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Microscopic and Macroscopic Thermodynamic Observations in Swollen Poly(dimethylsiloxane) Networks

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ABSTRACT: Poly(dimethylsiloxane) (PDMS) networks swollen in toluene are investigated both by small-angle neutron scattering (SANS) and by swelling pressure measurements. The scattering signal from the gels, measured as a function of swelling, is resolved into two components, a solution-like part and a static part. The forward scattering intensity of the solution-like part contains all the thermodynamic information relevant to the gel. The absolute intensity is obtained by calibrating against that of a standard water sample. The Flory–Huggins theory of polymer solutions is adopted to derive the swelling pressure of the gel from the scattering measurements. In addition, the swelling pressure is determined independently at different degrees of dilution of the gels. A comparison is made between these direct macroscopic observations and the results deduced from the scattering intensity.

Introduction

When cross-links are introduced in sufficient number to form a gel out of a dense array of polymer coils, the thermodynamic response of the resulting network swollen in a solvent is in general different from that of the equivalent solution.[1,2] Although such differences may be attributed to anomalous elastic effects,[3-6] it has nevertheless become increasingly clear that the underlying reason is more complex.[7,8] The response seems more consistent with a modification of the polymer–solvent mixing interaction.[9]

Small-angle neutron scattering techniques reveal the distribution of polymer segments on a short-range scale (5–100 Å). It is found that, due to gelation, the correlation lengths between chain segments are significantly larger in the case of a swollen network than in the solution of the same polymer at the same concentration.[10,11] Recent neutron scattering observations on poly(dimethylsiloxane) (PDMS) networks swollen to equilibrium in octane have shown that the fine-scale polymer distribution involves at least two characteristic lengths.[12] The shorter correlation length (ξ) was assumed to describe the rapid fluctuations in the position of the polymer chains that ensure thermodynamic equilibrium, while a longer distance (denoted here by Ξ) is needed to account for the static accumulations of polymer pinned down by junction points or clusters of such points. For that particular system, in which the two lengths were distinctly resolved, the numerical value of ξ exceeded that of the equivalent polymer solution by a factor of almost 2. If one pursues the analogy between gels and polymer solutions, scaling theories,[13-15] which relate the osmotic pressure Π to the energy density of the fluctuations kT/ξ^3, would imply that such a shift in the value of ξ should be accompanied by a decrease in the osmotic pressure exerted in the gel.

The redistribution of the polymer chain segments induced by cross-links at a microscopic level is expected to modify the macroscopic mechanical and swelling properties of the gel. Our purpose here is to examine the structure of a gel system using neutron scattering results in a wide range of wave vectors and hence evaluate the thermodynamic properties. These results will be compared with macroscopic swelling pressure observations performed on similar gels.[16] The swollen network system investigated here is end-linked PDMS with toluene as the diluent.

Scattering Formalism

Small-angle neutron scattering is a powerful tool for the investigation of small-scale structure of polymer solutions and gels.[17-21] The intensity $I(Q)$ of elastically scattered neutrons is measured as a function of the transfer wave vector $Q = (4\pi/\lambda)\sin(\theta/2)$, λ being the incident wavelength of the neutrons and θ the scattering angle. $I(Q)$ is proportional to the frequency at which a given spatial separation $1/Q$ arises among the different constituent particles in the sample. The wide range of Q available in small-angle neutron scattering allows the possibility of characterizing structural features of polymer systems over an extended scale of distances.

For a neutral polymer solution at equilibrium, the scattering intensity in the region $Q\xi \leq 1$ is described by the Lorentzian form[13]

$$I(Q) = a(\rho_p - \rho_d)^2 \frac{kT\varphi}{(\partial\Pi/\partial\varphi)} \frac{1}{1 + Q^2\xi_s^2}$$

$$\propto a(\rho_p - \rho_d)^2 \left(\frac{2}{\pi}\right)^{1/2} \frac{\varphi^2\xi_s^3}{1 + Q^2\xi_s^2} \qquad (1)$$

where a is an instrumental constant, ρ_p and ρ_d are the scattering densities of the polymer and solvent, respectively, φ is the polymer volume fraction in the solution, Π is the osmotic pressure, and ξ_s is the polymer–polymer correlation length of the solution. It has been shown[17] that in semidilute solutions in a good solvent, ξ_s varies as $\varphi^{-3/4}$.

