Dynamic Light Scattering from Swollen Poly(dimethylsiloxane) Networks

Suman K. Patel and Claude Cohen*

School of Chemical Engineering, Cornell University, Ithaca, New York 14853-5201

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ABSTRACT: Poly(dimethylsiloxane) (PDMS) networks which contain various amounts of pendant chains are prepared by end-linking mixtures of difunctional PDMS (B_2), monofunctional PDMS (B_1), and a tetrafunctional cross-linker (A_4). Dynamic light-scattering (DLS) experiments are performed on the toluene-swollen networks and on PDMS/toluene solutions. The magnitude of the scaling exponents of the cooperative diffusion coefficient versus the equilibrium concentration in swollen networks and versus concentration in solutions are in good agreement with Freed and Edwards' ideal chain predictions assuming no excluded volume in the length scale of the hydrodynamic correlation length ξ_H. The ratio of the diffusion coefficient in a network to that in solution of equal concentration, $D_{\mathrm{network}}/D_{\mathrm{solution}}$, appears to be constant and is found to be 1.45 ± 0.14, in good agreement with the estimate of 1.5 obtained on the basis of the Flory-Rehner expression.

Introduction

In this work, poly(dimethylsiloxane) (PDMS) networks are prepared with a broad range of structures. The variety in structure is achieved by varying both the amount and size of chains that can attach to the network at only one of their ends. This leads to networks having various amounts and sizes of pendant chains with different extents of branching. The types of structures which can be obtained with these methods are inherently quite different from the structures of networks prepared by more conventional means and certainly quite different from the idealized model used in establishing the scaling laws. In the previous article, we reported the swelling and mechanical properties of such networks[1] and found good agreement with the classical Flory-Rehner model based on Flory-Huggins thermodynamics. This result implies negligible excluded volume effects. In this paper, we report dynamic light-scattering (DLS) measurements on these swollen networks for the purpose of (1) examining the effect of network structure on the dynamics of concentration fluctuations as observed by DLS and (2) establishing the extent of excluded volume effects in these systems. Previous workers[2] have reported limited DLS data on swollen model PDMS networks with inconclusive results as far as the extent of excluded volume effects.

The quantity determined in a DLS experiment on polymer solutions or swollen networks is the correlation function of the intensity of the scattered light, $C(q,\tau)$, where τ is the delay time and q is given by $q = 4\pi n \sin(\theta/2)/\lambda$, where θ is the scattering angle, λ is the wavelength of the incident light in a vacuum, and n is the index of refraction of the scattering medium. $C(q,\tau)$ is related to the correlation function of the scattered electric field, $g^{(1)}(q,\tau)$. The form of $g^{(1)}(q,\tau)$ depends upon the system studied.

Tanaka et al.[3] developed a phenomenological model which treats the DLS from equilibrium swollen polymer networks. They assume that the wavelength of light is much greater than the average distance between cross-links and treat the swollen network as a continuous medium. They show that the electric field correlation function will have the form of an exponential decay with a decay rate of $\Gamma = D_c q^2$, where D_c is the cooperative diffusion coefficient in the "fixed-volume" frame of reference.

The scaling behavior of D_c of semidilute polymer solutions and, by analogy, that of swollen polymer networks has been analyzed by de Gennes.[4,5] de Gennes arrives at

$$D_c^{\,s} = kT/6\pi\eta_s\xi_H \tag{1}$$

where $D_c^{\,s}$ is the diffusion coefficient in the frame of reference in which the solvent does not move (often denoted as the "fixed-solvent" frame of reference), η_s is the viscosity of the solvent, and ξ_H is the hydrodynamic screening or correlation length. The factor of 6π in the denominator of eq 1 was introduced for convenience and by analogy to the Stokes-Einstein relation. In the blob picture of a semidilute solution, a polymer molecule can be considered as a group of spheres of radius ξ_H; the motion of these spheres is uncorrelated, but the motion of the monomers within a given sphere is correlated. Equation 1 can be used to determine the dependence of ξ_H on c, the concentration of polymer, once the dependence of $D_c^{\,s}$ on c is obtained experimentally. Models of the dependence of ξ_H on c have been discussed by several workers for the dilute[6] and the semidilute[7,8] cases, and the results are nicely summarized by Cukier.[9]

Hydrodynamic interactions between the monomers must be accounted for when calculating the dependence of ξ_H on c. Specifically, the motion of a given monomer creates a back-flow in the solvent, coupling the motion of a given monomer to the motion of the rest of the monomers. Debye and Bueche[6] calculated the screening length, $\kappa^{-1} \equiv \xi_H$, within a single polymer coil in dilute solution. For this case, the interactions between monomers are assumed to be approximately given by the Oseen tensor, which goes as $1/r$. Their result is that κ goes as

$$\kappa = (\zeta c/\eta_0)^{1/2} \tag{2}$$

where ζ is the monomer friction coefficient and η_0 is the viscosity of the pure solvent.

