

Neutron Scattering Investigations on a Bimodal Polymer Gel

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This study investigates structural similarities in polyfluorosilicone (PFSi) gels made by different cross-linking procedures, using small-angle neutron scattering (SANS). The scattering properties of gels prepared from long and short precursor chains and of the un-cross-linked polymer solutions are reported. The gel samples were cross-linked by two methods, hydrosilylation, and condensation curing. The scattering response of a bimodal gel made by hydrosilylation is compared with that of a monomodal gel made by condensation curing having nearly identical shear moduli. Significant differences in the microscopic structure are revealed by SANS. In the bimodal gels made by hydrosilylation, the scattering spectrum can be described by two characteristic length scales, one dynamic and one static. The condensation cured sample contains in addition very large structures, possibly due to solid precipitation as a byproduct of the condensation reaction. For this system at least three correlation lengths are thus required to define the scattering curve.

Introduction

Two of the major factors controlling the mechanical properties of elastomeric materials are the molecular weight and the distribution of the network chains.^{1,2} These parameters determine the architecture of the system at the molecular level. It is known that suitable combinations of polymer chains of different molecular weights yield elastomers having improved mechanical performance, in particular, enhanced ultimate properties.^{3,4} Mark et al. demonstrated that the yield strength of bimodal PDMS networks is significantly greater than that expected from simple additivity. The mechanism of this reinforcing process and the associated structures formed during cross-linking have not been studied in detail. The aim of this paper is to examine the structure of polymer gels made from a blend of low and high molecular weight polymer chains. The characteristic size of the spatial features that are generated during cross-linking are determined by small-angle neutron scattering (SANS). The macroscopic swelling and mechanical properties of bimodal gels are compared with gels prepared from monodisperse chains.

The system studied here is a fluorinated silicone, poly-(trifluoropropylmethyl-siloxane) (PFSi), swollen in acetone. This polymer displays improved resistance to most of the common solvents (e.g., hydrocarbons). For this reason, it is a desirable candidate in replacement of methyl silicones in applications where solvent resistance is at a premium. In the absence of reinforcing filler, however, this polymer exhibits poor mechanical behavior, with low elastic yield stress.

Theoretical Background

To find the relationship between the microscopic structure and the large-scale properties of amorphous polymer systems, it is desirable to combine high-resolution experimental techniques with macroscopic observations. The use of complemen-

tary techniques to probe different length scales reduces the inherent arbitrariness associated with the interpretation of either set of experiments taken singly.

Structural information from SANS in the range of length scales relevant to the macroscopic mechanical properties of amorphous polymer systems in many cases requires the introduction of a low molecular weight solvent. The role of the solvent is 2-fold: first, swelling separates regions of the sample having different structural properties; second, the solvent provides a background of uniform contrast against which features of different density are visible.

In the framework of the Flory–Huggins theory,¹ the osmotic pressure of a polymer solution is expressed as

$$\Pi = -(RT/v)[\ln(1 - \varphi) + (1 - P^{-1})\varphi + \chi_0\varphi^2 + \chi_1\varphi^3] \quad (1)$$

where v is the molar volume of the solvent, χ_0 and χ_1 are the second- and third-order interaction parameters and P is the degree of polymerization.

In swollen networks, the osmotic pressure of the network is assumed to have the same form as eq 1, but with $P = \infty$. In addition, however, an elastic pressure arises from the deformation of the chains and acts in opposition to the osmotic pressure.² The difference between these two terms yields the swelling pressure of the gel,

$$\omega = \Pi - G \quad (2)$$

The neutron scattering response of swollen polymer gels displays at least two characteristic distance scales, one related to the osmotic properties, describing the thermodynamic concentration fluctuations.^{5–13} The second length is related to the static elastic properties that are frozen in when the gel is cross-linked and therefore depends on the type and chemical details of cross-link formation. Other structural features, e.g., crystallization, chain aggregation etc, have different physical origins that require further length scales for their description.