In a gel, the polymer chains lose their individuality due to cross-links that bind them together. When the network is swollen, these cross-links generate elastic constraints that cause nonuniformities in the polymer concentration and exclude certain arrangements that would be explored by the polymer chains in a solution. As a result, the

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scattering intensity can no longer be described by eq 1: a contribution from the regions of the sample whose movement is restricted by the cross-links must also be included. The approximation adopted here assumes that these regions have a Gaussian spatial distribution that can be modeled by the concentration correlation function[12]

$$g_1(r) = \frac{\langle \delta\varphi^2 \rangle}{\langle \varphi \rangle^2} \exp\left(-\frac{r^2}{2\Xi^2}\right) \qquad (2)$$

In eq 2 $\langle \delta\varphi^2 \rangle$ is the mean square amplitude of the concentration excursions due to the effects of cross-linking, Ξ is their mean size, and $\langle \varphi \rangle$ is the average concentration. In addition to the long-distance fluctuations in the local concentration described in eq 2, short-range fluctuations occur as in a polymer solution. These two contributions are assumed to be decoupled. The total scattering intensity thus contains two terms. The first arises from the solution-like part of the gel and is of the form of eq 1. The second, due to the static concentration variations caused by the puckering of the network by the cross-links, is the spatial Fourier transform of eq 2. Thus the total scattering intensity is

$$I(Q) \propto a(\rho_p - \rho_d)^2 \left[\left(\frac{2}{\pi}\right)^{1/2} \frac{\langle \varphi \rangle^2 \xi_g^{\,3}}{1 + Q^2 \xi_g^{\,2}} + \langle \delta\varphi^2 \rangle \Xi^3 \exp\left(-\frac{Q^2 \Xi^2}{2}\right) \right] \qquad (3)$$

where ξ_g is the correlation length in the solution-like part of the gel.

In eq 1 the scattering intensity at small angles from a solution is inversely proportional to the osmotic modulus $K = \varphi(\partial\Pi/\partial\varphi)$. In a swollen network, the counterpart of the osmotic pressure is the osmotic swelling pressure ω. Due to the nonvanishing shear modulus (G_s) of such systems, the forward scattering intensity is governed by the longitudinal osmotic modulus

$$M_{os} = (\varphi\partial\omega/\partial\varphi) + 4G_s/3 \qquad (4)$$

Inserting M_{os}, the intensity of the solution-like part, $I_L(0)$ (the subscript L referring to the Lorentzian form of eq 1) becomes

$$I_L(0) = a(\rho_p - \rho_d)^2 kT\varphi^2/[(\varphi\partial\omega/\partial\varphi) + 4G_s/3] \qquad (5)$$

The swelling pressure is[9,22]

$$\omega = \Pi_m - G_s \qquad (6)$$

where Π_m is the osmotic contribution arising from the mixing of the cross-linked polymer and the solvent, and G_s is the shear modulus of the gel. According to the classical rubber elasticity theory,[23,24] G_s varies with polymer volume fraction φ as

$$G_s = G_0\varphi^{1/3} \qquad (7)$$

where G_0 is a constant that depends on the network structure.

The validity of eq 6 has been confirmed experimentally for several different gel systems swollen in a variety of diluents.[9,16,22,25,26]

Experimental Procedure

As reported elsewhere,[12,16] the gels were prepared from a melt of α,ω-dihydroxy-terminated PDMS chains, kindly supplied by Rhône Poulenc Département Silicones. The viscosity-average molecular weight of the precursor chains was $M_v = 40\,000$. The cross-linking agent, ethyltriacetoxysilane (ETAS), was mixed under a dry nitrogen atmosphere to produce a parent mixture that develops cross-links when exposed to atmospheric water. The parent mixture was diluted in chlorobenzene at 40% (gel 1), 60% (gel 2), and 100% (pure polymer, gel 3) by volume and then placed in PTFE molds and left for 2 months in a closed jar. Excess water and chlorobenzene were included to ensure that cross-linking took place and to prevent solvent evaporation during the network formation.

