Scattering Properties of Polymer Gels at the Θ Temperature

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ABSTRACT: Small-angle elastic neutron scattering (SANS) measurements of polystyrene gels swollen to equilibrium in cyclohexane at the Θ temperature are reported. Comparison of the SANS spectra with similar measurements in un-cross-linked solutions reveals that in the intermediate Q region the gels behave like solutions of lower concentration than the equivalent solutions. It is supposed that the structure factor for the gels is composed of a static component plus a dynamic, or solution-like part. By a suitable fitting procedure, the former can be estimated, yielding the mean square static concentration fluctuation $\langle \Delta\varphi^2 \rangle_s$ generated by cross-linking constraints in the gel. Independent measurements of the swelling pressure of the same gels permits an estimate to be made of the scattering intensity $I(Q=0)$ of the dynamic part of the spectrum. When allowance is made for the static concentration fluctuations, which scatter strongly in the low-Q region of the SANS spectra, plausible agreement is found between the macroscopic and microscopic estimations of the osmotic compressibility.

Introduction

Recently, we have reported comparative investigations for several polymer gel systems swollen in a good solvent, using scattering techniques and osmotic pressure measurements.[1-6] As a first approximation, gels may be thought of as being equivalent to polymer solutions of infinite molecular weight. Indeed, many gels display scaling properties that are qualitatively similar to those of polymer solutions. They do, however, exhibit features that are significantly different.

First, the osmotic component of the swelling pressure in a gel tends systematically to be lower than in the solution. This fact has been known for some time[7-12] and has been attributed to the interaction between the solvent and the cross-links.[8,10-13] The latter observations[8,10-12] conducted on fully swollen gels, can be interpreted[13] in terms of a Flory interaction parameter χ_1 that varies linearly with the density of cross-links in the gel ν^* (i.e. $\chi_1 = \chi + \alpha\nu^*$). Many of these observations are open to an alternative interpretation, however, namely that χ_1 is a function only of the polymer volume fraction φ (e.g., $\chi_1 = \chi + w\varphi$), where φ is in turn limited by the elastic modulus, i.e. the cross-link density, of the network. Previous results[3,14,15] (and indeed those of McKenna et al.[12]), involving coordinated swelling pressure and mechanical measurements on gel homologs at different degrees of swelling, show that the osmotic pressure (or Flory interaction parameter) in the gel follows a master curve that is independent of cross-linking density, thereby favoring the latter interpretation. Since even in polymer solutions the interaction parameter is concentration dependent, it follows that there is no particular physical reason to ascribe the observed variation of χ_1 in gels directly to the cross-links. The osmotic discrepancy between gels and solutions therefore requires another explanation.

Second, in the presence of a diluent, the equilibrium between the osmotic swelling force and the elastic constraint field produces a spread in local polymer concentration. The resulting average behavior therefore depends upon the quantity being measured. For example, the osmotic modulus of a gel in swelling equilibrium, M_{os}, varies with polymer volume fraction φ as φ^n, where the exponent n depends upon the nature of the polymer–solvent interaction. The average osmotic modulus measured in this way is thus different from that deduced from dynamic scattering techniques, where the scattered intensity is proportional to φ^2/M_{os}, i.e. to φ^{2-n}. It follows that the effective polymer concentration defining the macroscopic osmotic pressure measurements in a gel is not equal to that controlling microscopic scattering observations.[16] This inequivalence of concentration has an exact counterpart in dilute polydisperse solutions, where osmotic pressure and scattering techniques yield different estimates of the molecular weight of a polymer.

Third, in small-angle neutron or X-ray scattering (SANS or SAXS) patterns from gels, a shift in the intensity distribution toward lower transfer wave vectors Q occurs: the static superstructure associated with the spread in concentration scatters strongly at low values of Q. At higher Q, the scattering intensity from the gel tends to be lower than in a solution of the same concentration. The static scattering pattern can adopt an infinite variety of forms, each reflecting a different organization of the polymer segments imposed by the constraint field of the cross-links in the gel. Bastide et al.,[17,18] and Mendes et al.[19] have examined certain theoretical cases of fractal organization in the static distribution.

