Thermal Fluctuations in Polymer Gels Investigated by Neutron Spin Echo and Dynamic Light Scattering

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ABSTRACT: Measurements are described involving neutron spin echo and quasi-elastic light scattering in an end-linked polyfluorosilicone (PFS) gel swollen in acetone as well as in the equivalent solution. Small-angle elastic neutron scattering measurements were performed on the same system. For the PFS−acetone system, both dynamic light scattering and neutron spin echo yield similar results for the characteristic relaxation rates and for the intensity scattered by concentration fluctuations. It is shown that the relaxing part of the spin echo decay is described by the same thermodynamic concentration fluctuations that define the osmotic modulus of the system. Both the collective diffusion coefficient and the intensity of the dynamically scattered light are found to be greater in the gel than in the solution. This difference indicates that the polymer solvent friction coefficient in the cross-linked network is lower than in the un-cross-linked solution.

Introduction

In swollen polymer networks both the static and the dynamic properties are sensitive to the structure of the polymer. In a semidilute polymer solution, the collective diffusion coefficient D_c is given as[1]

$$D_c = (\partial\Pi/\partial\varphi)/f \quad (1)$$

where φ is the volume fraction of polymer, Π is the osmotic pressure, and f is the friction coefficient between the polymer segments and the solvent molecules. In gels, a similar relation applies, but the driving potential is then governed by the longitudinal osmotic modulus,[2]

$$M_{os} = \varphi(\partial\omega/\partial\varphi) + 4G/3 \quad (2)$$

Here, ω is the swelling pressure of the network and G is the shear elastic modulus. For a wide variety of different gel systems, it is found that the osmotic contribution of the network polymer Π_{mix} can be expressed as[3]

$$\Pi_{mix} = \omega + G \quad (3)$$

It follows from eqs 1 and 3 that in ideally homogeneous systems where cross-linking affects neither the osmotic properties nor the friction coefficient,

$$D_c^{gel} = M_{os}/\varphi f \quad (4)$$

is greater than $D_c^{solution}$. In practice, both quantities may in general be modified, thus making it difficult to make any prediction for D_c in gels.

No systematic investigations using quasi-elastic techniques at spatial resolution beyond that of light scattering have been devoted to the effect of network inhomogeneity on the dynamics of polymer solutions and gels.[4] Neutron spin echo and dynamic light scattering are techniques that are capable of distinguishing between the components in the system that fluctuate in time from those that are time invariant.[5] By normalizing by the appropriate contrast factor, analysis of the intensity autocorrelation function of light scattered by a gel allows the osmotic compression modulus to be determined.[6] This provides a basis for comparison of the thermodynamic measurements obtained by different techniques.

The goal of this study is to determine the dynamic response in a fluorinated silicone polymer solution and gel. The system investigated here is poly(methyltrifluoropropylsiloxane) (PFS) with acetone as solvent. In this polymer, segment rotation is sterically hindered by the large side groups. It is therefore expected that the dynamics of the segmental motions will be slower than in the more flexible polymer, poly(dimethylsiloxane) (PDMS).[4] A further goal is to estimate the ratio of the fluctuating and the nonfluctuating contributions by means of static and dynamic measurements using neutron spin echo and dynamic light scattering.

Experimental Section

PFS gels were made by cross-linking vinyl-terminated chains of molecular weight 26 000 with silicone hydride using hydrosilylation in the presence of a platinum catalyst, following a method described previously.[7] The gels were swollen to equilibrium in deuterated acetone (Acros).

Neutron spin echo experiments were carried out on the IN15 instrument at the Insititut Laue Langevin (ILL), Grenoble, France. The time delays explored in these experiments extended from 5 to 170 ns with a q range between 0.02 and 0.1 Å^{-1}. Small-angle neutron scattering measurements in the q range 3×10^{-3}Å$^{-1} \leq q \leq 0.2$ Å^{-1} were made on the NG3 instrument at the National Institute of Standards and Technology, Gaithersburg, MD. In all cases, the sample temperature was maintained at 25 °C.