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The thermal contribution to scattering in a polymer solution of volume fraction φ is governed by the osmotic compression modulus,^{14,15} K_{os}

$$I(q) = \frac{kT\Delta\rho^2\varphi^2}{K_{os}} \frac{1}{1 + q^2\xi^2} \quad (3)$$

where $K_{os} = \varphi(\partial\Pi/\partial\varphi)$, ξ is the polymer–polymer correlation length and $\Delta\rho^2$ is the neutron scattering contrast factor between polymer and solvent. The transfer wave vector is $q = (4\pi/\lambda)\sin(\theta/2)$, where λ the incident wavelength and θ is the scattering angle.

The static contribution can frequently be described by a Debye-Bueche expression.¹⁶ In situations where different types of inhomogeneity are present (e.g., crystallites, molecular aggregates, cross-link clusters etc), this contribution may formally be expressed as a sum

$$I(q) = \Delta\rho^2 \sum_j \frac{8\pi\Xi_j^3 \langle \delta\varphi^2 \rangle_j}{(1 + q^2\Xi_j^2)^2} \quad (4)$$

where Ξ_j is the characteristic length of the j th species of static inhomogeneity with a mean square amplitude $\langle \delta\varphi^2 \rangle_j$. The total scattering intensity of the gel thus is given by¹³

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

where M_{os} is the longitudinal osmotic modulus.¹⁷

Other more elaborate theoretical descriptions for the scattering response of gels have been proposed in the literature, notably by Onuki¹⁸ and, more recently, by Panyukov and Rabin.^{19,20} Although the expressions derived from these theories account qualitatively for some of the observed experimental features, the fits they provide to the data are poor and hence they cannot be used quantitatively to analyze the present scattering measurements. For this reason, we resort to expression 5 as the basis of our analysis.

In the description of eq 5, only the first term (i.e., eq 3) has a straightforward macroscopic interpretation: this equation predicts that an increase of the osmotic modulus produces a corresponding reduction in the scattering intensity. Such changes can be induced, for example, by varying the cross-link density, the polymer–solvent interaction or the temperature. The dependence of the scattering response on the static structure and its relationship to the mechanical properties is, however, less well established. Our purpose here is therefore to study a series of gels in which the molecular architecture was varied in a controlled manner.

Experimental Section

Gel Preparation. Fluorinated silicone gels were made from poly-3,3,3-trifluoropropylmethylsiloxane chains (Gelest Inc.) using two different cross-linking methods: (i) hydrosilylation, and (ii) condensation curing. In the first case 20% w/w low molecular weight ($M_w = 3300$) and 80% w/w high molecular weight ($M_w = 28\,000$) vinyl-terminated chains were blended and cross-linked by hydride functional poly(dimethylsiloxane) using Pt-divinyltetramethyl disiloxane complex as a catalyst. The hydride-to-vinyl ratio was 1.1. Gels were also prepared by this method from the pure high molecular weight chains. In the second case, linear silanol terminated chains ($M_w = 26\,000$)

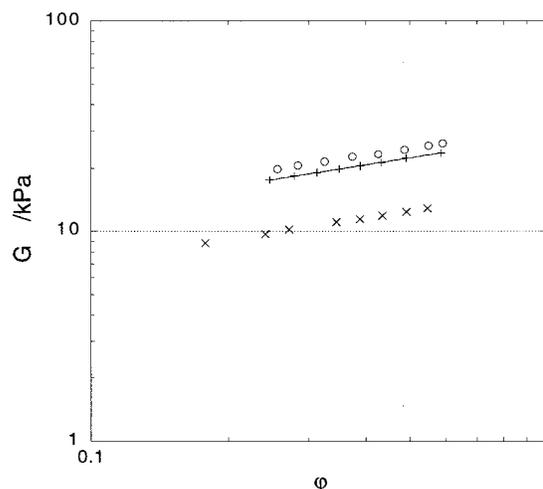


Figure 1. Shear modulus G of PFSi gels swollen in acetone as a function of polymer volume fraction: (+) addition cured bimodal gel, (x) addition cured monomodal gel, o: condensation cured gel. The slope of the least-squares straight line through the bimodal data points is 0.34.

were cross-linked with methyltriacetoxysilane in the presence of tin octoate. Samples were also prepared by hydrosilylation of the low and high molecular weight components alone.