Present understanding of these systems is that the phenomena described above are interrelated. In certain systems, such as polyacrylamide–bis(acrylamide) copolymer hydrogels, lower solubility of the cross-linking molecules and their ensuing aggregation must contribute to a reduction of the polymer solvent attraction. In a majority of cases, however, the observed modification of the polymer solvent interaction and the scattering behavior of the gel corresponding to a solution-like behavior of lower concentration are principally the result of two effects: a reduced degree of freedom for a fraction of the polymer and nonuniform concentration in the sample.

This article extends our previous analysis to a gel system near the Θ temperature. Here it is understood that the Θ condition is defined by the dilute and semidilute solution behavior (extrapolated to infinite molecular weight), where the second virial coefficient $A_2 = 0$ (i.e. the second-order

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Table I
Swelling Pressure Measurements

PSD2 (390 MGy)			PSD4 (590 MGy)			PSD6 (800 MGy)		
φ	G/kPa	ω/kPa	φ	G/kPa	ω/kPa	φ	G/kPa	ω/kPa
0.121	2.34	0	0.179	7.59	0	0.254	22.9	0
0.129		0.470	0.183		0.490	0.256		0.500
0.136	2.44	0.948	0.188	7.72	1.14	0.259	23.1	1.29
0.143		1.47	0.196		2.26	0.263		2.36
0.155	2.55	2.56	0.201	7.89	3.03	0.266	23.2	3.21
0.164		3.48	0.207		4.01	0.270		4.36
0.171		4.30	0.212	8.02	4.89	0.273		5.24
0.178	2.67	5.21	0.214		5.24	0.276	23.6	6.15

Flory–Huggins interaction parameter $\chi = {}^1/_2$). Our measurements were made in the system polystyrene–cyclohexane (PS–CH). The Θ temperature of protonated PS in protonated CH is close to 35 °C; that of protonated PS in deuterated CH is 38 °C.[20] Cross-linking can in addition displace the Θ temperature, but for the low cross-linking densities investigated here, this effect is expected to be small and moreover is not of major significance in the analysis that follows.

The arguments presented below, which depend on certain simplifying assumptions, are arranged in the following way. First, measurements of the swelling pressure and of the elastic shear modulus are used to derive the osmotic mixing pressure in three polystyrene gels swollen in cyclohexane. This information provides an a priori estimate of the intensity of SANS patterns from the same gels; the estimate is, however, uncorrected for nonuniformities of concentration present in the gels. SANS measurements from solutions are then compared with those of the gels, and the concentration of the solution is adjusted to obtain coincidence at high Q with the network spectra. The residual difference at low Q between these spectra is then integrated to yield the mean square static concentration fluctuation in the swollen network, which in turn is used to correct the a priori estimate of the scattering intensity. If this procedure is consistent, then the corrected scattering intensity calculated from the macroscopic parameters is expected to coincide with that measured for the solution-like part of the gel spectrum.

Experimental Details

The polymer networks, generously provided by Dr. N. Davidson, were prepared by γ-irradiation of dry polystyrene pellets. These consisted of heat-pressed disks containing fractionated polystyrene of molecular weight $M_w = 64\,000$, $M_n = 58\,000$. Three sets of samples were used, cross-linked with γ-ray doses of 3.9, 5.9, and 8.0 MGy, respectively. After irradiation, the samples were washed repeatedly in toluene for several months to remove the sol fraction and then dried. They were then cut into disks of diameter such that they could reach swelling equilibrium with the deuterated solvent inside the neutron scattering cells. The measured shear moduli of these gels swollen to equilibrium in the Θ state were approximately 2.3, 7.6, and 23 kPa, respectively (Table I).

For the neutron observations, the gels were held between two quartz windows separated by a Viton O-ring 1.8 mm thick. Deuterated cyclohexane was introduced into the cells, and the samples were held in thermostated baths at 38 °C for 72 h before the neutron measurements started. For incoherent backgrounds, mixtures of cyclohexane D-12 and H-12 at the same temperature were used.