In a semidilute solution, eq 2 is assumed to be valid, but ζ is now a function of the monomer concentration. Freed and Edwards[7] argued that in a semidilute solution, the monomer interactions cannot be accurately described by the Oseen tensor because a given polymer coil is not surrounded by solvent but is in an environment of other polymer coils and solvent. A monomer on a given polymer chain feels the effect of monomers of other chains as well as the effect of other monomers on the same chain. As a result, hydrodynamic interactions exist over a shorter

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length scale than they do in dilute solution. Freed and Edwards argued that the interactions could be described by a screened Oseen tensor and obtained

$$\kappa \propto \left(\frac{\zeta(c)c}{\eta_0}\right)^{1/2} \propto c \qquad (3)$$

for ideal chains (chains without excluded volume).

de Gennes[8] used scaling arguments to determine the dependence of ζ on c in semidilute solutions with excluded volume on the length scale of ξ. He makes a number of approximations and arrives at

$$\kappa \propto c^{\nu/(3\nu-1)} \qquad (4)$$

where ν is the scaling exponent relating the radius of gyration of a single polymer molecule to the degree of polymerization ($R_g = aN^{\nu}$).

Comparison of eq 4 with the well-established[4] scaling law for the static correlation length, ξ

$$\xi \propto c^{-\nu/(3\nu-1)} \qquad (5)$$

leads to

$$\kappa^{-1} \propto \xi \qquad (6)$$

Since $\kappa \equiv \xi_H^{-1}$, de Gennes concludes that the static and hydrodynamic screening lengths have the same scaling behavior, i.e.

$$\xi_H \propto \xi \qquad (7)$$

Furthermore, for a polymer/solvent system in which the solvent is a good one, $\nu \approx 0.6$, and from eqs 4 and 5 we get

$$\xi \text{ and } \kappa^{-1} \propto c^{-3/4} \qquad (8)$$

It should be noted that Freed and Edwards' result for an ideal chain can also be obtained from eq 4 by using $\nu = 0.5$.

From eqs 1, 7, and 8, D_c^s is expected to go as

$$D_c^s \propto c^{3/4} \qquad (9)$$

for a semidilute solution with excluded volume within the correlation length ξ, and as

$$D_c^s \propto c \qquad (10)$$

for a system without excluded volume.

Various scaling laws for swollen networks have been proposed on the basis of the analogy between semidilute solutions of high molecular weight polymers and swollen polymer networks.[4] Semidilute solutions can be considered as networks whose cross-links have finite lifetimes, where the cross-links are the entanglements between polymer chains. In a swollen polymer network, ξ will depend upon the concentration which the network assumes at equilibrium, c_e. With the analogy and the result of eq 7, ξ_H in a swollen network scales as

$$\xi_H \propto c_e^{-3/4} \qquad (11)$$

for a swollen network with excluded volume within the length scale ξ. For a swollen network with no excluded volume we would expect from Freed and Edwards' calculation that

$$\xi_H \propto c_e^{-1} \qquad (12)$$

From eqs 1, 11, and 12, D_c in a swollen network is expected to go as

$$D_c^s \propto c_e^{3/4} \qquad (13)$$

and as

$$D_c^s \propto c_e \qquad (14)$$

for a system with and without excluded volume within the correlation length ξ_H, respectively. On the basis of the aforementioned analogy, D_c^s for semidilute solutions and D_c^s for swollen polymer networks are expected to scale with the polymer concentration in a similar manner.

The phenomenological model developed by Tanaka et al.[3] results in an expression relating the diffusion coefficient to the macroscopically observable quantities, K, the bulk modulus, and G, the shear modulus of the network, f, the friction factor of a polymeric segment in the given solvent also enters into the relation which is expressed as

$$D_c^s = \frac{K + \frac{4}{3}G}{f} \qquad (15)$$

Semidilute polymer solutions can be envisioned as swollen polymer networks with cross-links having a finite lifetime. With this analogy, semidilute solutions are expected to behave on short time scales similarly to a gel with permanent cross-links. Then displacement fluctuations will also be expected to diffuse with a diffusion coefficient similar to the expression given by eq 15.

By de Gennes' scaling arguments discussed above, the diffusion coefficient of both semidilute solutions and swollen polymer networks are expected to scale with the polymer concentration to the 0.75 power. Polyacrylamide gels have been studied by Geissler and Hecht[10,11] and more recently by Takebe et al.,[12] and scaling exponents of 0.65–0.77 have been observed. The system of polystyrene in benzene was studied by several groups, and scaling exponents of approximately 0.68 were observed for both semidilute solutions and swollen networks.[13,14] For the system polystyrene in ethylacetate, an exponent of 0.66 was obtained for both solutions and networks.[13] For the PDMS/toluene system, an exponent of approximately 0.77 was observed for semidilute solutions and a somewhat higher exponent was observed for the swollen networks.[2] However, with the exception of the results by Geissler and Hecht,[11] the values of these exponents have been obtained for D_c, as directly measured by DLS, and not D_c^s. We shall see later that the difference can be appreciable.

Although semidilute solutions and swollen polymer networks exhibit similar DLS behavior, it has been observed that the magnitude of the diffusion coefficient in a swollen network is larger than the magnitude of the diffusion coefficient in a corresponding solution of the same concentration as the swollen network. Various arguments have been proposed to explain this, including the presence of microheterogeneities due to nonrandom cross-linking[15,16] and the absence of a shear modulus in semidilute solutions.[17] Our results will shed some light on this problem.

