where τ is the reduced temperature, $\nu = {}^1/_2$ in the Θ state, and $\nu = {}^3/_5$ in the good solvent limit. This gives the result

$$R_t^2 \propto (\tau/c)^{(2\nu-1)/(3\nu-1)} \qquad (A8)$$

Registry No. (VA)(glutaraldehyde) (copolymer acetate), 114718-88-6.

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Compressional Modulus of Swollen Polyacrylamide Networks

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ABSTRACT: For a set of nominally identical polyacrylamide–water gel samples an experimental comparison is made between the values of M_{os}, the longitudinal osmotic modulus observed by quasi-elastic light scattering, the osmotic modulus K_{os}, observed by swelling pressure measurements, and the shear modulus G, measured by mechanical deformation. From theoretical considerations it is shown that in inhomogeneous gels $K_{os} + {}^4/_3G > M_{os}$. The difference observed experimentally is, however, larger than expected from the heterogeneity of these gels and is attributed to the calibration method used in the light-scattering technique. The present results can thus be used as a calibration for the latter method. All the results are consistent with good solvent scaling predictions, which apply for the osmotic deswelling measurements, up to concentrations of 0.25 g cm^{-3}. Moreover, the osmotic Poisson ratio adopts a value 0.275 ± 0.011, in agreement with that expected for fully swollen gels in a good solvent, namely, 0.278.

Introduction

The swelling properties of gels are determined by two opposing effects, the osmotic pressure and the elastic restraining force of the network. The characteristic coefficient of these forces, i.e., the osmotic modulus K_{os} and the shear modulus G, can be measured in a variety of ways, each tributary to its own sources of systematic and observational errors. There is now a large body of work on diffferent gel systems that provides convincing evidence that K_{os} and G each vary with concentration and temperature according to the predictions of scaling theory,[1-2] as also does the longitudinal osmotic modulus[3]

$$M_{os} = K_{os} + {}^4\!/_3G \qquad (1)$$

In an earlier paper[4] M_{os} obtained from quasi-elastic light scattering in polyacrylamide gels was compared with the uniaxial swelling pressure. The latter was found to be about 12% greater than M_{os}, an acceptable agreement which seemed to corroborate the light-scattering results. Two objections may nonetheless be levelled at the swelling pressure measurements. The analysis of the deswelling data was made in terms of the Flory theory, including the well-known logarithmic term. Many observations in gels indicate that this term is negligible or absent.[5,6] Other sources of error included the possibility of the gel adhering to the containing glass cell walls as the semipermeable membrane advanced. Although care was taken to minimize such sources of error, it remained possible that agreement between experimental techniques was more apparent than real. For this reason we have undertaken a new test of light-scattering measurements, using this time polyacrylamide gels swollen to equilibrium. Direct measurements were made of the shear modulus G, and the longitudinal modulus M_{os} was measured by a quasi-elastic light-scattering technique described previously,[7] using as a standard a solution of polystyrene in cyclohexane. Swelling pressure measurements were made on the same

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gels, using a semipermeable membrane surrounded by polymer solutions of known activity to generate the required deswelling.

A source of systematic error that we have not previously investigated concerns the effect of cross-linking heterogeneities in the network, with their attendant static deviations from uniformity in the polymer concentration. Such permanent network defects are a counterpart of molecular weight polydispersity found in dilute polymer solutions. As the latter shows up in the different concentration averages intrinsic to osmotic pressure and light-scattering experiments, it may be expected that similar experiments in gels may reveal the degree of nonuniformity of concentration.

In the next section, certain theoretical aspects of these two types of measurements in inhomogeneous gels are described, and, after a brief description of the experimental conditions, the results are discussed in terms both of scaling and of the Flory theory.

Theory

Light passing through a refracting medium is scattered by spatial fluctuations in the refractive index n. In swollen polymer gels such fluctuations arise both from static heterogeneities, such as suspended dust particles or intrinsic defects in the gel structure, and from local time-dependent thermal fluctuations in the polymer concentration, the mean-square amplitude of which is proportional to the osmotic compressibility.[8] For light of incident wavelength λ, scattering through an angle θ occurs when the transfer wave vector of the light $\mathbf{Q}$

$$|\mathbf{Q}| = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \qquad (2)$$

coincides with the wave vector of a plane wave of concentration variation. The modulus defining the amplitude of such a plane wave is just the longitudinal osmotic modulus, M_{os}, so that the intensity of the fluctuating part of the scattered light is given by[9]

$$\frac{I_{\mathrm{f}}}{I_0} = fkT\frac{(\partial\epsilon/\partial c)^2 c^2}{M_{\mathrm{os}}} \qquad (3)$$

where ϵ is the dielectric permittivity of the gel medium at the wavelength λ, c is the polymer concentration in the gel, and f is an instrumental factor that depends upon the wavelength and the scattering geometry. I_0 is the incident light intensity.