The neutron small-angle scattering measurements were made at the D11 spectrometer at the Institut Laue Langevin, Grenoble, using an incident wavelength of 6 Å and two sample detector distances, 16.5 and 4.0 m. The counting times were either 1 h or 20 min, depending on the sample detector distance. Standard ILL programs were used to regroup the two-dimensional spectra. The corrections employed for incoherent scattering have been detailed elsewhere,[5] and normalization of the scattered intensities was performed using a 1-mm-thick water sample together with the data of Ragnetti et al.[21]

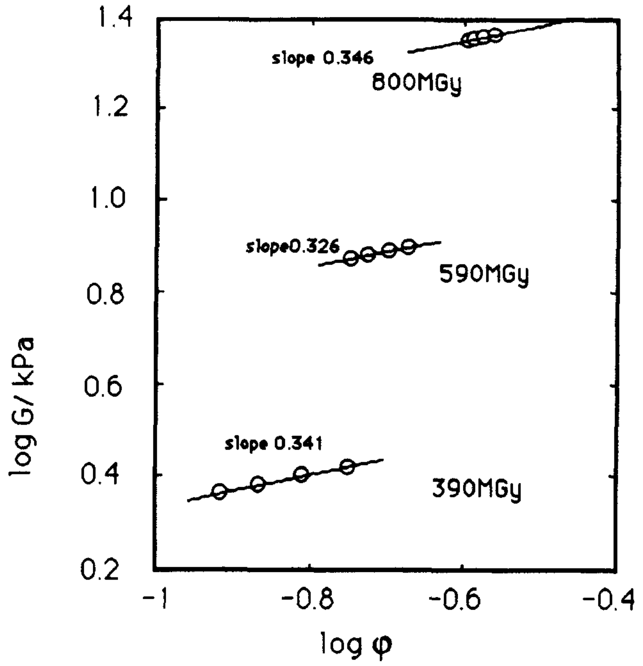

Figure 1. Shear modulus G of three PS gels of different degrees of cross-linking, swollen in cyclohexane-H at 37 °C, as a function of polymer volume fraction φ. The straight lines shown through the points are least squares fits to eq 2.

Table II
Results of Shear Modulus Data Fit to Equation 2

	PSD2	PSD4	PSD6
G_0/kPa	4.81	13.3	36.8
m	0.341 ± 0.004	0.326 ± 0.006	0.347 ± 0.05

The swelling pressure of the gels was measured as a function of polymer concentration using a modified deswelling method.[22] Gels were equilibrated with polymer solutions of known osmotic pressure.[23] A semipermeable membrane was inserted between the gel and the solution to prevent the diffusion of the polymer molecules into the swollen network. In the present case poly(vinyl acetate) (M_n = 120.000) was used to adjust the toluene activity.

The 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. The results were analyzed using the Mooney–Rivlin relation

$$\sigma = C_1(\Lambda - \Lambda^{-2}) + C_2(\Lambda - \Lambda^{-2})/\Lambda^{-1} \qquad (1)$$

where σ is the nominal stress (related to the undeformed cross-section of the gel cylinder) and $2(C_1 + C_2) = G$, the shear modulus of the swollen network. The value of C_2 proved to be negligibly small for the gels studied.

Results and Discussion

Swelling Measurements. In Figure 1 the measurements of the shear modulus G are displayed as a function of the polymer volume fraction φ, in a double-logarithmic representation. The data are listed in Table I. For neutral gels where chain association and crystallization effects are negligible, the theoretical expectation for the concentration dependence of G is[24]

$$G = G_0\varphi^m \qquad (2)$$

with $m = {}^1/_3$. Table II lists the values of G_0 and m found by linear regression for the three gels, the quoted errors

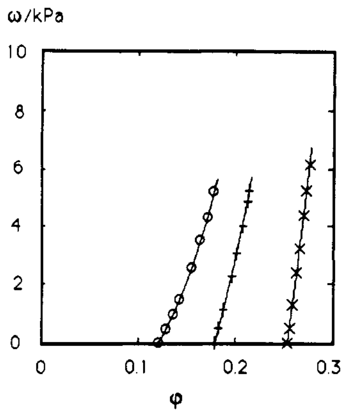

Figure 2. Measured swelling pressure ω of three PS gels with irradiation doses 390, 590, and 800 MGy (left to right), as a function of polymer volume fraction φ.

Table III
Fitting Parameters of Swelling Pressure Data to Equation 3

	PSD2	PSD4	PSD6
A/kPa	1847	1810	1556
n	3.17	3.20	3.06
G_0/kPa	4.66	13.1	37.3

simply being the statistical standard deviations. It is clear that the observed values of m show no significant deviation from standard theory.

In the swelling behavior of gels, it is a central assumption in the Flory–Rehner theory[25] that the free energy consists of two separable terms, one osmotic and one elastic. This hypothesis, which is consistent with our own observations,[1–6,14–16] has been carefully examined by other authors[10,11] and, in the following analysis of the swelling pressure measurements, we simply assume its validity.

