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Nanoscale Inhomogeneities and Thermodynamics of Unfilled Polymer Gels

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The description of the structure of swollen polymer networks and its relationship with mechanical and thermodynamic properties has been an unresolved problem for a long time. In spite of a number of theoretical approaches, no simple formalism has been found that captures the structural variety of real gels. Here we report a new approach to describe inhomogeneities in the nanometer size range that develop in the course of the cross-linking process, and their relationship with the macroscopic elastic properties. Experimental data from small angle neutron scattering (SANS), osmotic swelling pressure, and elastic modulus measurements were obtained on polyfluorosilicone (PFSi) gels prepared by different cross-linking processes from precursor chains of monomodal and bimodal distributions. The neutron scattering response of these gels reveals two types of concentration fluctuations, namely, those originating from nanoscale frozen-in constraints generated by the cross-links and the time-dependent thermodynamic fluctuations associated with the osmotic properties of the network chains. The amplitude of the frozen-in concentration fluctuations deduced from small angle neutron scattering measurements is found to be proportional to the ratio of the macroscopic elastic shear modulus to the osmotic compression modulus. The thermodynamic concentration fluctuations are in agreement with the results of dynamic light scattering and macroscopic osmotic pressure measurements. The present approach describes the effect of the nanoscale features on the macroscopic properties of the gel.

Keywords SANS, inhomogeneities, polymer gels, osmotic modulus

Introduction

Swollen polymer networks are always inhomogeneous, i.e., the local polymer concentration differs from the average. The size and amplitude of the inhomogeneities depend on the detailed mechanism of the cross-linking process. Because the cross-links are randomly distributed, certain chains contain more cross-links than others and

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consequently swell less. The impact of these nanoscale structures on the macroscopic responses such as swelling, elasticity, rupture strength, transport, and optical properties, is incompletely understood.

Scattering techniques provide a powerful tool to gain information on the structure over an extended length scale range. Several theoretical models have been proposed in the literature to describe the scattering response of gels.[1,2] These theories contain a number of parameters whose values are difficult either to estimate experimentally or to predict from the material properties. Existing models successfully describe the shape of the scattering curves from certain types of gel, but do not address explicitly the relationship between the scattering response and the elastic and thermodynamic properties. Here we report a systematic study to investigate the effects of different cross-linking methods on the nanoscale frozen-in inhomogeneities and an attempt to relate them to the results of independent osmotic and mechanical measurements performed on the same samples. In this study, polyfluorosilicone (PFSi) gels with monomodal and bimodal chain distributions were prepared by end-linking and by two different cross-linking methods, namely hydrosilylation and condensation.

Theoretical Background

In general, for weakly cross-linked polymer gels the swelling pressure ω can be expressed as the difference between the osmotic pressure Π exerted by the network polymer and the counteracting elastic pressure, which is defined by the shear modulus G.[3,4]

$$\omega = \Pi - G \tag{1}$$

Different cross-linking methods result in gels with inhomogeneities of different size and distribution. Owing to these variations in the nanostructure, chemically similar networks can exhibit different macroscopic properties. Cross-links permanently fix the configuration of the network, thus freezing-in the inhomogeneous regions. Densely cross-linked regions swell less than those where the elastic modulus is lower, thus giving rise to local variations in concentration. The local value of the elastic modulus, however, differs from the average (macroscopic) value in the sample. The size of these zones can be determined by scattering measurements. At equilibrium, ω is uniform throughout the sample, despite these local inhomogeneities. The amplitude of the frozen-in concentration fluctuations can be expressed in terms of the mean-square fluctuation $\langle \delta\varphi^2 \rangle$ of the polymer volume fraction φ. The value of $\langle \delta\varphi^2 \rangle$ is governed by the competition between the swelling and the elastic pressure. The condition of uniformity of the swelling pressure is[5]

$$\begin{aligned} \delta\omega &= (\partial\Pi/\partial\varphi)\delta\varphi - \delta G - (\partial G/\partial\varphi)\delta\varphi \\ &= 0 \end{aligned} \tag{2}$$

where δG is the local deviation in the value of G due only to differences in cross-link density. In a network in which Gaussian statistics are obeyed, its mean square deviation is