At the end of this process, the samples were removed from their molds and washed in octane, and the diluent was replaced by toluene, which is also a good solvent for PDMS at 25 °C. The extractable material, removed by successive solvent exchanges, did not exceed 4–5% by weight. The swelling equilibrium concentration of the samples in excess toluene was measured.

The swelling pressure was measured by enclosing the gels in dialysis bags and allowing them to come to equilibrium with a solution of poly(vinyl acetate) in toluene of known osmotic pressure.[27,28] After equilibrium was reached (1–4 weeks, depending on the sample size), the concentration of both the solution and the gel was measured. The swelling pressure of the PDMS gels was calculated from the osmotic pressure of the equilibrium polymer solution. The polymer volume fractions were calculated from the known densities at 25 °C of PDMS[29] ($\rho_{PDMS} = 0.97$ g cm^{-3}) and protonated toluene ($\rho_{TolH} = 0.861$ g cm^{-3}),[30] using the assumption of volume additivity.

The small-angle neutron scattering measurements were made on the D11 instrument at the Institut Laue Langevin, Grenoble. An incident wavelength of 6 Å was used, with two sample–detector distances, 1.2 and 4 m. The Q range explored was $0.013 \leq Q \leq 0.3$ Å^{-1}, and counting times of between 20 min and 1 h were used. The ambient temperature during the experiments was 25 ± 1 °C. After radial averaging, standard corrections for incoherent background, detector response, and cell window scattering were applied. Calibration of the scattered neutron intensity was performed by using the signal from a 1-mm-thick water sample in conjunction with the absolute intensity measurements of Ragnetti et al.[31]

The analysis of the scattering spectra thus obtained was performed in the case of the gels by a nonlinear fitting procedure[12] to

$$I(Q) = I_L(0)(1 + Q^2\xi^2)^{-1} + I_G(0)\exp(-Q^2\Xi^2/2) \qquad (8)$$

in which $I_L(0)$ (Lorentzian) and $I_G(0)$ (Gaussian) are linear coefficients and ξ and Ξ were varied iteratively to minimize the variance between the experimental data and eq 8. In eq 8 the first term arises from the solution-like part of the gel. The stability of the resulting values of ξ and Ξ was checked by successively reducing the Q range of the data used for the fitting procedure. A previous investigation[12] of these PDMS networks has demonstrated that, in the Q range explored in the present case, the gels are chemically homogeneous; i.e., the cross-linker makes no observable contribution to the scattering intensity.

Results and Discussion

In Figure 1 is displayed the scattering intensity $I(Q)$ for a PDMS network swollen in toluene and for the corresponding polymer solution. Data measured at both the 1.2- and 4-m sample–detector distances are shown. In the double-logarithmic representation, the excess scattering from the gel (open circles) at small Q values indicates the presence of large static scatterers. At increasing Q, the discrepancy between the gel and the solution decreases, and at $Q \approx 0.08$ Å^{-1}, the two curves cross over so that at higher Q values the scattering from the solution exceeds that of the gel. In this figure is also plotted the Lorentzian curve (dotted line) obtained by fitting eq 1 to the experimental data from the solution in the small-Q region of the spectrum. At high Q values, the observed intensity falls below the calculated line. This so-called intermediate regime, which has been investigated by Rawiso,[32] is influenced by several factors, such as finite chain dimensions, persistence length, etc.

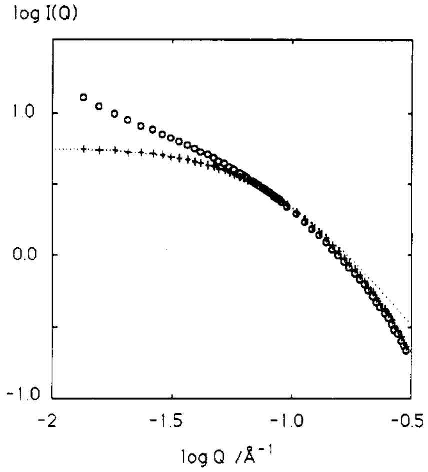

Figure 1. Double-logarithmic representation of the corrected scattering intensity $I(Q)$ for a PDMS–toluene solution at volume fraction $\varphi = 0.155$ (+) and for PDMS gel 3 swollen in toluene at $\varphi = 0.166$ (O). The dotted line is the least-squares fit of the solution data to eq 1 in the Guinier range $Q\xi < 1$.