Osmotic and Mechanical Measurements. The swelling pressure of the gels was measured as a function of the polymer concentration using a modified deswelling method.^{21,22} Gels were brought to equilibrium with polymer solutions of known osmotic pressure.²³ 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 performed on isometric cylindrical gel specimens prepared in a special mold. Swollen networks were uniaxially compressed (at constant volume) between two parallel flat plates. The stress–strain data were determined in the range of deformation ratio $0.7 < \Lambda < 1$. The absence of volume change and barrel distortion was checked by determining the dimensions of the deformed and undeformed gel cylinders.

Small-Angle Neutron Scattering Measurements. The SANS measurements were performed on the NG3 instrument at NIST, Gaithersburg, using an incident wavelength of 6 \AA and selector bandwidth of 10%. The detector was placed at two distances, 3 and 13 m, from the sample. The q range explored was $0.004 \text{ \AA}^{-1} \leq q \leq 0.23 \text{ \AA}^{-1}$, with counting times of between 10 min and 1 h. The ambient temperature during the experiments was $25 \pm 1 \text{ }^\circ\text{C}$.

Deuterated acetone was used as solvent. The sample cell consisted of 1 mm thick quartz windows separated by a 1 mm thick spacer, sealed by a Viton O-ring. After radial averaging, corrections for incoherent background, detector response and cell window scattering were applied. Calibration of the scattered neutron intensity was performed using the signal from standard samples of silica aerogel.²⁴

Results and Discussion

Figure 1 shows the concentration dependence of the shear modulus G of three PFSi networks as a function of the swelling ratio in acetone. In this double logarithmic representation straight-line behavior is observed for all three gels with a slope close to 0.33; this finding is consistent with the prediction of rubber elasticity,^{1,2} i.e.,

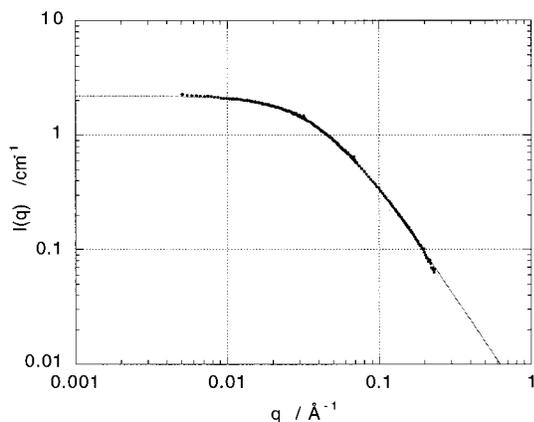


Figure 2. SANS spectrum from a semidilute solution of fluorinated silicone in deuterated acetone at volume fraction $\phi = 0.08$. The continuous line is the best fit to eq 3 with $\xi = 23.7$ Å.

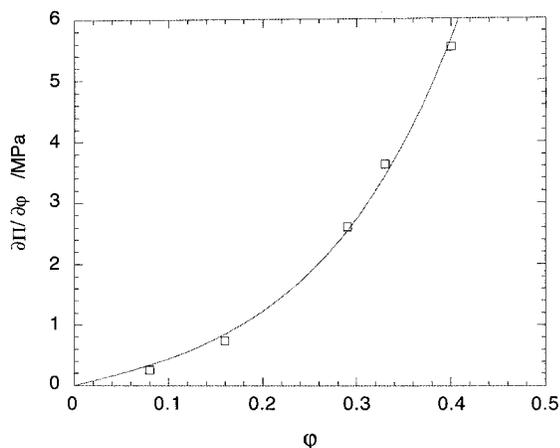


Figure 3. Plot of $\partial\Pi/\partial\phi$, calculated from SANS intensity measurements for fluorosilicone-acetone solutions as a function of polymer volume fraction. The continuous curve is the least-squares fit of eq 6 through the data points.

$$G \propto \phi^{1/3} \quad (6)$$

The values of G for the bimodal network cross-linked by hydrosilylation are close to those of the condensation cured gel and are significantly higher than those prepared from the precursor of molecular weight 28 000. The similarity in macroscopic response of the first two is unexpected, given that the structure of these systems is supposed to be quite different.