$$\langle \delta G^2 \rangle^{1/2} = CG \tag{3}$$

where C is a constant ($C \leq 1$) that depends on the mechanism of the cross-linking process (e.g., structure and spatial extent of the cross-link zone). In conjunction with the standard

expression for the elastic modulus of a swollen rubber, $G \propto \varphi^{1/3}$, Eq. (3) yields

$$\frac{\langle \delta\varphi^2 \rangle^{1/2}}{\varphi} = C\frac{G}{\varphi(\partial\omega/\partial\varphi)} = CR \tag{4}$$

where R is the ratio of the shear elastic modulus G to the osmotic compression modulus $\varphi\partial\omega/\partial\varphi$. Equation (4) provides a simple relationship between the nanosized inhomogeneities, which can be observed by scattering techniques, and the macroscopic swelling and elastic properties. Since the constant, C, depends on the distribution of the cross-links, its value should increase with increasing inhomogeneity of the network. The constant is also expected to depend not only on the cross-linking mechanism but also on the chemical structure of the polymer.

The neutron scattering response of swollen polymer gels displays at least two characteristic distance scales. The first, ξ, is related to the osmotic properties and describes the thermodynamic concentration fluctuations.[6,7]

$$I(q) = \Delta\rho^2\left[\frac{kT\varphi^2}{M_{os}}\frac{1}{1+q^2\xi^2} + \frac{8\pi\Xi^3\langle\delta\varphi^2\rangle}{(1+q^2\Xi^2)^2} + f(q, \Xi_j)\right] \tag{5}$$

where $\Delta\rho^2$ is the neutron scattering contrast factor between polymer and solvent. The amplitude of the transfer wave vector is $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident wavelength and θ is the scattering angle, while φ is the polymer volume fraction and M_{os} $[=\varphi(\partial\omega/\partial\varphi) + 4G/3]$ is the longitudinal osmotic modulus.[8] The second term[9] in Eq. (5) describes the concentration fluctuations frozen-in by the cross-links, the length of which, Ξ, measures their spatial range. Other structural features, e.g., crystallization, chain aggregation, etc, have different physical origins that require further length scales Ξ_j for their description.

Experimental Section

Gel Preparation

Gels were prepared from poly-3,3,3-trifluoropropylmethylsiloxane chains (Gelest Inc.) by two different cross-linking routes: 1) hydrosilylation, and 2) condensation curing. In route 1, vinyl-terminated precursor chains ($M_w = 28{,}000$, $M_w/M_n < 1.1$) were cross-linked by hydride functional polydimethylsiloxane using Pt-divinyltetramethyl disiloxane complex as a catalyst. The hydride to vinyl ratio was 1.1. In the second case, linear silanol terminated chains ($M_w = 26{,}000$, $M_w/M_n < 1.1$) were cross-linked with methyltriacetoxy silane in the presence of tin octoate. Samples were also made from a bimodal distribution containing 20% w/w low molecular weight ($M_w = 3300$) and 80% w/w high molecular weight ($M_w = 28{,}000$) vinyl-terminated chains, cross-linked by hydrosilylation.[10]

Osmotic and Mechanical Measurements

The swelling pressure of the gels was measured as a function of polymer concentration by bringing them to equilibrium with polymer solutions of known osmotic pressure.[11,12] A semipermeable membrane was inserted between the gel and the solution to prevent diffusion of the polymer molecules into the swollen network.

Shear modulus measurements were made on isometric cylindrical gel samples prepared in a special mold. Swollen networks were compressed uniaxially (at constant volume) between two parallel flat plates. The stress-strain data were determined in the deformation ratio range $0.7 < \Lambda < 1$. Absence of volume change and barrel distortion was verified by determining the dimensions of the deformed and undeformed gel cylinders.

Small Angle Neutron Scattering Measurements

The small angle neutron scattering (SANS) measurements were performed on the NG3 instrument at NIST, Gaithersburg, MD, using an incident wavelength of 6 Å and selector bandwidth of 10%. The detector was placed at two distances from the sample, 3 m and 13 m. The q range explored was $0.004\,\text{Å}^{-1} \leq q \leq 0.23\,\text{Å}^{-1}$, with counting times of between 10 min and 1 h. The sample temperature during the experiments was maintained at 25°C ± 1°C.