In Figure 2 the measured values of the swelling pressure are plotted as a function of φ. The continuous curves through the data points are fits to the following equation[26–28] for the swelling pressure ω, based on the hypothesis of separability

$$\omega = A\varphi^n - G_0\varphi^m \tag{3}$$

where, in order to limit the number of free parameters, m is set equal to $^1/_3$. In a Θ system, the value of n is expected[29] to be equal to 3, a result that is also consistent with experimental observations.[30] By variation of n a nonlinear least squares fit of eq 3 to the swelling pressure data is obtained, which yields the values for A, G_0, and n listed in Table III. Inspection of Tables II and III reveals agreement between the values of G_0 in the two measurement techniques, with a value of n that is slightly, but not outrageously, higher than expected for a semidilute Θ solution. The coefficient A, which is sensitive to variations in n, exhibits a certain scatter from one sample to another. If, in eq 3, the exponent m is allowed to vary as a free parameter, the resulting values of m lie between 0.31 and 0.35, thus providing independent justification for taking $m = {}^1/_3$.

Equation 3 can be rewritten in the form

$$\omega = \Pi_m - G \tag{4}$$

where the mixing pressure Π_m describes the osmotic interaction between polymer and solvent. Thus

$$\Pi_m = \omega + G \tag{5}$$

is the resultant of two independent measurements, the swelling pressure and the shear modulus.

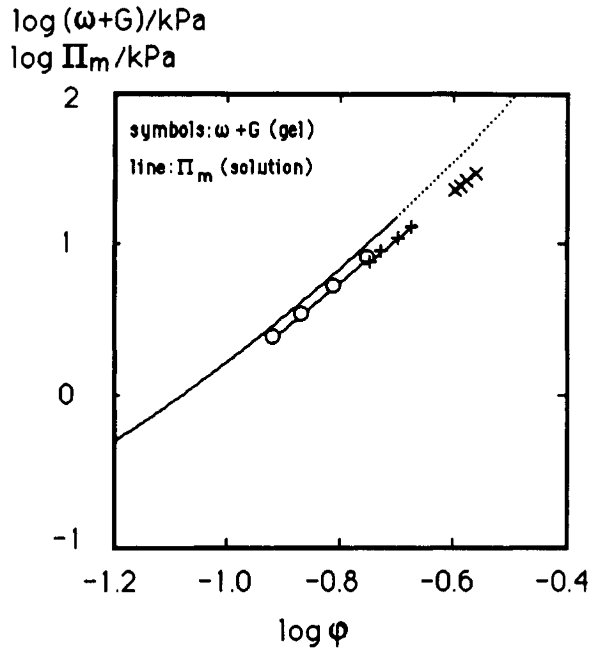

Figure 3. Mixing pressure (Π_m) of protonated PS–cyclohexane solutions[23] (continuous line with dashed extrapolation) at 37 °C and of protonated PS–cyclohehane gels ($\omega + G$) at the same temperature. (The deviation of 2 °C from the known Θ condition implies a negligibly small correction in the calculations presented here.) The interpolations between the gel data points are obtained by fitting to eqs 3 and 5.

For polymer solutions in the higher concentration range of interest here, Π_m is better described by a modified Flory–Huggins expression[31] (in which χ and w are respectively the second- and third-order interaction parameters)

$$\Pi_m = -(RT/v_1)[\ln(1-\varphi) + \varphi + \chi\varphi^2 + w\varphi^3] \tag{6}$$

Π_m is the osmotic pressure of a solution extrapolated to infinite molecular weight.

In Figure 3 the data of Vink[23] for Π_m are shown as a function of polymer volume fraction at 37 °C (continuous line), i.e. slightly above the Θ temperature for the purely protonated PS–CH system. The experimental points shown in the same figure are the measured values of $\omega + G$ for the three gels at various degrees of swelling, at the same temperature. The straight lines through the gel data points are those calculated from the fitting parameters in Table III. As has been observed for other systems in good solvent conditions,[2–4,11,12,15] the mixing pressure for the gels is lower than that of the solution.