Experimental Section

Materials. The divinyl precursor (B_2) was prepared by polymerizing hexamethylcyclotrisiloxane (D_3) in toluene, using methyl sulfoxide as a promoter, and benzyltrimethylammonium bis(*o*-phenylenedioxy)phenylsiliconate as a catalyst.[18-21] The amounts of the above materials used were 5 g of toluene, 0.002 26 g of catalyst, and 0.2202 g of DMSO/5 g of D_3. The polymerizations were allowed to run for approximately 2 h, after which the polymers were endcapped with vinyl groups using vinyldimethylchlorosilane and pyridine as an acid scavenger. B_2 was washed with water and then dissolved and reprecipitated with toluene and methanol. B_2 was dried in a vacuum oven at 60 °C for 3 days.

Table I
Molecular Weight Data for Polymer Precursors from Gel Permeation Chromatography

series designation	$10^{-3}M_{n,B_2}$	$M_{w,B_2}/M_{n,B_2}$	$10^{-3}M_{n,B_1}$	$M_{w,B_1}/M_{n,B_1}$
Q	18.5	1.18	19.8	1.26
R	18.5	1.18	36.1	1.16

Table II
Experimental Characteristics of Networks

network	x	r	10^2w_{sol}	v_2
Q-1	0.0	1.91	0.744	0.259
Q-2	0.148	1.79	4.09	0.242
Q-3	0.289	1.84	5.37	0.211
Q-4	0.437	1.88	9.19	0.179
Q-5	0.573	1.86	12.1	0.153
R-1	0.0	1.77	0.499	0.259
R-2	0.165	1.81	3.79	0.217
R-3	0.341	1.84	7.04	0.170
R-4	0.458	1.82	8.02	0.143

The monofunctional precursor (B_1) was synthesized by polymerizing D_3 in cyclohexane, using n-BuLi as an initiator and methyl sulfoxide as a promoter. Cyclohexane (12 mL) was used per 15 g of D_3. B_1 was endcapped, washed, and dried using the same methods as were used in the preparation of B_2.

B_2 and B_1 were characterized using gel permeation chromatography (GPC). Mark-Houwink parameters obtained by Lapp et al.[22] were used in the GPC molecular weight determination. The results are reported in Table I.

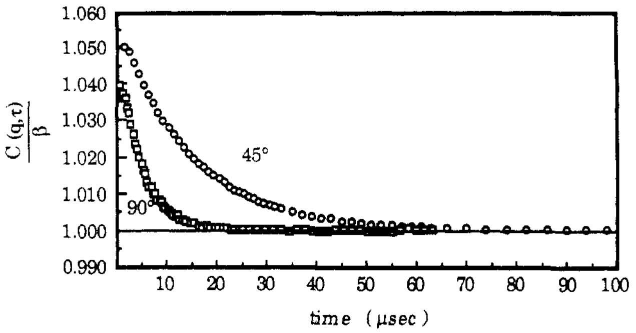
The networks were synthesized using methods which have been well established.[23-25] The networks are formed using a hydrosilylation reaction, a platinum-catalyzed addition of a silane group, present on the cross-linker molecule, tetrakis(dimethylsiloxy)silane (A_4), to the vinyl groups at the ends of the polymer molecules.

To prepare the networks, the required amount of B_2, B_1, and A_4 was first diluted with toluene to a PDMS volume fraction of 0.10 and stirred overnight. The end-linking reaction was catalyzed with *cis*-dichlorobis(diethyl sulfide)platinum(II) in toluene to achieve a concentration of 20 parts platinum/10^6 parts PDMS. After the addition of the catalyst, each sample was filtered through 0.20-μm FP-Vericel syringe filters into glass vials which had been rinsed with filtered toluene. The vials were then placed in a vacuum oven and the solvent was flashed off as quickly as possible. The samples were allowed to cure in the vacuum oven for 3 days at a temperature of 35 °C. After this curing procedure, the vials were carefully broken and the networks were removed.

Two series of networks were prepared. The amounts of the precursor and cross-linker used are given in the first two columns of Table II in the form of x and r, where x is the mole fraction of B_1 and r is the ratio of silane hydrogens to vinyl groups. As noted in the preceding article, the relatively large value of r (1.8–1.9) was selected on the basis that it leads to model networks (of the type Q-1 and R-1) that have the minimum amount of swelling in toluene and thus are expected to be to the most perfect model networks possible.

Experimental Apparatus. The light source was a Lexel Model 85 argon ion laser operated at a wavelength of 488 nm. The scattering cell was inserted into a brass jacket whose temperature was maintained at 25 ± 0.1 °C with a circulating bath. Photon counting was performed with an EMI 9789B photomultiplier tube, which was mounted on a rotary table. The signal from the photomultiplier tube was sent to a Pacific Instruments Model 3470/AD6 amplifier–discriminator. The signal from the amplifier–discriminator was sent to a Brookhaven Instruments BI-2030AT correlator. Software supplied by Brookhaven Instruments was used to analyze the data.