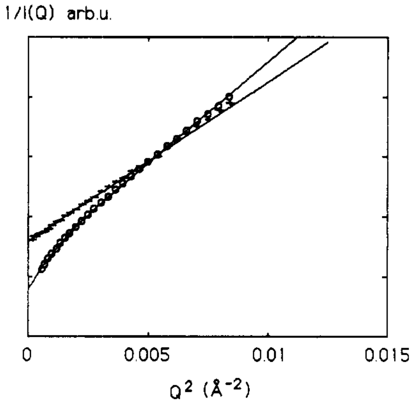

Figure 2. Zimm plot of same data as in Figure 1: gel (O); solution (+). The height of the vertical bars of the crosses shows statistical error of the measurements. The Q range explored here is that obtained from the 4-m sample–detector position on D11. The straight line through the solution data points is the same Lorentzian fit as shown in Figure 1. The curve drawn through the gel data points is the fit to eq 8 with the parameters listed in Table I ($\varphi = 0.166$).

Figure 2 shows the data from the same samples in a Zimm representation, obtained at the 4-m sample–detector distance. The straight line passing through the data points from the solution (crosses) is the least-squares fit to the Lorentzian line shape of eq 1, from the region $Q\xi < 1$. The same Lorentzian fit is displayed in Figure 1.

For the gel, the extra scattering at small Q values does not permit a linear Zimm fit to be used. The procedure employed here was to fit eq 8 to the data points obtained from the 4-m detector position, using a nonlinear least-squares method, as in ref 12. (The data at higher Q values is, as in the solution, contaminated by the local structure of the monomers.) The parameters deduced from the fits of the neutron spectra to eq 8 are summarized in Table I. The last column of this table lists the calculated ratios of $\langle \delta\varphi^2 \rangle / \langle \varphi \rangle^2$, which decrease strongly as the gel is deswollen, indicating that the static concentration fluctuations diminish with increasing polymer volume fraction.

Figure 3 shows the values of the correlation length ξ_s for the PDMS solutions (open circles). In the double-logarithmic representation of this figure, the equation of the straight line through the experimental points is

$$\log \xi_s = (0.504 \pm 0.012) - (0.74 \pm 0.01) \log \varphi \qquad (9)$$

The slope of eq 9 is in agreement with the theoretically expected good-solvent value of $-^3/_4$ and is close to the value found by Munch et al.[33] for the hydrodynamic correlation length in quasi-elastic light scattering. [The ratio of the hydrodynamic correlation length (ref 33) to the static correlation length reported here is 1.7. This ratio is comparable with those reported by Brown and Mortensen[34] for other polymer–solvent systems.]

Also shown in Figure 3 is the variation of the short-range and the long-range correlation lengths in the gel, ξ_g and Ξ, as a function of φ. The two points at the smallest concentration refer to gel samples 1 and 2, while the rest are obtained at different degrees of swelling from gel sample 3. The lower limits of the vertical bars denoting ξ_g are the fits of the data to eq 8. Fitting these data to a Zimm plot in the quasi-linear $Q\xi_g < 2$ region yields rather similar values (upper limits of vertical bars). Both ξ_g and Ξ decrease with increasing polymer volume fraction, the variation being less pronounced for the long-range correlation length. Expressed as power laws, these two parameters vary with deswelling as

$$\log \xi_g = (0.45 \pm 0.04) - (1.01 \pm 0.07) \log \varphi \qquad (9a)$$

and

$$\log \Xi = (1.69 \pm 0.04) - (0.12 \pm 0.06) \log \varphi \qquad (9b)$$

The concentration dependence of ξ_g is stronger than found for the polymer solution. This result implies that the concentration of the solution-like regions is lower, and varies faster, than the average concentration of the sample. In contrast, the variation of Ξ with φ described in eq 9b is weaker than might be expected from the separation of densely cross-linked regions in a uniformly expanding matrix: such a situation would give rise to a distance variation of the form $\Xi \propto \varphi^{-1/3}$. The exponent appearing in eq 9b is in better agreement with the concentration dependence of a linear chain[17] or a star[35] molecule in a good solvent ($\Xi \propto \varphi^{-1/8}$).