Scattering Measurements. Figure 4 shows the SANS spectra of the three swollen gels at 38 °C in a Zimm representation. The responses qualitatively resemble the Ornstein–Zernike behavior of solutions, i.e.

$$1/I_L(Q) = (1 + Q^2\xi^2)/I_L(0) \tag{7}$$

where ξ is the polymer–polymer correlation length and the subscript L stands for liquid. The straight line fits shown, which include data lying outside the usual Guinier region $Q\xi < 1$, yield the parameters listed in Table IV. The numerical values both of $I_L(0)$ and ξ are, however, significantly larger than in solutions of the same concentration.[32]

As a comparison, Figure 5 shows the scattering spectrum of the most concentrated gel (PSD6) in a double logarithmic representation (circles). The crosses are the spectrum of a PS–CH solution at a somewhat higher

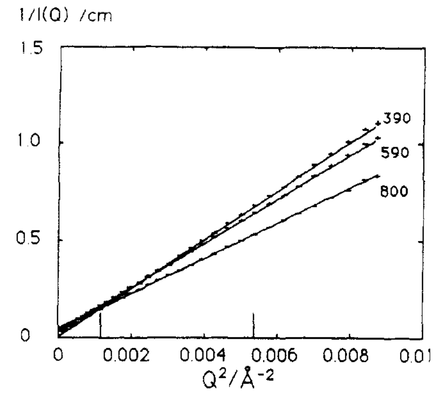

Figure 4. Zimm representations of SANS spectra from the three polystyrene gels in deuterated cyclohexane at 38 °C. The apparent intensities and correlation lengths extracted from these fits are listed in Table IV.

Table IV
Apparatus Intensities and Correlation Lengths from Figure 4

	φ	ξ/Å	$I_L(0)$/cm^{-1}	$\xi Q_{\min}$	$\xi Q_{\max}$
PSD2	0.1399	132.5	140.4	4.49	9.7
PSD4	0.1985	55.3	27.06	1.87	4.05
PSD6	0.2565	41.6	19.3	1.41	3.05

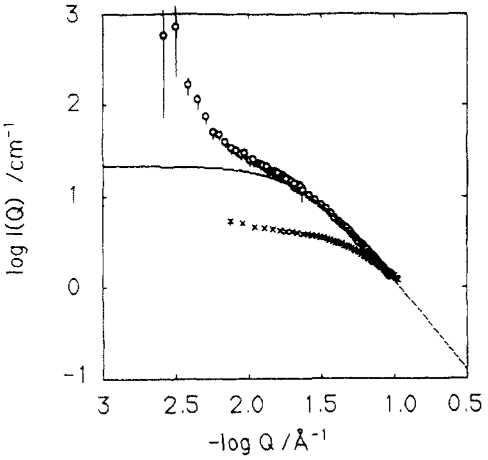

Figure 5. log $I(Q)$ (cm^{-1}) vs log Q for gel PSD6 (O). Crosses: scattering spectrum from un-cross-linked PS/CH solution at 38 °C (φ = 0.348). Continuous line: fit to Zimm plot from data of Figure 4.

concentration (φ = 0.348). The continuous line is the Zimm fit shown in Figure 4.

For concentrated PS–CH solutions it was found[32] that the scattering intensity obeys a relation of the form (7), in which

$$\xi = 5.57\varphi^{-1.13}\ \text{Å} \tag{8a}$$

and

$$I(0) = \frac{1.125}{\varphi}\left(\frac{1}{(1-\varphi)} - 0.83\right)^{-1} \tag{8b}$$

On substituting the values of the polymer concentration φ of each gel into eq 7 and 8, one obtains scattering curves represented by the dotted lines in Figure 6a–c. At small Q the interpolated intensities for the solutions (dotted curves) are lower than the measurements from the gels; at high Q they overshoot.