Deuterated acetone was used as solvent. The sample cell consisted of 1 mm thick quartz windows separated by a 2 mm thick spacer, sealed by a Viton O-ring. After radial averaging, corrections for incoherent background, detector response, and cell window scattering were applied. The scattered neutron intensity was calibrated using the signal from standard samples of silica aerogel.[13]

Results and Discussion

The SANS measurements reveal structural details over the length scale range 1–100 nm. Figure 1 shows the SANS spectra from the three types of PFSi gel fully swollen in deuterated acetone. Significant differences in the characteristic features of each response are apparent. The differences are most pronounced in the lower to intermediate q range where excess scattering from the frozen-in inhomogeneities dominates. The gel

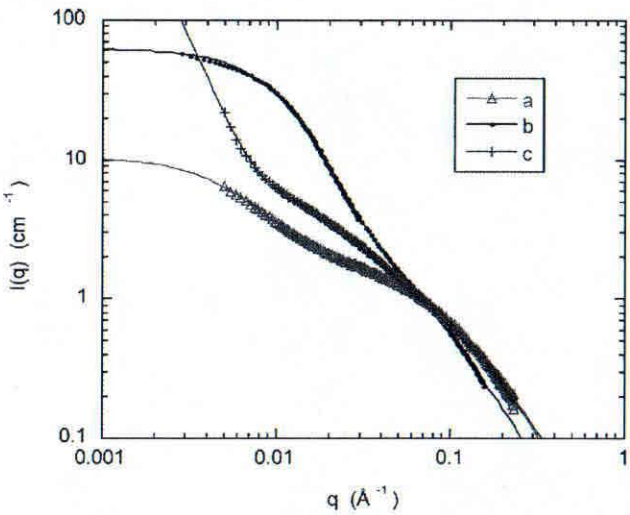

Figure 1. The SANS response of three different fluorosilicone gels fully swollen in deuterated acetone. a: hydrosilylation cured, monomodal; b: hydrosilylation cured, bimodal; c: condensation cured. Continuous curves are fits to Eq. (5) in which the additional term Eq. (6) is required for a and c.

prepared from monomodal precursor chains by hydrosilylation displays a shoulder near $0.1\,\text{Å}^{-1}$ and an increase in intensity as q decreases. The excess intensity at low q is stronger in the corresponding gel prepared by condensation reaction, where a second shoulder appears around $0.02\,\text{Å}^{-1}$, with an abrupt upturn at the lowest values of q, indicating the formation of large-scale superstructures that extend into the visible light scattering region. Three length scales are required to describe the scattering from both types of monomodal gel. The continuous curves through the data points are the fits to Eq. (5), where the third term is approximated by

$$f(q, \Xi_2) = \frac{8\pi\Xi_2^3\langle\delta\varphi^2\rangle_2}{(1+q^2\Xi_2^2)^2} \tag{6}$$

Owing to the large values found for Ξ_2 in the present gels ($\Xi_2 \approx 50\,\text{nm}$, compared to $\Xi_1 \approx 5\,\text{nm}$), $\langle\delta\varphi^2\rangle_2$ is very small and can be neglected.

Figure 2 shows SANS data from the fully swollen bimodal network, together with the fit to Eq. (5). The scattering signal from this sample differs from those of the monomodal gels: 1) at low q the scattering intensity tends to a plateau; 2) the two shoulders are well separated; 3) only two length scales are necessary to describe the curve. The dashed curve in the figure is the first term in Eq. (5), corresponding to the scattering intensity from osmotic fluctuations in the gel. The arrow on the left axis of the figure is the intensity at $q \to 0$ estimated from direct osmotic pressure measurements. The filled circle shows the dynamic light scattering intensity from this sample, normalized by the ratio of the neutron and light scattering contrast factors. Within experimental error, this data point lies on the same curve. The agreement between the calculated curve and two experimental osmotic observations indicates that the thermodynamic contribution to the scattering