To reveal differences in the local organization of the network chains in these gels made by different cross-linking procedures, we investigated them using SANS. We consider first the uncross-linked solutions and then proceed to the case of the gels.

Figure 2 shows the neutron scattering spectrum of an uncross-linked semidilute solution of a fluorinated silicone sample (molecular weight 28 000) at polymer volume fraction 0.08. It can be seen that the experimental data are adequately described by eq 3, with a correlation length ξ equal to 23.7 Å. The plateau response in the low q region implies that the concentration is uniform at large length scales.

According to eq 3, the intensity $I(0)$ is inversely proportional to the osmotic modulus of the solution. In Figure 3 the quantity $\partial\Pi/\partial\phi = \Delta\rho^2 kT\phi/I(0)$ is plotted for PFSi-acetone solutions at five different polymer volume fractions ϕ . For this system, the calculated value of the scattering contrast factor is $\Delta\rho^2 = 1.618 \times 10^{21} \text{ cm}^{-4}$. The continuous curve shown in Figure 3 is the least-squares fit through the data points using the derivative of eq 1, i.e.,

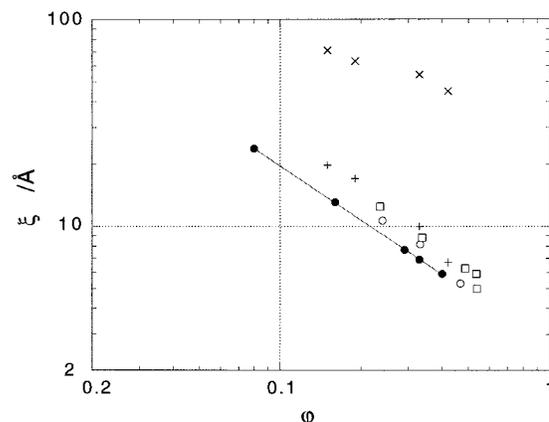


Figure 4. Variation of the correlation length ξ as a function of polymer volume fraction ϕ for the PFSi/acetone solutions (filled circles) and bimodal hydrosilylation gels (+); high molecular weight monomodal hydrosilylation gels (□); condensation cured gel (○). The symbol (×) denotes the static correlation length Ξ_1 of the bimodal gel.

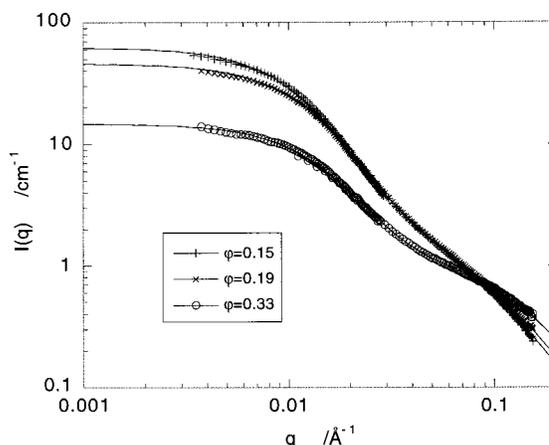


Figure 5. SANS curves for bimodal PFSi/acetone gels at various degrees of swelling. (+) $\phi = 0.15$; (×) $\phi = 0.19$; (○) $\phi = 0.33$.

$$\partial\Pi/\partial\phi = \phi (RT/v)[1/(1 - \phi) + P^{-1} - 2\chi_0 - 3\chi_1\phi] \quad (7)$$

which yields the values

$$\chi_0 = 0.446 \quad (8)$$

$$\chi_1 = 0.296$$

In Figure 4 the correlation length, ξ , is plotted as a function of the polymer volume fraction for these solutions (filled circles). The slope of the straight line through the experimental points is equal to -0.86 , i.e., somewhat larger than the exponent $-3/4$ predicted by scaling theory for good solvent conditions.¹⁵