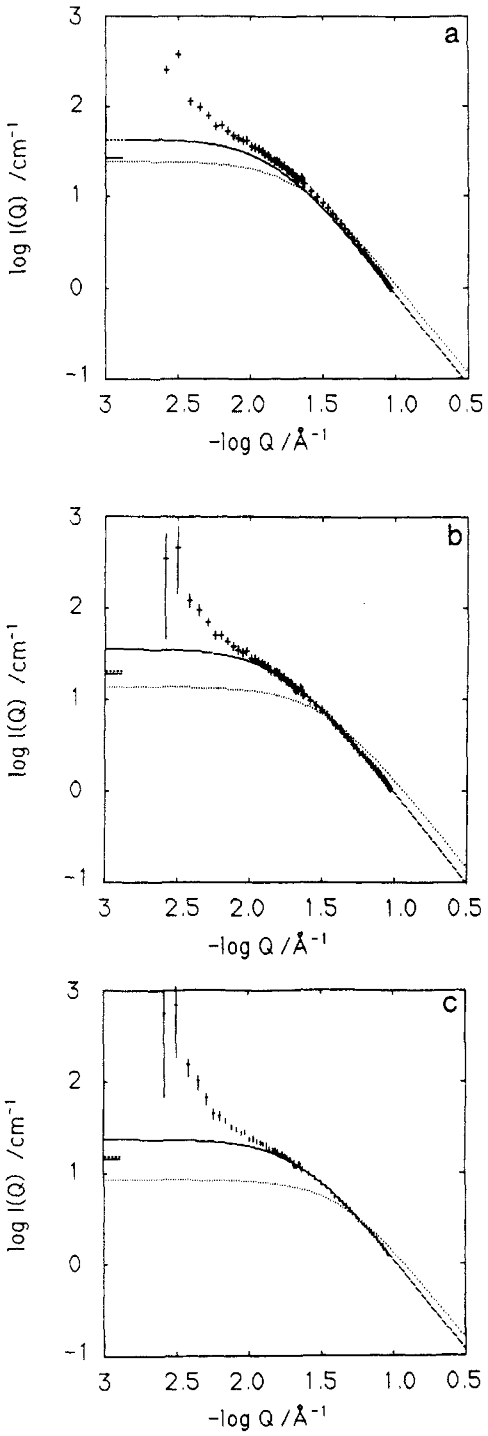

Figure 6. (a) Scattering spectrum for PSD2 (+). Dotted line: interpolated spectrum of solution at same concentration φ = 0.1399. Continuous line: spectrum of solution giving best fit to data at high Q, i.e. φ = 0.100. Horizontal lines at the ordinate axis are the expected intensity at Q = 0 from gel PSD2 at φ = 0.1399, using $M_{os} = \varphi\partial\omega/\partial\varphi + 4G/3$ (continuous line) and using $M_{os} = [\varphi\partial\omega/\partial\varphi + 4G/3]/(1 + \langle\Delta\varphi^2\rangle/\langle\varphi\rangle^2)^4$ (dashed line). (b) Scattering spectrum for PDS4 (+). Dotted line: interpolated spectrum of solution at same concentration φ = 0.199. Continuous line: spectrum of solution giving best fit to data at high Q, i.e. φ = 0.105. Horizontal lines at the ordinate axis are the expected intensity at Q = 0 from gel PSD4 at φ = 0.199, with the same symbols as in (a). (c) Scattering spectrum for PSD6 (|). Dotted line: interpolated spectrum of solution at same concentration φ = 0.257. Continuous line: spectrum of solution giving best fit to data at high Q, i.e. φ = 0.15. Horizontal lines at the ordinate axis are the expected intensity at Q = 0 from gel PSD6 at φ = 0.257, with same symbols as in (a).

Improvement in the fit is obtained if, in addition to the liquidlike spectrum (7), it is recognized that large-scale static nonuniformities in polymer concentration contribute to the scattering. Such static superstructures, also present in gels swollen in good solvents,[1–6,16–19] are the result of cross-link density fluctuations in the network; their sizes, as can be seen from inspection of Figure 6, have a broad distribution and are of the order of several hundred Angström units. Given such static fluctuations, the

Table V
Calculated Partial Second Moments of PS–CH Gels
[PS–Cyclohexane D12: $(\rho_p - \rho_s)^2 = 2.66 \times 10^{21}$ cm^{-4} at 37 °C]

	φ	$10^{-20}M_2$/cm^{-4}	$\langle\Delta\varphi^2\rangle_s$	$\langle\Delta\varphi^2\rangle_s/\langle\varphi\rangle^2$
PSD2	0.1399	1.28	2.44×10^{-3}	0.125
PSD4	0.1985	0.183	0.35×10^{-3}	0.009
PSD6	0.2565	0.536	1.02×10^{-3}	0.016

concentration of the liquidlike regions is not necessarily equal to the average gel concentration. We assume here that large-scale static nonuniformities in the gel do not contribute to the spectrum at high Q: in this range, therefore, the experimental curves may still be represented by eq 7. At lower Q values, however, the large static structures generate scattering in excess of the Ornstein–Zernike contribution (7).