In Figure 4 are displayed the absolute intensities of the solution-like contribution from the gel $I_L(0)$ (open circles), compared with those of the polymer solutions (crosses). In this double-logarithmic representation, the latter (including the most concentrated sample, $\varphi > 0.2$) can be approximated by a simple power dependence with an apparent exponent -0.44 ± 0.05. In a good solvent in the semidilute regime, the expected exponent[36] is approximately -0.31. In the gel the intensity of the Lorentzian component decreases much faster than for the solution, and its behavior cannot be described by a simple relation of the same form.

From eq 1 or 3, it follows that the quantity $I_L(0)/\xi^3$ should be proportional to φ^2. The experimental dependence of this ratio upon φ is shown in Figure 5, both for the solution and for the gel. The slopes of the resulting two straight lines in this log–log plot are almost identical (ca. 1.8) but differ from the expected value of 2. In addition, the value of $I_L(0)/\xi^3$ for the gel is shifted along the concentration axis by a factor of approximately 1.35 with respect to that of the solution. This finding is in qualitative agreement with previously reported osmotic observations, according to which the osmotic contribution of the cross-linked polymer follows a concentration dependence similar to that of the solution. Generally, however, the mixing pressure Π_m in the gel is smaller than that of the solution of infinite polymer molecular weight.[9]

Table I
Scattering Parameters from PDMS Networks and Solutions in Toluene at 25 °C

sample	vol fract φ	ξ/Å	Ξ/Å	$I_L(0)$/cm^{-1} [a]	$I_G(0)$/cm^{-1} [a]	$(\langle\delta\varphi^2\rangle/\langle\varphi\rangle^2)/10^{-3}$
sol	0.085	20.0		3.21		
sol	0.115	15.9		2.90		
sol	0.155	12.9		2.59		
sol	0.206	10.3		2.15		
gel 1	0.129	21.8	67.5	4.40	2.24	13.7
gel 2	0.130	18.6	67.9	3.74	1.54	6.8
gel 3	0.166	16.7	59.5	3.43	1.77	9.1
gel 3	0.177	15.6	63.6	3.40	1.75	6.0
gel 3	0.223	13.4	57.5	2.92	1.27	4.4
gel 3	0.254	11.1	57.3	2.26	0.97	2.5
gel 3	0.353	7.8	56.3	1.35	0.35	0.6

[a] Intensities calibrated with respect to 1 mmH_2O for incident neutron wavelength 6 Å ($d\sigma/d\Omega$ = 0.857 cm^{-1}).[31]

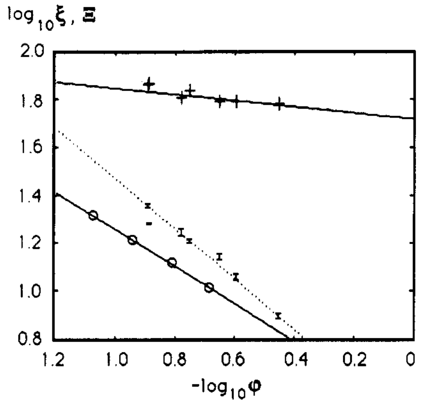

Figure 3. Double-logarithmic plot of correlation length ξ_s as a function of polymer volume fraction φ in PDMS–toluene solutions (O) with corresponding straight-line fit (eq 9). Vertical bars denote short-range correlation length for the gels, ξ_g; crosses refer to long-range correlation length Ξ.