Dynamic light scattering measurements were made using a 488 nm argon ion laser (Spectra Physics 1162) working at

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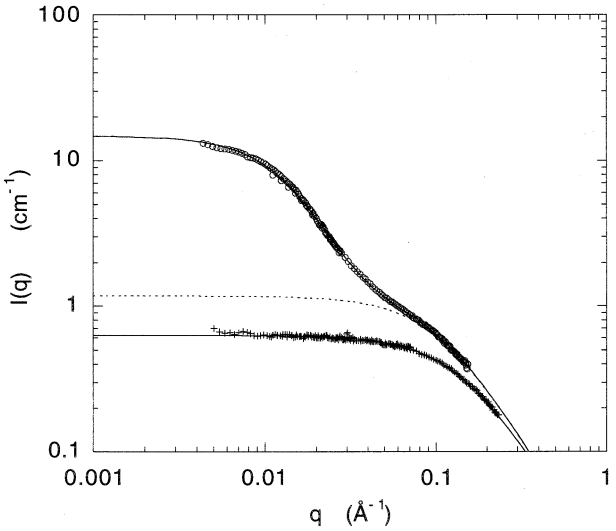

Figure 1. Small-angle neutron scattering spectra from poly(fluorosilicone) solution (crosses) and gel (circles) in acetone at polymer volume fraction $\varphi = 0.33$. Continuous curves are fits of eq 5 and 7 through the data. The dotted line is the fluctuating component in the fit to the gel data.

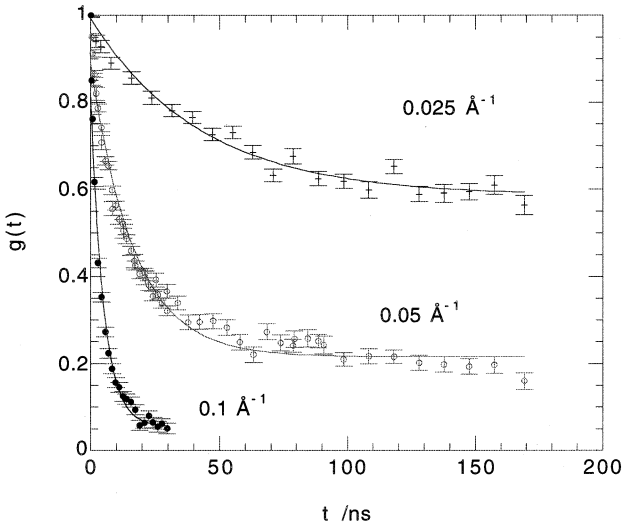

Figure 2. Neutron spin echo decays from a poly(fluorosilicone) gel swollen in acetone at $\varphi = 0.16$ for three different wavevectors q.

100 mW and an ALV E5000 multi-tau correlator. To enhance signal intensity and reduce relaxation rates, observations were made in the angular range 20°−45°. The refractive index increment for PFS−acetone, determined using a Brice-Phoenix differential refractometer at 25 °C, was found to be $dn/d\varphi = 0.0178$.

Results and Discussion

Figure 1 shows the results of SANS measurements for a PFS solution and the corresponding gel, swollen in acetone. The lower continuous line is the fit of the solution data to the expression[1]

$$I_f(q) = \Delta\rho^2 \frac{kT\varphi^2}{\varphi\, \partial\Pi/\partial\varphi} \frac{1}{1 + q^2\xi^2} \tag{5}$$

where $\Delta\rho^2$ is the contrast factor between polymer and solvent and ξ is the thermodynamic correlation length of the polymer. It can be seen that for the solution at small values of q a horizontal plateau is reached, indicating that the system is uniform at longer length scales.

In the case of the gel, however, the scattering intensity exhibits excess scattering in the low q region. This feature, which is generally observed in polymer gels, is the signature of static concentration fluctuations that are frozen-in by the cross-links.[8] The cross-linking process leads to formation of structural heterogeneities consisting of regions of short and longer regions of mobile chains sequences. The regions of shorter chains have higher polymer density and give rise to excess scattering in the q range corresponding to their spatial dimensions. The dynamics of the localized motion of the polymer in such a heterogeneous system, however, is expected to display a wide range of relaxation rates.