Experimental Methods. For each network, the soluble fraction was extracted, and the weight fraction of soluble material, w_{sol}, and the volume fraction of polymer in the equilibrium swollen network, v_2, was determined gravimetrically. The networks were allowed to equilibrate to an excess of toluene. The swollen networks were carefully sliced into sections by making two parallel cuts with a razor blade. The middle section were used for the scattering experiments. It was placed in the scattering cell with the cut surfaces parallel with the bottom of the cell. The position of the sample within the cell was such that the incoming beam hit the sample at a smooth, uncut surface. The outgoing and scattered beams also passed through uncut surfaces. By varying the position of the sample within the scattering cell, a scattering volume was selected which resulted in a minimum of excess scattering. The scattering experiments were performed after the sample was allowed to equilibrate for a minimum of 1 h.



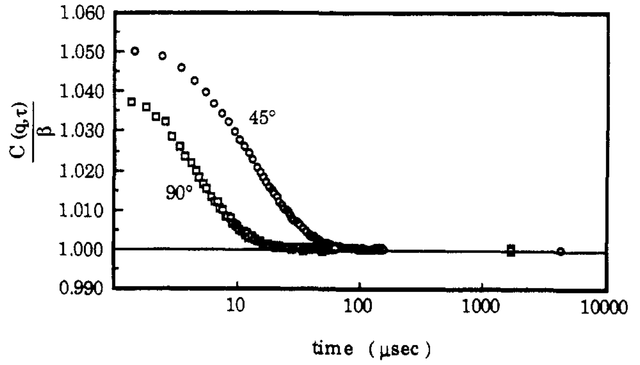


Figure 1. Typical normalized correlation functions obtained from equilibrium swollen networks. The correlation functions shown are for scattering angles of 45 and 90° from sample Q-1.

Experiments on polymer solutions were also performed on PDMS chains with a weight average molecular weight of 173K, as determined by low-angle light scattering. The sample had a polydispersity of 1.66, as determined by gel permeation chromatography. The solutions were prepared, stirred overnight, and filtered through 0.2-μm filters into clean centrifuge tubes. The tubes were cleaned by soaking them overnight in Chromerge, followed by successive rinses of deionized water, acetone, methanol, and toluene. After rinsing, they were further cleaned by inverting the tubes over a stream of refluxing toluene for 1 h. In this procedure, the tube acted as a condenser for the toluene. The centrifuge tubes were sealed and placed into the scattering cell, which contained a refractive index matched glycerin bath. The experiments were performed after allowing the sample to equilibrate for a minimum of 1 h and were performed within 1 day of sample preparation.

Results and Discussion

Typical normalized correlation functions obtained from an equilibrium swollen network are shown in Figure 1, where $C(q,\tau)/\beta$ is plotted versus τ for scattering angles of 90 and 45°. In the upper figure, a linear time scale is used and the behavior of $C(q,\tau)/\beta$ is shown for the first 100 ms. In the lower figure, a logarithmic time scale is used to show the long-time behavior of $C(q,\tau)/\beta$. β is the long-time asymptote of $C(q,\tau)/\beta$ and is obtained by averaging six values of $C(q,\tau)$ at times corresponding to approximately 1000 times the same time of the last regular (nondelay) channel of the correlator.

Data such as that reported in Figure 1 can be analyzed with a cumulant analysis[26] or with a nonnegative least-squares (NNLS) fitting routine.[27,28] The results of the cumulant analysis for samples Q-1, Q-3, and Q-5 for the

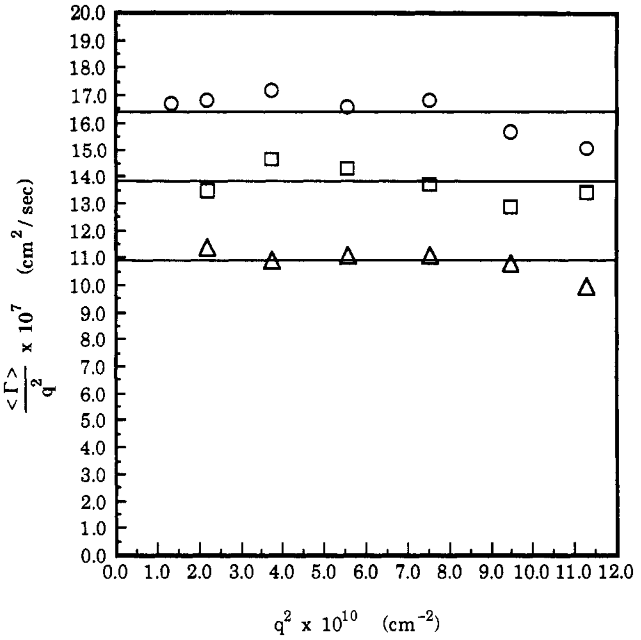


Figure 2. Typical plots of $\langle \Gamma \rangle / q^2$ from the cumulant analysis versus q^2. The results shown are for networks Q-1, Q-3, and Q-5, represented by the symbols ○, □, and △, respectively.

angles shown in Figure 1 as well as for five other angles are given in Figure 2 where $\langle \Gamma \rangle / q^2$ is plotted versus q^2, where $\langle \Gamma \rangle$ is the mean decay rate determined from the cumulant analysis.