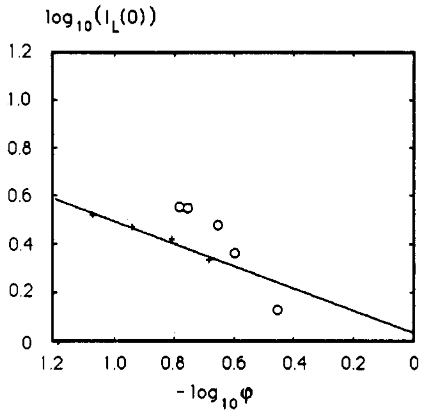

Figure 4. Double-logarithmic plot of the Lorentzian intensity $I_L(0)$ as a function of φ for PDMS–toluene solutions (+) and gel 3 (O). The power law fit shown for the solution data has a slope of –0.44.

In the light of these earlier results, the parallel found here between the solution and the gel behavior provides support for our hypothesis that the thermodynamic properties of the swollen network are contained in the Lorentzian component of the gel signal. The Gaussian contribution has much less influence on the osmotic response.

Comparison of the scattering intensity from the gel with the macroscopic osmotic observations provides a unique test of the consistency between the macroscopic and microscopic results. The PDMS gels investigated here seem to be a good model system for this comparison, since the small values of $\langle\delta\varphi^2\rangle/\langle\varphi\rangle^2$ found, even at the lowest polymer concentration (Table I), imply that the osmotic properties are not expected to be strongly influenced by the nonuniformities of the gel structure.[25]

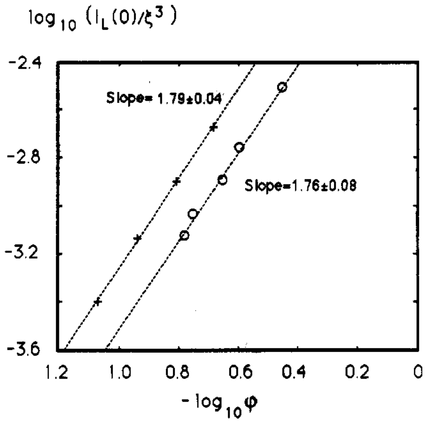

Figure 5. log–log plot of $I_L(0)/\xi^3$ vs φ for PDMS solutions (+) and gel 3 undergoing deswelling (O).

The thermodynamic properties of the swollen network are governed by the swelling pressure (eq 6), which is directly related to the scattering intensity. In view of the relatively high concentrations investigated, we pursue the analogy of a solution-like component of the gel by adopting the Flory–Huggins expression[37] for the mixing contribution Π_m. This gives

$$\Pi_m = -(RT/v_1)[\ln(1-\varphi) + \varphi + \chi_1\varphi^2 + \chi_2\varphi^3] \quad (10)$$

where v_1 is the partial molar volume of the solvent and χ_1 and χ_2 are constants. Insertion of this expression into eq 6, together with eq 7, gives

$$M_{os} = -(RT/v_1)[(\varphi/\varphi_0)^{1/3}\log(1-\varphi_0) - \varphi^2/(1-\varphi) + \varphi_0^{2/3}\varphi^{1/3}] + b_2[2\varphi^2 + \varphi_0^{5/3}\varphi^{1/3}] + b_3[3\varphi^3 + \varphi_0^{8/3}\varphi^{1/3}] \quad (11)$$

in which φ_0 is the polymer volume fraction of the gel at swelling equilibrium with the pure diluent. RT/v_1 = 2.319 × 10^4 kPa, and the coefficients b_2 and b_3 ($-b_2v_1/RT = \chi_1$, $-b_3v_1/RT = \chi_2$) are obtained by fitting the measured intensities to

$$I_L(0) = a(\rho_p - \rho_d)^2kT\varphi^2/M_{os} \quad (12)$$

The constant factor $\mathcal{A} = a(\rho_p - \rho_d)^2kT$, evaluated from the intensity of the calibrated water sample,[31] together with the known scattering densities ρ_p = 6.34 × 10^{12} m^{-2} and ρ_d = 5.63 × 10^{14} m^{-2} for PDMS and deuterated toluene, respectively, is $\mathcal{A}$ = 1.27 × 10^6 kPa·m^{-1}.