The gel spectrum in Figure 1 displays a shoulder at high q similar to that in the solution, but at lower q it exhibits an increased scattering intensity. This extra contribution can be described by including an additional term in the scattering function[9]

$$I_s(q) = \Delta\rho^2 \frac{8\pi\Xi^3\langle\delta\varphi^2\rangle}{(1 + q^2\Xi^2)^2} \tag{6}$$

where Ξ is the spatial range of the static inhomogeneities and $\langle\delta\varphi^2\rangle$ is their mean-square amplitude. Thus, the total scattering function for the gel is the sum of the static and time-fluctuating term

$$I(q) = I_s(q) + I_f(q) \tag{7}$$

where, in accordance with eq 2, the fluctuating component $I_f(q)$ must be redefined as

$$I_f(q) = \Delta\rho^2 \frac{kT\varphi^2}{M_{OS}} \frac{1}{1 + q^2\xi^2} \tag{8}$$

The continuous line through the gel data points shows the least-squares fit of eq 7. The quality of the fit indicates that the functional dependence of the gel response is adequately described by the two terms defined in eqs 6 and 8.

The dynamic response of a polymer system is governed by the mobility of the segments of the chains. In a network, however, cross-links constrain the local motion of the segments. It therefore follows that the overall dynamic response of a gel will not relax completely to zero as in a solution owing to the presence of a constant local elastic constraining field frozen-in by the cross-links. This latter contribution depends on the specific properties of the particular system such as the spatial extent of the cross-linked zones, chain rigidity, local cross-link density, etc., and corresponds to the static term $I_s(q)$ in eq 7.

Figure 2 shows the neutron spin echo decays at various values of q for the PFS gel. For the corresponding solution (not shown here) the polarization echoes relax to zero, while the gel echoes decay to a finite residual constant that increases with decreasing q. The results for the PDMS system reported earlier are qualitatively similar.[4]

In the Guinier region ($q\xi < 1$) neutron spin echo measurements detect collective diffusion, which is described by the diffusion coefficient D_c. The decay rate Γ of the relaxation is then governed by the relation

$$\Gamma = D_c q^2 \tag{9}$$

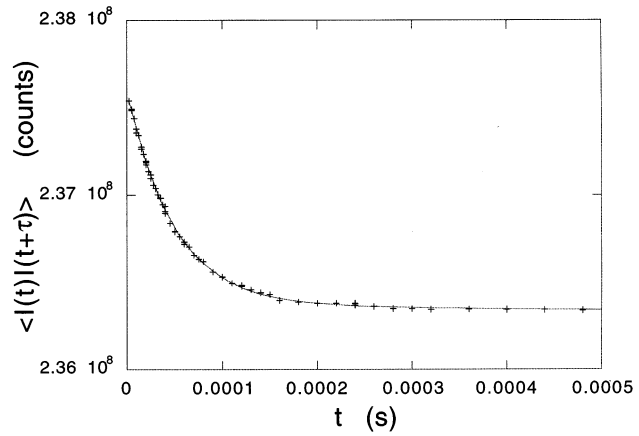

Figure 3. Light scattering intensity correlation function at 30° scattering angle from a poly(fluorosilicone) gel at $\varphi = 0.2$. The relative strength of the dynamic fluctuations to the statically scattered light can be appreciated from the unnormalized intensity scale on the ordinate axis.

For the PFS solution the following value of D_c is found:

$$D_c = (1.9 \pm 0.4) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}} \qquad (10)$$

In the case of the gel the amplitude of the spin echo signal $A(t)$ decays to a constant baseline $A_s(q)$, which can be determined by fitting the data to an expression of the form

$$A(t{=}0) = A_s(q) + A_f(q)\exp(-\Gamma t) \qquad (11)$$

where $A(0) = 1$ and $A_f(q)$ is the relative amplitude of the fluctuating component.