The networks designated Q-2 thru Q-4 and R-1 thru R-2 exhibited behaviors similar to that exhibited by Q-1. The correlation functions decayed nicely to the baseline, and there was no shift or discontinuity between the last few regular channels of the correlator and the delay channels, which are used to determine the long-time asymptote of $C(q,\tau)$. On the other hand, the more highly swollen networks exhibited a different behavior. For these, the values of $C(q,\tau)$ at the last regular data channels were significantly greater than the values of $C(q,\tau)$ for the delay channels, indicating the presence of heterogeneities with very slow decay rates. For these networks, the baseline corresponding to an average of the last six regular channels was used. The behavior of $C(q,\tau)$ between the last regular channels and the delay channels was neglected on the assumption that this slow decay of $C(q,\tau)$ does not affect the fast decay observed with the regular channels. The results reported in Table III for samples Q-5, R-3, and R-4 were obtained by using this modified method of analysis.

The results of all of the experiments on swollen networks are summarized in Figure 3, where $\langle \Gamma \rangle / q^2$ is plotted versus v_2. The values of $\langle \Gamma \rangle / q^2$ reported in Figure 3 are an average of values of $\langle \Gamma \rangle / q^2$ for five to six different scattering angles, and the error bars represent their standard deviation. The individual values of $\langle \Gamma \rangle$ and μ, the polydispersity, are given in Table III. Some of the correlation data were also analyzed using the NNLS method of Morrison et al.,[27,28] and the results for $\langle \Gamma \rangle$ were in good agreement with the results from the cumulant analysis. The results from solutions of high molecular weight PDMS in toluene were analyzed in the same manner as the swollen networks were.

It has been established that scattering experiments from swollen networks are typically heterodyned because of the invariable presence of heterogeneities. Thus, values of D_c for the swollen networks are taken as equal to $2\langle \Gamma \rangle / q^2$. The values obtained in this manner are consistent with the limited results of previous workers for $D_c(c_e)$ for PDMS networks in toluene.[2] The solution experiments were assumed to be homodyne, and D_c was taken as $\langle \Gamma \rangle / q^2$.

Table III
Light-Scattering Results

sample designation	$10^{10}q^2$ (cm^{-2})	$10^7\langle \Gamma \rangle / q^2$ (cm^2/s)	μ (s^{-2})
Q-1	1.36	16.7	0.156
	2.21	16.8	0.108
	3.76	17.2	0.109
	5.58	16.6	0.0872
	7.53	16.8	0.165
	9.48	15.7	0.152
	11.3	15.1	0.117
		16.4 ± 0.74	
Q-2	2.21	15.5	0.0770
	3.76	16.6	0.178
	5.58	17.0	0.171
	7.53	15.0	0.165
	9.48	15.4	0.174
	11.3	14.9	0.162
		15.7 ± 0.87	
Q-3	2.21	13.5	0.141
	3.76	14.7	0.154
	5.58	14.3	0.171
	7.53	13.7	0.170
	9.48	12.9	0.184
	11.3	13.4	0.175
		13.8 ± 0.65	
Q-4	3.76	12.8	0.158
	5.58	13.3	0.174
	7.53	11.6	0.181
	9.48	11.3	0.185
	11.3	11.7	0.205
		12.1 ± 0.86	
Q-5	2.21	11.4	0.231
	3.76	10.9	0.138
	5.58	11.1	0.135
	7.53	11.1	0.178
	9.48	10.8	0.167
	11.3	9.96	0.140
		10.9 ± 0.50	
R-2	2.21	15.1	0.163
	3.76	14.6	0.184
	5.58	14.7	0.207
	7.53	14.3	0.204
	9.48	13.0	0.201
	11.3	13.0	0.190
		14.1 ± 0.90	
R-3	2.21	11.7	0.138
	3.76	11.8	0.129
	5.58	11.3	0.158
	7.53	11.2	0.169
	9.48	10.6	0.181
	11.3	10.6	0.183
		11.3 ± 0.52	
R-4	2.21	10.3	0.148
	3.76	9.54	0.155
	5.58	9.80	0.170
	7.53	9.45	0.183
	9.48	9.26	0.189
	11.3	9.11	0.184
		9.57 ± 0.41	

In Figure 4, D_c obtained from $D_c = \langle \Gamma \rangle / q^2$ is reported for the polymer solutions along with D_c obtained from $D_c = 2\langle \Gamma \rangle / q^2$ for the swollen networks. In agreement with the reports of previous workers,[2] the values of D_c for the solutions are lower than the values for the networks at equivalent concentrations. Also, within experimental error, the scaling relationships between D_c and concentration is the same for both the solutions and the swollen networks. From a least-squares fit of the data in the linear regime, the scaling exponent of D_c versus c for the semidilute solutions is approximately 0.73 ± 0.14. The $D_c(c_e)$ scaling relationship appears to be approximately the same for the swollen networks; a least-squares fit gives an exponent of 0.87 ± 0.14. This larger exponent for the