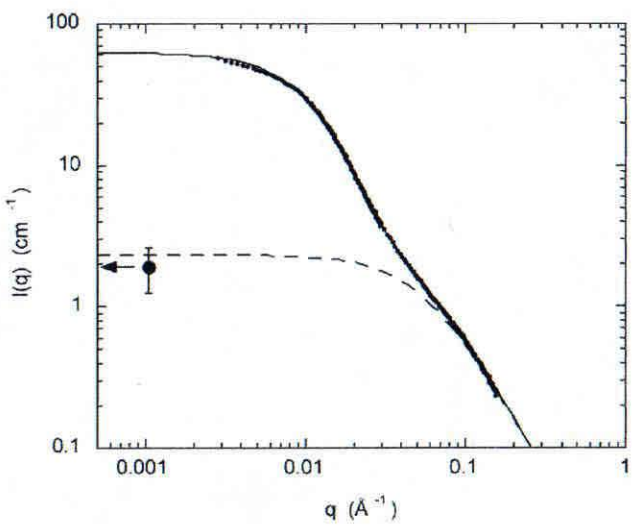

Figure 2. The SANS spectra from poly(fluorosilicone) bimodal gel (dots) in denatured acetone at polymer volume fraction $\varphi = 0.15$. Dashed line is the dynamic component in the fit to the gel data. Arrow on left is the intensity calculated from osmotic swelling pressure measurements. Filled circle is the intensity estimated from dynamic light scattering measurements, expressed in the same neutron scattering units.

intensity is separable from the static structure factor. This observation is consistent with previous measurements on other systems.[7,10]

Figure 3 shows the variation of the relative amplitude, $\langle\delta\varphi^2\rangle^{1/2}/\varphi$, of the frozen-in concentration fluctuations as a function of φ. For all three samples, $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ decreases monotonically with increasing concentration. The data suggest that the inhomogeneity decreases in the order: bimodal > monomodal condensation > monomodal hydrosilylation. At a high degree of swelling, $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ for the monomodal sample made by hydrosilylation is almost an order of magnitude smaller than for either the bimodal sample or the condensation cross-linked monomodal gel. Since concentration differences disappear as φ approaches unity, $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ must vanish at high polymer concentration.

In Fig. 4, the same values of $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ as shown in Fig. 3 are plotted according to Eq. (4). In this representation, the data for each type of PFSi sample lie on a separate straight line, the slope of which, C, increases with increasing inhomogeneity. In Fig. 4 similar data obtained for two other polymer gel systems, namely poly(dimethyl siloxane) in toluene (PDMS/toluene) and poly(vinyl acetate) in toluene are also displayed. The linearity found between $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ and the modulus ratio R in each of these different systems suggests that the relationship may be general.

To illustrate the validity of the present approach, it may be remarked from Eq. (5) that the ratio of the scattering intensities at $q = 0$ from the frozen-in fluctuations to the osmotic fluctuations enables an estimate to be made of the absolute value of the shear elastic modulus. From Eqs. (1), (3), and (4), this ratio is,

$$\frac{I_{frozen}(0)}{I_{osm}(0)} = \frac{8\pi\Xi^3\langle\delta\varphi^2\rangle}{kT\varphi^2}M_{os} = \frac{8\pi\Xi^3C^2R(1+4R/3)}{kT}G \tag{7}$$

At swelling equilibrium in good solvent conditions, $R = 0.522$.[5] The left hand side of Eq. (7) and the value of Ξ are found from the analysis of the SANS scattering response in

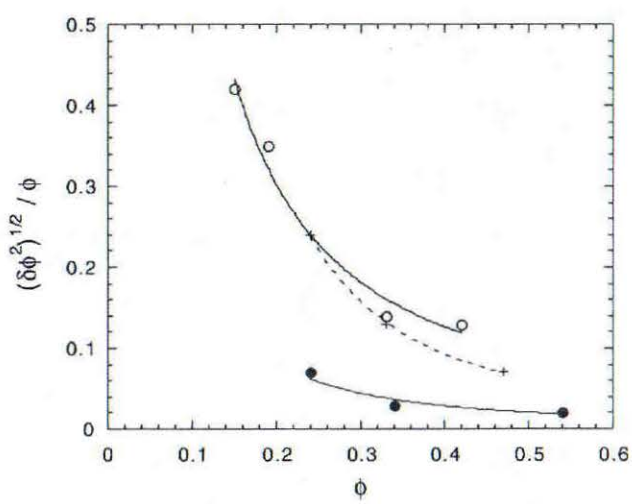

Figure 3. Variation of $(\langle\delta\varphi^2\rangle)^{1/2}/\varphi$ with φ for the three FSil samples. (○): bimodal hydrosilylation cured; (+): condensation cured; (•): monomodal hydrosilylation cured.

