in the figure corresponds to the $D(\phi)$ calculated for N_b = 759 when B = 0. The corresponding diffusion profile (dashed line in Figure 4) shows the sensitivity of the calculated profile to variation of the assumed value of B. From eq 1, it can be shown that the coexistence concentration,[6,18] ϕ_c, for all N_b considered here

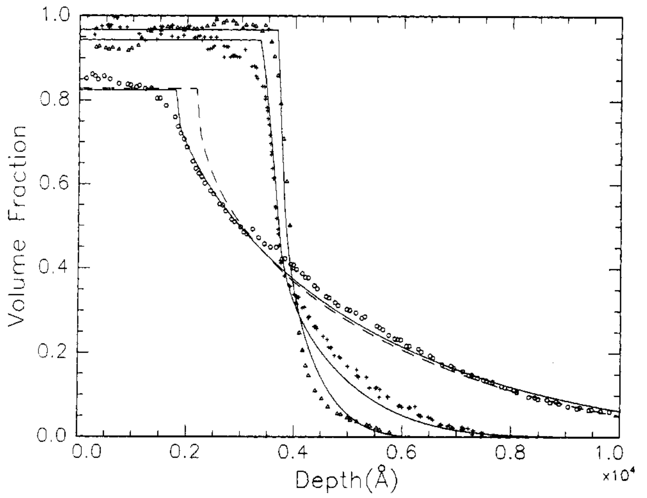

Figure 4. DPS volume fraction vs depth for DPS films of $Mw = 85\,000$ (○), 303 000 (+), and 550 000 (△) allowed to diffuse at 150 °C for 24 h, 24 h, and 10 days, respectively, into a cross-linked PS matrix having $N_c = 4900$. The dashed line corresponds to setting $B = 0$ in eq 5 for $N_b = 817$.

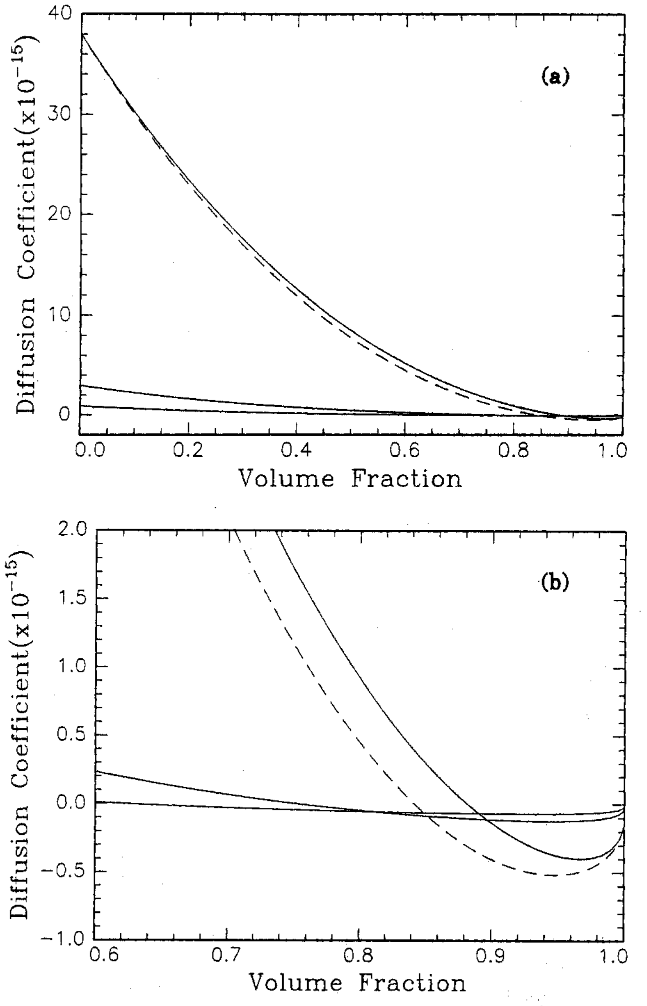

Figure 5. (a) $D(\phi)$ obtained from eq 5 vs ϕ corresponding to $M_w = 85\,000$ (A), $M_w = 303\,000$ (B), and $M_w = 550\,000$ (C) of DPS homopolymer and $N_c = 4900$. The dashed line corresponds to setting $B = 0$ for $N_b = 759$ ($M_w = 85\,000$). (b) Expanded portion of the figure in the vicinity of the spinodal concentration.