Figure 6 shows the fit of eq 12 to the experimental values of $I_L(0)$ in gel 3 at different degrees of deswelling. The best fit to the data points of Figure 4 is obtained for

$$b_2 = -11486 \text{ kPa}$$

$$b_3 = -3716 \text{ kPa} \quad (13)$$

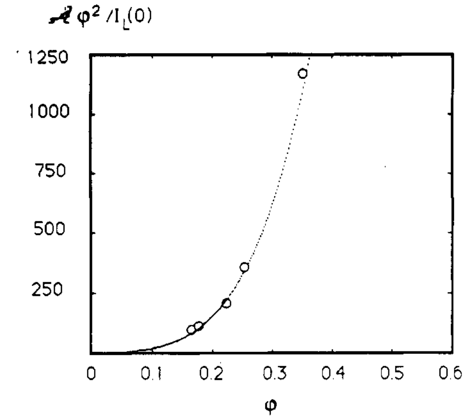

Figure 6. Least-squares fit to eq 12 of the experimental values of $\mathcal{A}\varphi^2/I_L(0) \propto M_{os}$ for PDMS gel 3 at various degrees of swelling in toluene. The constant $\mathcal{A}$ = 1.27 × 10^6 kPa·m^{-1}.

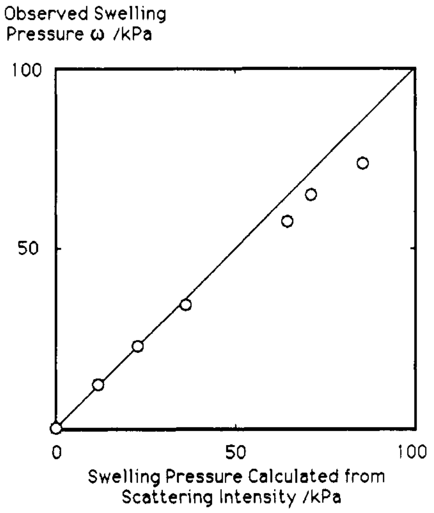

Figure 7. Measured swelling pressure in toluene of PDMS gel cross-linked in the dry state plotted as a function of calculated swelling pressure (eq 15). For the calculation the fitting parameters of eq 13 were used.

which correponds to the second- and third-order interaction parameters

$$\chi_1 = 0.495$$

$$\chi_2 = 0.160 \qquad (14)$$

The swelling pressure, ω, from which eq 11 is derived, is

$$\omega = -(RT/v_1)[\log(1-\varphi) - (\varphi/\varphi_0)^{1/3}\log(1-\varphi_0) + \varphi - {\varphi_0}^{2/3}\varphi^{1/3}] + b_2[\varphi^2 - {\varphi_0}^{5/3}\varphi^{1/3}] + b_3[\varphi^3 - {\varphi_0}^{8/3}\varphi^{1/3}] \qquad (15)$$

Figure 7 shows the swelling pressure data[16] obtained from macroscopic measurements for the sample prepared in the dry state as a function of the swelling pressure calculated from eq 15 using the parameters of eq 13. In view of the fact that the two techniques employed to investigate the system probe very different characteristic lengths and are completely independent, the agreement is substantial. The deviation observed at higher swelling pressures, however, shows the limitations of the model.

Conclusions

The neutron scattering measurements of poly(dimethylsiloxane) networks swollen in toluene described here are consistent with a model for the gel in which densely cross-linked regions give rise to excess static scattering at small transfer wave vectors Q, while at higher Q values the scattering is dominated by the surrounding swollen matrix, which exhibits solution-like behavior.

The two regions can each be described by a correlation length, Ξ and ξ_g, respectively. The short-range correlation length ξ_g can be approximated by a power law behavior as a function of polymer volume fraction φ, with an exponent −1, i.e., a stronger dependence than in the solution ($\varphi^{-0.74}$). In addition, the value of ξ_g is significantly greater than that of the solution, ξ_s, the difference becoming smaller for increasing φ. This behavior is consistent with the existence of a solution-like fraction with diminished polymer concentration in the gel. The long-range correlation length Ξ varies much more weakly with φ, the apparent exponent being −0.12.

It is shown that the thermodynamic properties of the gel are contained principally in the solution-like (Lorentzian) part of the total scattering spectrum, which in the present samples can be resolved from the static part. An attempt is made to compare the osmotic swelling pressure of the gel deduced from the intensity of this component with that measured on the swollen macroscopic gel. In the light of the uncertainties of the independent observations, the agreement found is reasonable.