The value obtained for D_c from eq 11 for the PFS gel is

$$D_c = (2.5 \pm 0.4) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}} \qquad (12)$$

The results for D_c indicate that the collective relaxation in the gel is faster than in the corresponding solution of the un-cross-linked polymer. As stated in the Introduction, this finding could be consistent with an increase of the osmotic modulus due to the presence of the elastic contribution in eq 2; i.e., the dynamic response of the gel is influenced by the presence of cross-links. From these results alone, however, it is not possible to reach a conclusion about the osmotic modulus. In what follows, it will be shown that, for this system, the osmotic modulus in fact decreases.

An independent estimate of the diffusion coefficient was made by dynamic light scattering. Figure 3 shows a typical light scattering intensity correlation function for the PFS gel swollen in acetone to a volume fraction $\varphi = 0.2$. The intensity of the dynamically scattered light in this system is extremely weak owing to the small refractive index increment, and much weaker than that scattered by the static inhomogeneities in the gel, as can be seen by inspection of the amplitude of the variation in Figure 3. Analysis of the intensity correlation function using the heterodyne scheme[10] yields values of D_c in reasonable agreement with those deduced from neutron spin echo measurements

$$\text{PFS gel:}\quad D_c = (3.0 \pm 0.5) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}} \qquad (13a)$$

$$\text{PFS solution:}\quad D_c = (1.9 \pm 0.5) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}} \qquad (13b)$$

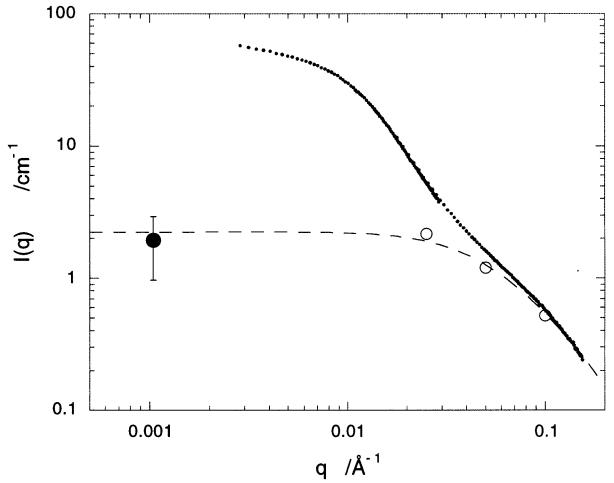

Figure 4. Small-angle neutron scattering spectra from poly(fluorosilicone) gel (small circles) in acetone at polymer volume fraction $\varphi = 0.2$. The dashed line is the dynamic component in the fit to the gel data. Open circles are the intensities calculated from the SANS and neutron spin echo data using eq 14. The filled circle indicates the intensity, expressed in the same neutron scattering units, estimated from dynamic light scattering measurements.

To interpret these differences, it is important to compare the above results with measurements of the scattering intensity. Since the static and dynamic scattering intensities $I_s(q)$ and $I_f(q)$ in eq 7 should be identical in the neutron spin echo and in the static SANS observations, a direct comparison can be made between these results. The fraction of the total intensity scattered dynamically, $r(q)$, can be estimated from the amplitude of the spin echo measurements shown in Figure 2. Thus

$$r(q) = A_f(q)/[A_s(q) + A_f(q)] = I_f(q)/[I_s(q) + I_f(q)] \qquad (14)$$

It follows therefore that the absolute value of $I_f(q)$ can be determined from $r(q)$ together with $I(q)$ measured by SANS; thus

$$I_f(q) = r(q)\, I(q) \qquad (15)$$

Figure 4 shows the SANS spectrum of the PFS gel at $\varphi = 0.2$ as well as the dynamic component of the least-squares fit to eq 7, displayed as a dashed curve. The open circles are the values of $I_f(q)$ deduced from the neutron spin echo results in conjunction with SANS. Clearly, the neutron spin echo results are in good agreement with the phenomenological model of eq 7.