wre approximately $\phi_c \geq 0.8$; i.e. the homopolymer network melt is in the one phase region over most of the diffusion range studied.[19] Expanding the lower portion of Figure 5a (see (b)), we can see that for $\phi > \phi_c$, $D(\phi)$ is positive. Consequently, penetration of the network by homopolymer is possible even for $N_b/N_c \geq 1$, in good agreement with Brochard's predictions.[5]

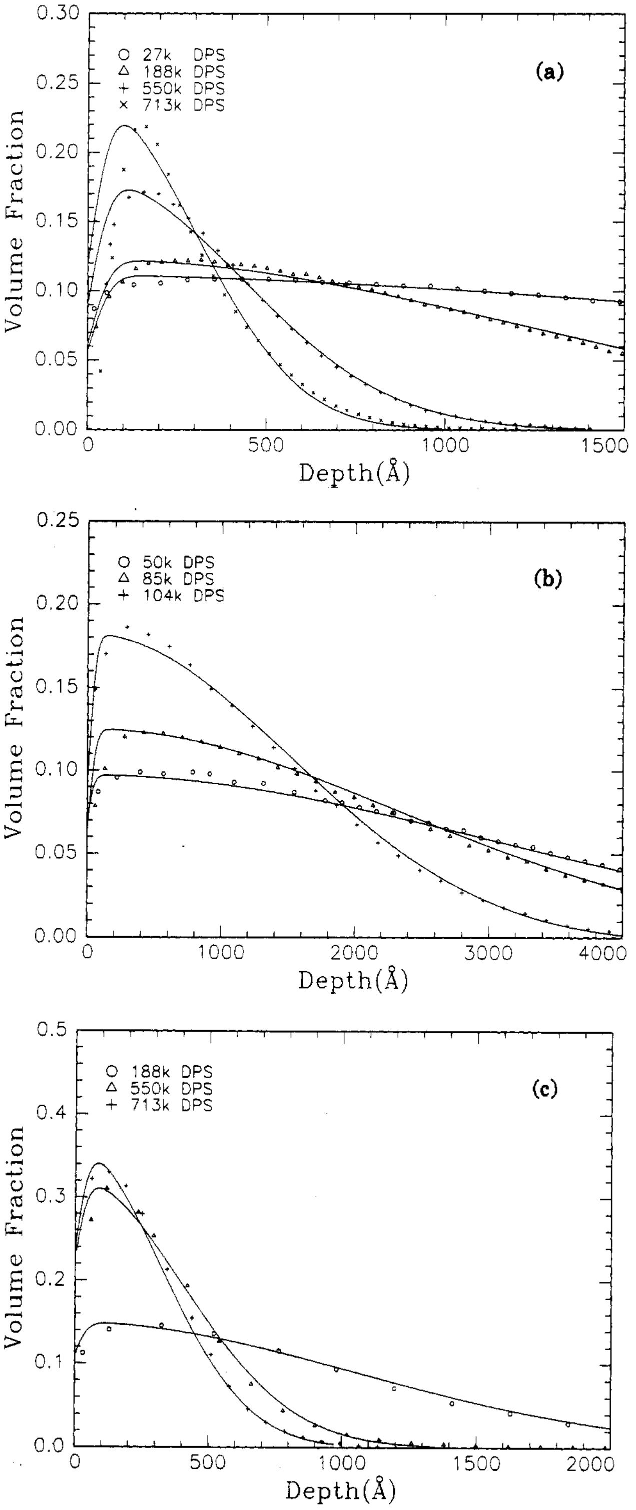

Figure 6. DPS volume fraction vs depth profiles for thin films of various molecular weights allowed to diffuse (a) for 0.5 h for DPS $M_w = 27\,000$ and 3.25 h for DPS $M_w = 188\,000$, 550 000, and 713 000 into a cross-linked matrix of $N_c = 9300$, the film thicknesses are 396, 195, 94, and 87 Å, respectively, (b) for 2 h into a cross-linked matrix having $N_c = 2400$ (DPS $M_w = 50\,000$, 85 000, and 104 000, the thickness are 381, 336, and 350 Å, respectively), and (c) for 3.25 h into the same network as in (b) (DPS $M_w = 188\,000$, 550 000, and 713 000, the thicknesses are 195, 162, and 135 Å, respectively).