Figure 5 shows the neutron scattering spectra of a cross-linked bimodal gel at three different concentrations. Two distinct shoulders can be seen, indicating that these gels exhibit two principal length scales. As the gel deswells, the intensity of both features decreases. This pattern is consistent with the expectation for a system containing two building blocks having different characteristic sizes. The continuous curves were calculated by least-squares fitting to eq 5 using a single static correlation length. The fitting parameters of these spectra are listed in Table 1. The quality of the fit shows that two length scales (ξ and Ξ_1) are sufficient to describe the scattering response of these bimodal systems. The values of ξ and Ξ_1 for these gels are also shown in Figure 4. Both of these length scales are decreasing

TABLE 1: Fitting Parameters to SANS Data (eq 5)

$$I(q) = a_0/(1 + \xi^2 q^2) + a_1/(1 + \Xi_1^2 q^2)^2 + a_2/(1 + \Xi_2^2 q^2)^2$$

$$a_0 = \Delta\rho^2 kT \varphi^2 / M_{os} \quad a_1 = \Delta\rho^2 8\pi \Xi_1^3 \langle \delta\varphi^2 \rangle_1 \quad a_2 = \Delta\rho^2 8\pi \Xi_2^3 \langle \delta\varphi^2 \rangle_2$$

sample	volume fraction (φ)	a_0 (cm ⁻¹)	ξ (Å)	a_1 (cm ⁻¹)	Ξ_1 (Å)	a_2 (cm ⁻¹)	Ξ_2 (Å)	$\langle \delta\varphi^2 \rangle_1^{1/2}/\varphi$	$\langle \delta\varphi^2 \rangle_2^{1/2}/\varphi$
solution	0.08	2.2	23.7						
	0.16	1.5	13.1						
	0.29	0.77	7.7						
	0.33	0.63	6.9						
	0.40	0.50	5.9						
bimodal gels (hydrosilylation)	0.15	2.2	19.8	60	71			0.42	
	0.19	1.9	17.0	44	63			0.35	
	0.33	1.1	10.0	14	54			0.14	
	0.42	0.8	6.7	12	45			0.13	
monomodal gels ($M = 28\,000$)	0.24	1.7	12.5	1.7	53	6.9	140	0.07	0.015
	0.34	1.1	8.8	1.0	62	82	510	0.03	0.004
	0.54	0.53	5.0	0.1	32	137	600	0.02	0.004
condensation cured gels	0.24	1.4	10.7	4.3	32	780	500	0.24	0.011
	0.33	0.9	8.2	1.4	26	220	450	0.13	0.004
	0.47	0.54	5.3	0.6	23	325	1600 ^a	0.07	1.1×10^{-4}

^a This result is obtained from the fitting procedure to eq 5. The numerical value lies beyond the resolution range of the neutron scattering experiment.

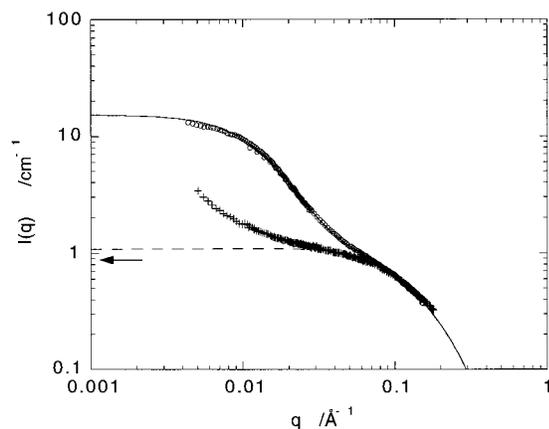


Figure 6. SANS spectrum from PFSi/acetone gels ($\varphi = 0.33$) prepared by hydrosilylation curing; (O) bimodal; (+) monomodal. Full curve is the fit of eq 5 to the bimodal data with a single static correlation length, the dashed curve being the first term in eq 5 describing the thermal concentration fluctuations in the gel. The horizontal arrow indicates the intensity calculated from swelling pressure and shear modulus measurements.

functions of the polymer concentration. The concentration dependence of the dynamic correlation length ξ in the gel is similar to that of the solution, but the numerical values are somewhat higher. This result may reflect that a certain fraction of the polymer in the network is immobilized in the static superstructure, the correlation length of which is described by Ξ_1 . The concentration dependence of the latter quantity is different and weaker than that of ξ . The fact that the static concentration fluctuations in this system are satisfactorily described by a single distance implies that the frozen-in elastic constraints are local and their spatial range does not extend beyond about 100 Å.