It follows from this approach that the high-Q region of the spectra should be fitted to an Ornstein–Zernike form (eqs 7 and 8) by modifying the apparent concentration φ. The continuous lines in Figure 6a–c show the results of this fit, with the values of φ modified as indicated. In each case the best fits are those of a polymer solution of lower concentration than the gel.

Our next task is to estimate the amplitude of the static concentration fluctuations. From the difference between the observed spectrum $I(Q)$ and the Lorentzian fit $I_L(Q)$ to the high-Q region, a partial second moment can be calculated

$$M_2 = \int_0^\infty [I(Q) - I_L(Q)]Q^2\,dQ \tag{9}$$

where, for a sample of unit volume[33]

$$M_2 = 2\pi^2\langle\Delta\varphi^2\rangle_s(\rho_p - \rho_s)^2 \tag{10}$$

Here the ρ_i are the scattering length densities of the polymer and solvent, respectively, and $\langle\Delta\varphi^2\rangle_s$ is the mean square amplitude of the static concentration fluctuations. Table V lists these values. Since this integral is most sensitive to the range of highest Q where the difference between $I(Q)$ and $I_L(Q)$ is small, the calculated values for $\langle\Delta\varphi^2\rangle_s$ are subject to large uncertainty. In the case of sample PDS2, however, there is an extended range in which the difference between the spectra is appreciable and more reliance can be placed on the estimate of $\langle\Delta\varphi^2\rangle_s$.

We open a parenthesis here to emphasize that eqs 9 and 10 are valid under three conditions: (i) The system is statistically isotropic. (ii) There is no long range order. (iii) The objects constituting the two phases (here, polymer and solvent) have well-defined boundaries. The first two conditions are clearly obeyed here; the third is not. This objection turns out to be immaterial, however, for the following reason. Low-resolution scattering experiments (i.e. with values of Q such that $Qa \leq 1$, where a is the size of a monomer) cannot distinguish between an object with sharp boundaries and one in which the electron (or nuclear) density is unevenly distributed within the region of size a. Thus, for measurements confined to this spectral region, the scattered intensity can indeed be considered as belonging to an invariant, even though the high spatial frequency contribution of the latter is not an observable quantity. Hence, although the *total* second moment of the scattering curve of complex liquids cannot be interpreted simply in terms of two phases, the procedure adopted here is valid because the differences in intensity that interest us are confined to $Qa \leq 1$. In a related parenthesis, it is also worth mentioning that the Ornstein–Zernike expression yields an infinite second moment owing to underlying assumptions that neglect the finite size of the molecules in a real system.

Returning now to the question at hand, radiation is scattered by dynamic concentration fluctuations in the gel with an intensity at $Q = 0$ given by[34]

$$I(0) = \mathbf{a}k_BT(\rho_p - \rho_s)^2\varphi^2/M_{os} \tag{11}$$

where k_BT is the Boltzmann energy, M_{os} is the longitudinal osmotic modulus

$$M_{os} = \varphi\partial\omega/\partial\varphi + 4G/3 \tag{12}$$

and $\mathbf{a}$ is an apparatus constant. According to eq 4, at swelling equilibrium with the pure solvent, $G = \Pi_m$, so that under conditions where scaling considerations apply,[29] both terms on the right-hand side of eq 12 are proportional to φ^n, where the exponent n is related to the excluded volume exponent ν by $n = 3\nu/(3\nu - 1)$. Thus, in excluded volume conditions $n = {}^9/_4$ ($\nu = 0.6$) and at the Θ temperature $n = 3$ ($\nu = 0.5$). If the concentration φ is not uniform throughout the gel, a measurement of φ will yield the spatial average $\langle\varphi\rangle$. Thus, from the concentration dependence of the swelling pressure, one gets for M_{os} at equilibrium in a pure solvent[35]

$$M_{os|swpr} \propto \langle\varphi^n\rangle \tag{13}$$

In contrast, from eq 11, a scattering experiment gives

$$M_{os|sc} \propto \langle\varphi\rangle^2/\langle\varphi^{2-n}\rangle \tag{14}$$

The ratio of the two quantities (13) and (14) is a function of the amplitude of the static concentration fluctuations in the sample. Its relation to $\langle\Delta\varphi^2\rangle_s$, however, requires a knowledge of the polymer concentration distribution.