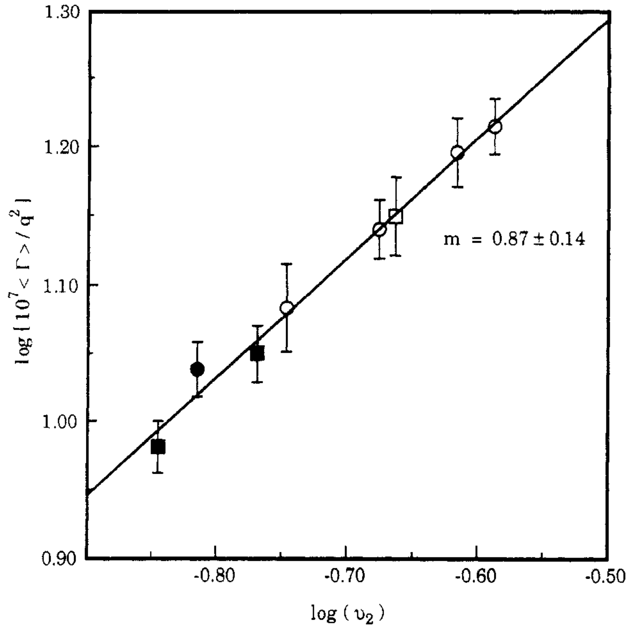


Figure 3. $\langle\Gamma\rangle/q^2$ from a cumulant analysis versus v_2. The circles correspond to networks from series Q and the squares correspond to networks from series R. The open symbols represent values calculated using the long-time asymptote for β, whereas the closed symbols represent values calculated using the average of the last six regular channels as β.

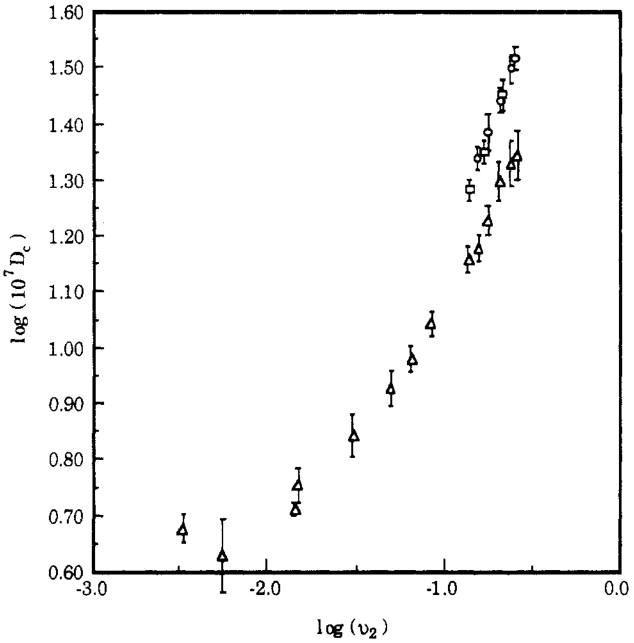


Figure 4. D_c of swollen polymer networks and polymer solutions, where the networks from series Q and R are represented by the symbols ○ and □, respectively, and the solutions are represented by △.

networks may be due to the narrower range of concentrations which were observed, and is in good agreement with the exponents of 0.9–1.0, which Munch et al.[2] observed from a least-squares fit of their limited data for swollen network results.

The networks examined here cover a very wide range of structures, from those similar to networks prepared by previous workers (Q-1 and R-1) to those containing very large branched structures. Despite this variation in structure, similar scaling exponents are observed for both the networks and the solutions. This indicates that the concentration fluctuations which are probed with DLS are not affected by the variations in the chain-level architecture produced in this work, at least as far as the fastest decay rate of $C(q,\tau)$ is concerned. For the most highly swollen networks, $C(q,\tau)$ did not decay to the baseline, but a slower decay was evident with a time scale much longer than the fast decay. The magnitude of q ranged from 1.2×10^5 to 3.1×10^5 cm^{-1} in this work. The length scale which is probed in a scattering experiment is given by $1/q$, corresponding to 300–900 Å. Because the details of the molecular chain level architecture do not appear to affect the magnitudes of D_c, it appears that concentration fluctuations over a length scale of 300–900 Å are not affected by the variations of chain-level architecture. Differences in concentration fluctuation behavior due to the differences in network structure may occur at shorter length scales but cannot be probed with the accessible range of q's of visible light.

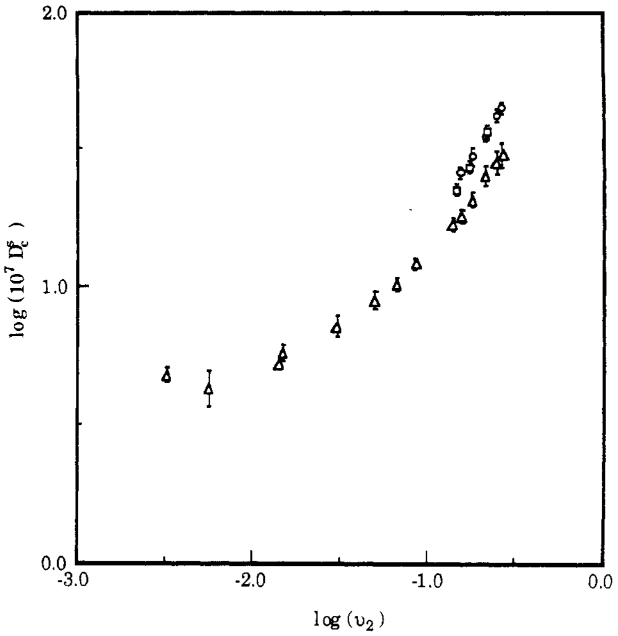


Figure 5. D_c^s from swollen polymer networks and semidilute solutions, where the networks from series Q and R are represented by the symbols ○ and □, respectively, and the solutions are represented by △.