Figure 6 displays the spectrum of a bimodal gel ($\varphi = 0.33$) with the fitting function (eq 5) through the data points, together with the thermal component (dashed line) corresponding to the first term in eq 5. The latter term represents the thermodynamic concentration fluctuations, which are governed by the longitudinal osmotic modulus¹⁷ of the gel,

$$M_{os} = \varphi \partial\omega/\partial\varphi + 4G/3 \quad (9)$$

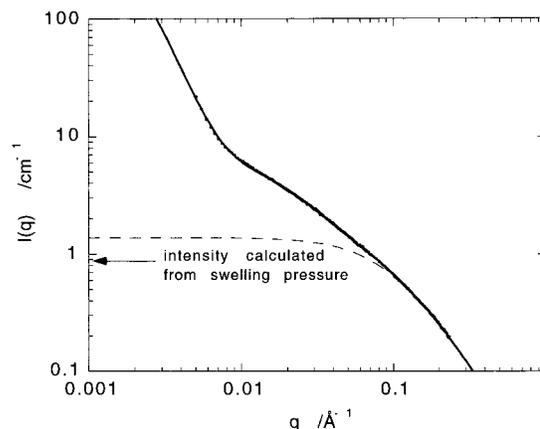


Figure 7. SANS spectrum of condensation cured fluorosilicone gel swollen in acetone. Full curve is fit to eq 5 with two static correlation lengths; dashed curve is first term of eq 5. Fitting parameters listed in last line of Table 1. Arrow shows intensity calculated from swelling pressure and shear modulus measurements.

The horizontal arrow in Figure 6 indicates the scattering intensity calculated from the osmotic swelling pressure and shear modulus measurements on the basis of eq 9 and the value of the neutron scattering contrast factor $\Delta\rho^2$. The amplitude of the concentration fluctuations indicated by the decomposition of the SANS spectrum tends to be somewhat larger than that calculated from the osmotic measurements. Similar agreement in the results obtained from these two independent techniques has been reported previously for other polymer gel-solvent systems.^{5,6,25} In Figure 6 is also shown the scattering spectrum of a gel prepared from vinyl terminated PFSi chains of molecular weight 28 000 swollen to the same concentration ($\varphi = 0.33$). In the intermediate q range where the elastic response of the other networks is visible, this sample exhibits a weak variation in intensity, corresponding to an almost uniform concentration, akin to the un-cross-linked solution (cf. Figure 2). The upturn in intensity at lower q , however, reveals the presence of other structures that are much larger than in the bimodal system.

Figure 7 shows the SANS spectrum of a PFSi/acetone gel, made by condensation curing from a monomodal hydroxyl-terminated polymer of molecular weight 26 000. The shape of

this curve differs from those of the bimodal system in several aspects: absence of plateau region and shoulder, strong increase in intensity at low q with a slope that is consistent with the scattering from a system of starlike clusters.²⁶ Owing to the upturn in the scattering intensity at low q , this curve cannot be described satisfactorily using only two correlation lengths as in the bimodal case: an additional length scale must be introduced. In the region $0.01 \text{ \AA}^{-1} < q < 0.1 \text{ \AA}^{-1}$, the scattering is dominated by the frozen-in elastic constraints. The continuous curve through the data points shows the least-squares fit with two static terms in eq 5. The corresponding parameters are also listed in Table 1. (It is important to note, however, that since the feature at the low q end of the spectrum is not resolved, the precision attached to the numerical values of Ξ_2 and the corresponding amplitude is poor: these values merely indicate the presence of very large structures.) Compared with the bimodal system, the smaller values of Ξ_1 observed here imply a more compact spatial distribution of the elastic constraints. It should be added that to fit the spectra of the monomodal hydrosilylation samples a second static correlation length is required as well, to take account of the large clusters.