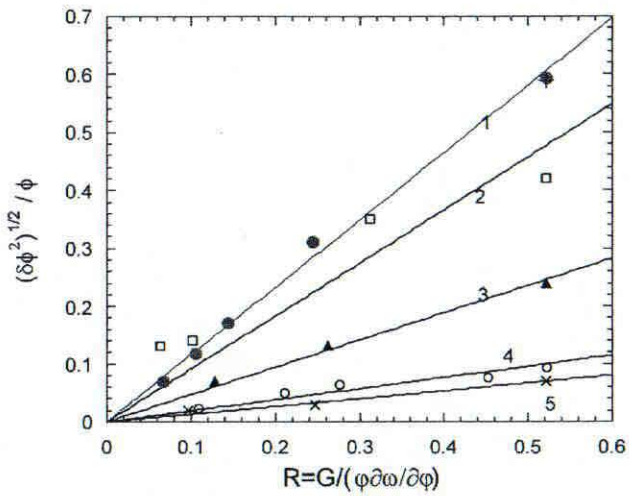

Figure 4. Dependence of $(\langle\delta\varphi^2\rangle)^{1/2}/\varphi$ on the modulus ratio R. 1 (●, +): PVAc-toluene; 2 (□): FSil (bimodal)-acetone; 3 (▲): FSil (condensation)-acetone; 4 (×): PDMS-toluene; 5 (5): FSil (monomodal)-acetone.

terms of Eq. (5). For the bimodal sample, which displays just two characteristic length scales, $I_{frozen}(0)/I_{osm}(0) = 27.3$, $\Xi = 7.1$ nm and $C = 0.91$. From Eq. (7) it follows that

$$G = 13.2\,\text{kPa} \tag{8}$$

at swelling equilibrium, which is in reasonable agreement with the macroscopically measured value of 16.8 kPa.

The above result illustrates how the neutron scattering spectrum of polymer gels in the nanoscale range is intimately related to the elastic constraints that cross-links impose on the network strands. Although the signal from the static constraints is separable from that of the osmotic fluctuations, the inhomogeneities are exposed to and respond to the same swelling forces. Their dominance in the scattering spectrum at low q reflects their low osmotic compressibility. Their contribution to the osmotic swelling pressure of the gel at high degrees of swelling, therefore, is much smaller than that of the osmotic fluctuations described by the first term in Eq. (5).

Conclusions

A new approach is proposed to describe the relationship between the nanosized inhomogeneities that are created by cross-linking and the macroscopic elastic and thermodynamic properties in highly swollen polymer networks. Experimental observations from SANS and osmotic and elastic modulus measurements are reported for polyfluorosilicone (PFSi) gels prepared by different cross-linking processes from precursor chains of monomodal and bimodal distribution. The neutron scattering responses of these gels made by different cross-linking techniques exhibit substantial differences. The scattering spectra are analyzed in terms of an equation that allows for the separation of the time-dependent thermodynamic fluctuations of the network chains and the frozen-in fluctuations. The thermodynamic component is in agreement with the results of the macroscopic osmotic measurements. The amplitude of the frozen-in concentration fluctuations is

proportional to the ratio of the macroscopic elastic modulus to the osmotic compression modulus, $R = G/[\varphi(\partial\omega/\partial\varphi)]$. The proportionality constant, which is governed by the network heterogeneity, correlates with improved mechanical properties. The present data in conjunction with previously published results for chemically different gel systems suggest that a universal relationship exists between $\langle\delta\varphi^2\rangle^{1/2}/\varphi$ and R.

The results of this investigation provide evidence that the neutron scattering spectrum of polymer gels in the nanoscale range is intimately related to the elastic constraints imposed on the gel structure by the cross-links.

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