(b) Tracer Diffusion Coefficient. The tracer diffusion coefficients were obtained by measuring the diffusion profiles of thin homopolymer films of different

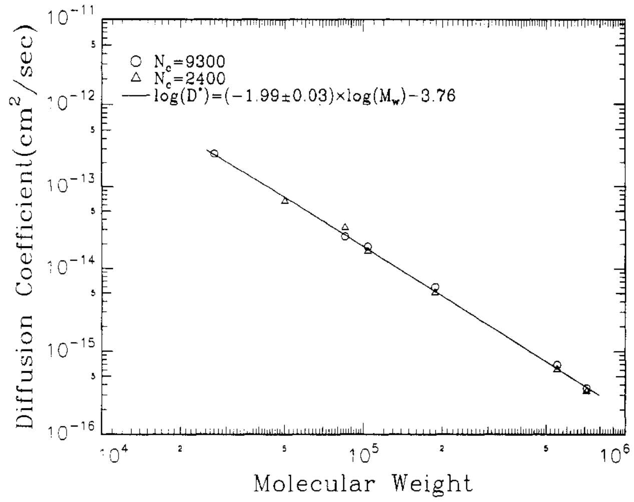

Figure 7. Log of the best fit values of the tracer diffusion coefficients in the N_c = 9300 (0) and in the N_c = 2400 network (Δ) vs the log of the homopolymer molecular weight.

molecular weights (Table II) into the cross-linked networks with the highest and lowest cross-linking densities, N_c = 2400 and 9300, respectively. The thickness of the homopolymer films was chosen such that the concentration of DPS would become very dilute and approximate as closely as possible noninteracting chain diffusion. The SIMS profiles obtained for the two networks are shown in Figure 6. The solid lines are fits to the solution of the Fickian diffusion equation for a thin film of thickness h into a semiinfinite medium[22] given by

$$\phi(z) = 0.5\ \mathrm{erf}\ \{(h - z)/2\sqrt{D_b t}) + 0.5\ \mathrm{erf}\ \{(h + z)/2\sqrt{D_b t}\} \qquad (7)$$

The best fit values of D_b for the different molecular weights in the two networks are listed in Table II together with the D_b value for DPS homopolymer (M_w = 104 000) into a PS (M_w = 1 030 000) homopolymer matrix. The tracer diffusion coefficient in the homopolymer matrix when approximately scaled by temperature and molecular weight[1] is in agreement with the previous results of ref 1. From the table we can see that the coefficients in the cross-linked networks are independent of cross-linking density and are only slightly smaller than those in the homopolymer matrix. In Figure 7 we plot log(D_b) vs molecular weight for all the data in the cross-linked matrices. The best fit slope to the data is −1.99 ± 0.03, the same as that measured previously in high molecular weight PS matrices.[1] de Gennes'[23] calculations for the mobility of isolated homopolymer chains in networks predict that if both N_b and N_c are greater than the homopolymer entanglement length, N_e, the motion proceeds by simple reptation which is independent of the cross-linking density. In his model the gels were already swollen and the diffusing chains produced no further deformation. Our case is analogous when we study the motion of dilute homopolymer chains where we assume negligible stretching of the network. Furthermore, since for polystyrene[24] N_e = 173 our studies are also in the regime where $N_c \gg N_e$ and the motion is constrained mostly by entanglements which occurs between cross-links. Our results, namely that D_b is relatively insensitive to the cross-linking density and scales as M^{-2}, are in good agreement with his prediction that the motion of individual chains is still dominated by reptation.

Conclusion

In conclusion, we have shown that individual chain diffusion proceeds by the usual reptation mechanism in cross-linked networks where the cross-linking density is greater than the entanglement length. The mutual diffusion coefficient can then be derived for all molecular weights from a Flory–Huggins potential incorporating elastic energy terms.

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