Returning to Figure 4, it can be observed that the values of ξ for the condensation cured gels (open circles) lie on the same line as the data from the bimodal gels as well as from the monomodal hydrosilylation samples of the same mass. This result shows that all the samples exhibit substantially the same thermodynamic response. Significant differences in the superstructure are, however, visible in the q -range below 0.1 \AA^{-1} , a region which plays a critical role in the elastic properties of the network.

Table 1 lists the relative amplitude of the concentration fluctuations due to elastic constraints, $\langle \delta\varphi^2 \rangle_1^{1/2}/\varphi$, calculated from the values of the corresponding intensity a_1 and correlation length Ξ_1 . This parameter, which is a measure of the coupling between the osmotic forces and the random local elastic strain from the cross-links, is a maximum when the gel is swollen to equilibrium with the pure solvent.⁷ For the condensation cured gel $\langle \delta\varphi^2 \rangle_1^{1/2}/\varphi$ is comparable in value to that of the bimodal system in its fully swollen state. In the monomodal hydrosilylation cured gel, however, this quantity is severely diminished, indicating a lower degree of elastic strain in the network chains. This result is in qualitative agreement with the lower value of shear modulus observed in the monomodal sample. Furthermore, the spectra of both the monomodal hydrosilylation cured gel and the condensation cured gel reveal additional structures at the lowest values of q , for whose description a second larger static correlation length Ξ_2 is required in expression 5. Inspection of Table 1, however, shows that the apparent concentration fluctuations associated with these secondary superstructures are significantly weaker than those due the primary elastic constraints.

These results suggest the following simple picture. The curing agent in the condensation cured system, methyltriacetoxysilane, not only forms simple trifunctional cross-links, but also nucleates and grows into polymerized clusters that act as multiple cross-links in the network. As these clusters are both large and chemically different from the surrounding polymer, they scatter strongly at small values of q , thereby giving rise to the feature described by the length Ξ_2 . Observations similar to these have been reported previously and described in detail in an analogous system.²⁷ In the monomodal system, however, growth of a cross-linked region around a nucleation point generates a significant fraction of loops and dangling chains, thus producing an array of polymer rich regions that are, however, relatively loosely

connected. In this case, Ξ_2 corresponds to the size of the microgel particles. The bimodal system, in contrast, can be understood as being similar in structure to the condensation cured gel. Mobile low molecular weight polymer chains form clusters that act as multifunctional cross-links. These dense regions are connected by the higher molecular weight chains. The fact that no large clusters are observed in the bimodal gels indicates that the spatial extent of the cross-linked zones is relatively small. Although such an aspect lies beyond the scope of the present investigation, the ratio of molecular weights in the bimodal distribution is expected to play a strong role in the properties of the resulting network.

Conclusions

The small-angle neutron scattering properties of PFSi gels, prepared by hydrosilylation from a blend of low and high molecular weight vinyl-terminated polymers and swollen in acetone, have been investigated and compared with a monomodal gel prepared by condensation curing. In the bimodal system, the scattering response can be described by two characteristic length scales, one dynamic and one static. The former has a similar concentration dependence to that in the solution of the un-cross-linked polymer, while the latter, resulting from frozen-in elastic constraints, is the result of competition between the osmotic and elastic pressures. Similar measurements on samples made by condensation curing showed that at least three characteristic lengths are required to describe the scattering curves. As in other condensation cured systems, these networks contain very large structures, probably due to solid precipitation as a byproduct of the condensation reaction. Additionally to these large objects, static concentration fluctuations can be observed in an intermediate q -range due to frozen-in elastic constraints, with comparable amplitude to, but more compact than, those in the bimodal system. In gels prepared by hydrosilylation of the neat high molecular weight vinyl-terminated polymer, the amplitude of the frozen-in elastic constraints is much smaller. This finding is a sign that the concentration of active network chains is significantly lower than in the corresponding gel made by condensation cure.

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