It should be noted that the scaling predictions derived by de Gennes for a good solvent are for the cooperative diffusion D_c^s using a fixed-solvent frame of reference. On the other hand, the D_c obtained from a DLS experiment is based on a fixed-volume frame of reference.[29,30] As shown by previous workers,[11,29,31] the two diffusion coefficients are related by

$$D_c^s = D_c/(1 - v_2) \qquad (16)$$

The correction factor of $(1 - v_2)$ is small for dilute systems as anticipated by de Gennes, but for the concentrations of the networks and solutions examined in this work, this factor is significant. D_c^s obtained from $D_c^s = \langle\Gamma\rangle/[q^2(1 - v_2)]$ for solutions and D_c^s obtained from $D_c^s = 2\langle\Gamma\rangle/[q^2(1 - v_2)]$ for the swollen networks are reported in Figures 5 and 6. A comparison of these figures with Figure 4 illustrates that the $(1 - v_2)$ factor has a significant effect on the scaling exponents. The magnitude of the values of the scaling exponents for D_c^s versus c is greater than that of the exponents for the scaling behavior of D_c versus c, and they are also greater than the values predicted by eq 13 for a system with excluded volume. The magnitude of the exponents observed in this work is in good agreement with the predictions of eqs 10 and 14 for a system without excluded volume and does not agree with de Gennes scaling predictions (eqs 11 and 13).

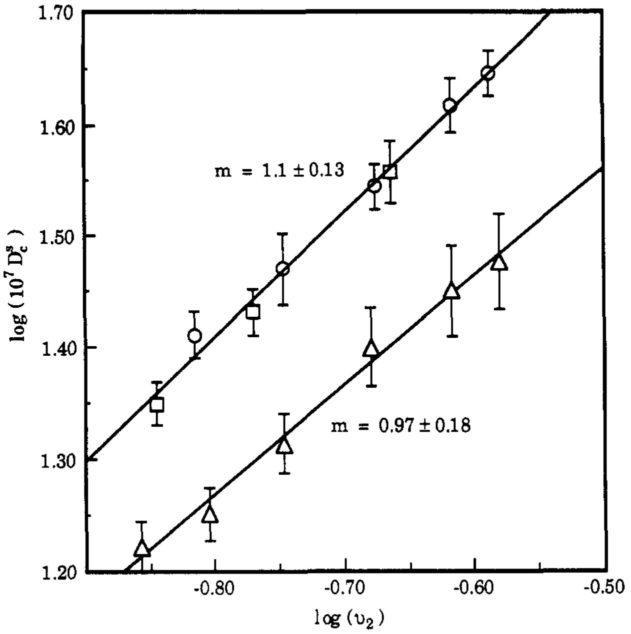


Figure 6. D_c^s from swollen polymer networks and semidilute solutions at equivalent concentrations, where the networks from series Q and R are represented by the symbols ○ and □, respectively, and the solutions are represented by △.

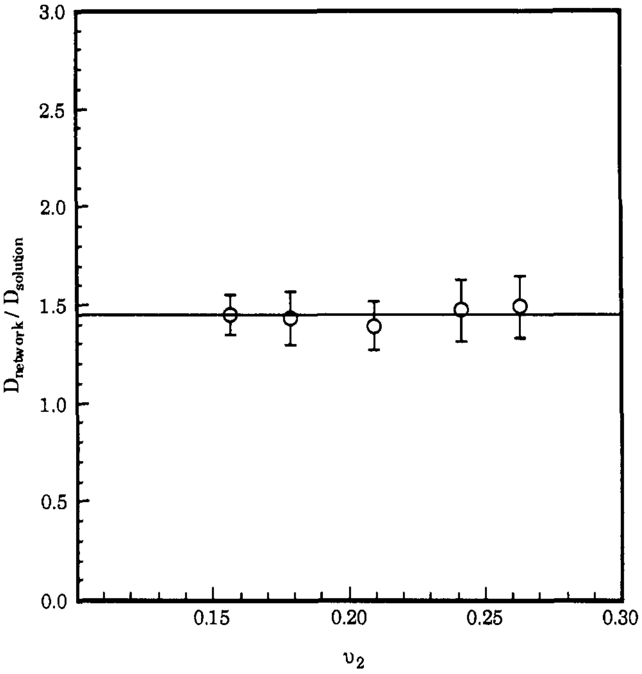


Figure 7. $D_{\mathrm{network}}/D_{\mathrm{solution}}$ versus υ_2.