Intensity measurements of quasi-elastic light scattering provide further evidence of the validity of this approach. The scattering intensities of the dynamic component in the PFS gel and solution were found to be

$$I^{sol}(0) = (2.9 \pm 0.6) \times 10^{-6}\ \mathrm{cm^{-1}} \qquad (16a)$$

$$I_f^{gel}(0) = (4.9 \pm 2.0) \times 10^{-6}\ \mathrm{cm^{-1}} \qquad (16b)$$

In Figure 4, the filled circle shows the value of the fluctuating intensity in the gel, calculated from eq 16b,[11] normalized by the contrast factors of the neutron[12] and light scattering experiments ($\Delta\rho^2 = 1.618 \times 10^{29}\ \mathrm{m^{-4}}$, $K = 4\pi^2(n\ \mathrm{d}n/\mathrm{d}\varphi)^2/\lambda^4 = 4.08 \times 10^{23}\ \mathrm{m^{-4}}$). Once again,

the agreement between the dynamic component in the light and neutron scattering results is satisfactory.

The enhancement in dynamic light scattering intensity in the gel over that of the solution, expressed in eq 16a,b, is equally striking in the SANS results of Figure 1, where the measurements were made at a higher concentration. In this respect, the PFS−acetone system contrasts with previous results obtained for PDMS−toluene.[4] In that case, the values of $I(0)$ and D_c were found to be practically identical for gel and solution, i.e., $I^{sol}(0) = 2.45\ cm^{-1}$ and $D_c = (1.5 \pm 0.2) \times 10^{-6}\ cm^2\ s^{-1}$. On correcting the latter value for the viscosity ratio of toluene and acetone, $\eta_{tol}/\eta_{acet} = 1.8$, it becomes apparent that the dynamic response of the PFS solution, defined by the quantity ηD_c, is some 30% weaker than that of PDMS. In addition, the osmotic moduli of these two different solutions may be compared by dividing $I^{sol}(0)$ by the corresponding contrast factors ($\Delta\rho^2 = 3.09 \times 10^{29}\ m^{-4}$ for PDMS−toluene): these two moduli differ by less than 10%. The difference in diffusion coefficients between PFS−acetone and PDMS−toluene is thus revealed to be essentially a frictional effect. It seems reasonable to conclude that the presence of side chains in PFS increases the friction coefficient of the polymer. Finally, it is noteworthy that, unlike the case of PDMS,[4] where in the higher q range the relaxation rates Γ of the spin echo decay were observed to vary as q^3, in the PFS samples only diffusive behavior was detected; i.e., relation 9 was found to hold in the whole q range explored. It is reasonable to suppose that this result corresponds to the presence of the bulkier side chains.

It is now possible to compare the results of the PFS gel with those of the un-cross-linked solution. Although the experimental error in the light intensity measurements of the gel is large, the product

$$I_f(0)D_c = KkT\varphi/f \tag{17}$$

which is independent of the osmotic properties, is clearly higher in the gel. Since cross-linking leaves the numerator of the right-hand side of eq 17 unchanged, it follows that the friction coefficient in the gel is significantly lower in the gel than in the solution.

Conclusions

For the PFS−acetone system, it is shown that the relaxing part of the neutron spin echo decay can be attributed to the thermodynamic concentration fluctuations that define the osmotic modulus. This result is confirmed by independent dynamic light scattering observations. In the gel, the relaxation limit of the decay corresponds to the static intensity scattered by the frozen-in concentration fluctuations.

A comparison between the present system and a PDMS−toluene solution previously studied reveals that the friction coefficient in the un-cross-linked PFS solution, after correction for solvent viscosity, is significantly higher. The difference is attributed to the steric hindrance of the large trifluoropropyl side groups in PFS.

In the PFS gel, both the collective diffusion coefficient and the dynamic component of the scattered intensity are found to be greater than in the equivalent un-cross-linked solution. This finding shows that the friction coefficient in the cross-linked system is lower than in the un-cross-linked solution.

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