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References and Notes

(1) Gee, G.; Herbert, J. B. M.; Roberts, R. C. *Polymer* **1965**, *6*, 541.
(2) Yen, L. Y.; Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 121.
(3) Brotzman, R. W.; Eichinger, B. E. *Macromolecules* **1981**, *14*, 1445; **1982**, *15*, 531; **1983**, *16*, 1131.
(4) Neuburger, N. A.; Eichinger, B. E. *Macromolecules* **1988**, *21*, 3060.
(5) Gottlieb, M.; Gaylord, R. J. *Macromolecules* **1984**, *17*, 2024.
(6) Gottlieb, M.; Gaylord, R. J. *Polymer* **1983**, *24*, 1644.
(7) McKenna, G. B.; Flynn, K. M.; Chen, Y.-H. *Polym. Commun.* **1988**, *29*, 272.
(8) Freed, K. F.; Pesci, A. I. *Macromolecules* **1989**, *22*, 4048.
(9) Horkay, F.; Hecht, A. M.; Geissler, E. *J. Chem. Phys.* **1989**, *91*, 2706.
(10) Geissler, E.; Hecht, A. M.; Duplessix, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 225.
(11) Brown, W.; Johnsen, R.; Stepánek, P.; Jakes, J. *Macromolecules* **1988**, *21*, 2859.
(12) Mallam, S.; Hecht, A. M.; Geissler, E.; Pruvost, P. *J. Chem. Phys.* **1989**, *91*, 6447.
(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(14) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(15) Muthukumar, M. *J. Chem. Phys.* **1986**, *85*, 4722.
(16) Horkay, F.; Geissler, E.; Hecht, A. M.; Pruvost, P.; Zrinyi, M. *Polymer*, in press.
(17) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(18) Hecht, A. M.; Duplessix, R.; Geissler, E. *Macromolecules* **1985**, *18*, 2167.
(19) Davidson, N. S.; Richards, R. W. *Macromolecules* **1986**, *19*, 434.
(20) Tsay, H.-M.; Ullman, R. *Macromolecules* **1988**, *21*, 2963.
(21) Bastide, J.; Boué, F.; Buzier, M. In *Molecular Basis of Polymer Networks*; Baumgärtner, E., Picot, C. E., Eds.; Springer Proceedings in Physics 42; Springer: Heidelberg, 1989.
(22) Horkay, F.; Zrinyi, M. *Macromolecules* **1982**, *15*, 1306.
(23) James, H. M.; Guth, E. J. *J. Chem. Phys.* **1943**, *11*, 455.
(24) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon: Oxford, 1975.

(25) Geissler, E.; Hecht, A. M.; Horkay, F.; Zrinyi, M. *Macromolecules* **1988**, *21*, 2594.
(26) Geissler, E.; Horkay, F.; Hecht, A. M.; Zrinyi, M. *J. Chem. Phys.* **1989**, *90*, 1924.
(27) Vink, H. *Eur. Polym. J.* **1974**, *10*, 149.
(28) Nagy, M.; Horkay, F. *Acta Chim. Acad. Sci. Hung.* **1980**, *104*, 49.
(29) Shih, H.; Flory, P. J. *Macromolecules* **1972**, *5*, 761.
(30) Langley, N. R.; Ferry, J. D. *Macromolecules* **1968**, *1*, 353.
(31) Ragnetti, M.; Geiser, D.; Höcker, H.; Oberthür, R. C. *Makromol. Chem.* **1985**, *186*, 1701.
(32) Rawiso, M.; Duplessix, R.; Picot, C. *Macromolecules* **1987**, *20*, 630.
(33) Munch, J. P.; Lemaréchal, P.; Candau, S.; Herz, J. *J. Phys. (Les Ulis)* **1977**, *38*, 1499.
(34) Brown, W.; Mortensen, K. *Macromolecules* **1988**, *21*, 420.
(35) Daoud, M.; Cotton, J. P. *J. Phys. (Les Ulis)* **1982**, *43*, 531.
(36) Le Guillou, J. C.; Zinn Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(37) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

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