In many cases a Gaussian distribution function is adequate to describe the static concentration fluctuations in polymer gels:[16]

$$\mathcal{P}(\varphi) = A' \exp[-(\varphi - \langle\varphi\rangle)^2/2\langle\Delta\varphi^2\rangle_s] \tag{15}$$

The difficulties of negative concentrations can, if desired, be avoided by using the log normal distribution:[36]

$$\mathcal{P}(\varphi) = A \exp[-\{\ln(\varphi) - \mu\}^2/2\langle\Delta\varphi^2\rangle_s] \tag{15'}$$

which has a mean concentration

$$\langle\varphi\rangle = \exp(\mu + \langle\Delta\varphi^2\rangle_s/2)$$

Use of the properties of the moments of (15′) gives for the ratio of the two longitudinal osmotic moduli M_{os}, estimated by swelling pressure measurements and by light scattering, respectively

$$\frac{M_{os|swpr}}{M_{os|sc}} = \left[1 + \frac{\langle\Delta\varphi^2\rangle_s}{\langle\varphi\rangle^2}\right]^{[1/(3\nu-1)]^2} \tag{16}$$

In the present case, the Θ condition implies $\nu = 0.5$, making the exponent in expression 16 equal to 4. For small values of $\langle\Delta\varphi^2\rangle_s/\langle\varphi\rangle^2$, such as calculated from the spectra of the present samples (Table V), the result is insensitive to whether a Gaussian or a log normal distribution function is assumed.

We are now in a position to calculate the scattering from osmotic fluctuations, corrected for the concentration inhomogeneities in the samples. Parts a–c of Figure 6 show the expected values of these intensities calculated using correction factor (16) (dashed horizontal lines at origin). In the most dilute gel the theoretical estimate coincides with the intensity obtained from the fit to the high-Q end of the scattering spectrum. In the other two cases the agreement is less good, but still reasonable. It should be borne in mind, however, that in the more concentrated gels the difference between the solution and the gel spectra is considerably smaller than in the most dilute sample: the relative error in the estimate of $\langle \Delta\varphi^2 \rangle_s$ is therefore much greater.

Independent information on $\langle \Delta\varphi^2 \rangle_s$ is difficult to extract from purely static scattering experiments. It would be incorrect, for instance, to deduce $\langle \Delta\varphi^2 \rangle_s$ from the definition of the invariant, using the total mean square concentration fluctuation in a binary solution

$$\langle \Delta\varphi^2 \rangle = \varphi(1 - \varphi) \qquad (17)$$

Since the gel displays a behavior analogous to a solution of lower concentration (say φ_1), it might be reasoned from the invariance of $\langle \Delta\varphi^2 \rangle$ that

$$\langle \Delta\varphi^2 \rangle_s = \varphi(1 - \varphi) - \varphi_1(1 - \varphi_1) \qquad (18)$$

The concentrations φ_1 appearing in Figure 6a–c, on insertion into eq 18, yield values of $\langle \Delta\varphi^2 \rangle_s$ that are 1 order of magnitude larger than those listed in Table V. Such a procedure is misguided, however, because the structure factor of the gel eventually rejoins that of the solution in the region $Qa \approx 1$, where the scattering is determined by the individual monomers. A more promising approach to an independent estimate of $\langle \Delta\varphi^2 \rangle_s$ is to use quasi-elastic light scattering.[35] Such an experiment is planned in the near future.

Conclusions

Measurements of the swelling pressure of gels in the Θ condition are compared with small-angle neutron scattering spectra from the same samples. The small-Q region of the SANS spectra is dominated by the static concentration fluctuations of the swollen networks, with a broad size distribution extending over hundreds of Angström units. In the intermediate-Q region, the scattering intensity from the gels is similar to that of a polymer solution of lower concentration.

The swelling pressure measurements enable an intensity to be calculated for the SANS spectra. This theoretical intensity is, however, lower than that expected of a uniform solution of the concentration indicated by the intermediate Q response of the gel. When the amplitude of the static concentration fluctuations caused by network constraints is taken into account, the agreement between these two calculated intensities improves, owing to the different concentration averages involved.

These observations suggest that in the present case of lightly cross-linked networks in a Θ solvent, the differences in the thermodynamic properties between the gel and solution are mainly the result of the static concentration fluctuations in the swollen network.

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