There are a few possible explanations for these results. Toluene is not particularly a very good solvent for PDMS, as indicated by the values of the interaction parameter reported in the preceding article.[1] The behavior of PDMS/toluene solutions may be intermediate between that for theta solvent and a good solvent. In this case, a scaling exponent between 0.75 and 1.0 would be expected. However, more importantly, we note that the power law observed in Figure 5 is for solutions and networks with $\upsilon_2 \geq 0.1$, which is beyond the true semidilute regime, $\upsilon_2 < 0.1$, as defined by de Gennes. The fact that no scaling law is apparent in the solutions data below $\upsilon_2 < 0.1$ could be due to the quality of solvent. For the networks, we have shown[1] that the chains are highly interspersed even at equilibrium swelling and this interspersion decreases any excluded volume effects that might have occurred otherwise.

The friction factor of a polymeric segment depends on the average concentration of segments and is expected to be the same for both networks and solutions at the same concentration. Thus, taking $f_{\mathrm{solution}} = f_{\mathrm{network}}$ and assuming, furthermore, that the shear modulus of the solution is zero, i.e. $G_{\mathrm{solution}} = 0$, it is straightforward to show from eq 15 that

$$\frac{D_{\mathrm{network}}}{D_{\mathrm{solution}}} = \frac{K_{\mathrm{network}}}{K_{\mathrm{solution}}} + \frac{4}{3}\frac{G}{K_{\mathrm{solution}}} \tag{17}$$

where $G_{\mathrm{network}} = G$. The values of $D_{\mathrm{network}}/D_{\mathrm{solution}}$ for the swollen networks and the analogous semidilute solutions of equal concentrations are plotted versus υ_2 in Figure 7. Within experimental error, it appears that for the concentration regime studied here, the ratio $D_{\mathrm{network}}/D_{\mathrm{solution}}$ is independent of concentration.

The Flory–Rehner[32] expression for a highly swollen network can be used to calculate K_{network}, K_{solution}, and G and obtain an estimate of $D_{\mathrm{network}}/D_{\mathrm{solution}}$; the results are

$$K_{\mathrm{network}} = \frac{5}{3}\frac{RT}{\mathrm{V}_1}\left(\frac{1}{2} - \chi\right)\upsilon_2^{\,2} \tag{18}$$

$$K_{\mathrm{solution}} = 2\frac{RT}{\mathrm{V}_1}\left(\frac{1}{2} - \chi\right)\upsilon_2^{\,2} \tag{19}$$

$$G = \frac{RT}{\mathrm{V}_1}\left(\frac{1}{2} - \chi\right)\upsilon_2^{\,2} \tag{20}$$

Equations 18–20 indicate that G and K scale with concentration in a similar manner. This similar scaling dependence was experimentally confirmed by Zrinyi and Horkay,[33] who measured K and G for poly(vinyl acetate) networks swollen with acetone and toluene. The substitution of eqs 18–20 into eq 17 gives

$$D_{\mathrm{network}}/D_{\mathrm{solution}} = 3/2 \tag{21}$$

Within experimental error, the value of $D_{\mathrm{network}}/D_{\mathrm{solution}} = 1.45 \pm 0.14$, obtained from Figure 7, is in good agreement with the prediction of eq 21, although the networks are not very highly swollen. This agreement is surprising, at first, in view of the higher concentrations of our solutions and networks ($\upsilon_2 \simeq 0.2$). However, one can keep the higher order corrections (υ_2^3 terms) to eqs 18–20 by taking into account the concentration dependence of χ reported earlier.[1] We find that because these corrections appear in both numerators and denominators on the right-hand side of eq 17, their effect is not appreciable. Keeping these terms, we calculate $D_{\mathrm{network}}/D_{\mathrm{solution}} \simeq 1.30$ for $\upsilon_2 = 0.2$.

Conclusions

DLS experiments were performed on toluene-swollen PDMS networks containing various amounts of pendant chains and varying widely in physical structure, as well as on semidilute solutions of high molecular weight PDMS in toluene. As stated in the Introduction, the purpose was to examine any possible effects that the network structure might have on the dynamics of concentration fluctuations observed by DLS and to establish the extent of excluded volume effects in these systems. All the networks exhibited a cooperative diffusion coefficient that scaled with the equilibrium swollen concentration c_e of the networks and was independent of the physical structure of the networks. The most imperfect networks, containing a large portion of highly branched pendant chains, exhibited a very slow relaxation (probably due to heterogeneities with very slow decay rates) in addition to the cooperative diffusion mode. The ratio of the diffusion coefficient in a network to that in solution of equal concentration, $D_{\mathrm{network}}/D_{\mathrm{solution}}$, was measured and found to be 1.45 ± 0.14, independent of concentration in the range of concentrations studied here. This is in good agreement with the estimate of 1.5 obtained on the basis of the Flory–Rehner expression for highly swollen networks. The magnitudes of the scaling exponents of the cooperative diffusion coefficient versus the equilibrium concentration in swollen networks and versus concentration in semidilute solutions were found to be 1.1 ± 0.13 and 0.97 ± 0.18, respectively. These results are in better agreement with Freed and Edwards's ideal chain predictions assuming no excluded volume than de Gennes predictions assuming excluded volume in the length scale of the hydrodynamic correlation length ξ_H. This is explained by the high degree of chain interspersion in the swollen networks and the fact that toluene is only a moderately good solvent for PDMS.

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