In many gels, as was the case for the poly(acrylamide–bisacrylamide) water samples investigated here, the intensity of the light scattered by the static heterogeneities far exceeded that from the concentration fluctuations of eq 3, so that direct observations of the total intensity I of the scattered light gives no useful information about M_{os}. This difficulty can be circumvented by use of photon correlation spectroscopy, in which a laser light source is used, with the scattered light being collected at the photomultiplier from one coherence area in the sample. In these conditions, the statically scattered light heterodynes with that from the concentration fluctuations, and the total intensity of the photon correlation signal is given by the product[7]

$$\begin{aligned}\langle I(t)\, I(t+\tau)\rangle = {} & \langle |E_{\mathrm{f}}(t)|^2 |E_{\mathrm{f}}(t+\tau)|^2\rangle + \\ & |E_{\mathrm{s}}|^2 \langle [E_{\mathrm{f}}(t)E_{\mathrm{f}}^*(t+\tau) + E_{\mathrm{f}}^*(t)E_{\mathrm{f}}(t+\tau)]\rangle + \\ & 2|E_{\mathrm{s}}|^2\langle |E_{\mathrm{f}}(t)|^2\rangle + |E_{\mathrm{s}}|^2|E_{\mathrm{s}}|^2 \qquad (4)\end{aligned}$$

in which $\langle |E_{\mathrm{f}}(t)|^2\rangle = I_{\mathrm{f}}$, and $|E_{\mathrm{s}}|^2$ is the mean intensity of the light scattering from the static heterogeneities. Since $|E_{\mathrm{s}}| \gg |E_{\mathrm{f}}|$, the first term of eq 4 is negligible, and the only time-dependent term is the second. The spectra are accumulated in a digital correlator, and low-incident light intensities are used, so that correlator saturation is avoided. The signals are then transferred to a computer and, after subtraction of the base line, fitted to a two-cumulant expansion.[10] The amplitude of the resulting correlation signal at $\tau = 0$ is thus[18]

$$S_{\mathrm{corr}} = 2E_{\mathrm{s}}^2 I_{\mathrm{f}} t \Delta \qquad (5)$$

where t is the time over which the spectrum is accumulated (ca. 1000 s) and Δ the clock period, i.e., the inverse of the analyzing frequency (ca. 10^{-5} s) of the correlator. The quantity $|E_{\mathrm{s}}|^2 t$, equal to the total integrated intensity of the light received at the photomultiplier, is obtained from a pulse counter that is started and stopped at the beginning and end of each spectrum. The incident light intensity I_0 is measured for each sample by reflecting a small fraction of the incident beam on to a photodiode. Many spectra are collected in order to average the statistical fluctuations due to interferences from the different pseudostatic scatterers. Calibration of the apparatus was made indirectly by using as a reference sample a solution of polystyrene in cyclohexane at 45 °C for which the osmotic modulus is known.[3]

Although the light-scattering experiment measures the mean-square amplitude of plane osmotic waves in the gel as described in eq 3, there is a significant conceptual difference between M_{os} measured in this way and that obtained from direct swelling pressure measurements. This difference, which we shall now describe, is equivalent to the well-known difference between the weight average and number average molecular weight in dilute polymer solutions.

As stated above, polymer gels with chemical cross-links are almost invariably inhomogeneous, as they contain permanent spatial variations in their concentration that arise from topological constraints around nonuniformities in the cross-linking density. In what follows, we shall assume, for the purposes of illustration, that such static concentration fluctuations have a Gaussian distribution about their mean value $\langle c\rangle$ and a mean-square amplitude $\langle \Delta c^2\rangle$. The probability of having a concentration c at any point in the gel is given by

$$p(c) = \frac{1}{(2\pi\langle\Delta c^2\rangle)^{1/2}} \exp[-(c - \langle c\rangle)^2/2\langle\Delta c^2\rangle] \qquad (6)$$

where the unphysical values $c < 0$ have negligible probability provided that $\langle\Delta c^2\rangle/\langle c\rangle^2$ is much smaller than unity.

Now the osmotic pressure of a gel or a polymer solution in a good solvent is given by[11]

$$\Pi(c) = Ac^{2.25}$$

where A is the second virial coefficient. In terms of the excluded volume exponent, ν (=0.6), this gives

$$\Pi(c) = Ac^{3\nu/(3\nu-1)} \qquad (7)$$

Neglecting for the moment the elastic contribution that is present in networks, the isotropic osmotic modulus is thus

$$K'_{\mathrm{os}} = \left\langle c\frac{\partial\Pi}{\partial c}\right\rangle = \frac{3\nu}{3\nu - 1}A\langle c^{3\nu/(3\nu-1)}\rangle \qquad (8)$$

where the average is taken over all the concentration states in the sample, and the prime in K'_{os} indicates that the elastic term has not yet been taken into account.

In cross-linked gels, an additional contribution to the osmotic modulus comes from the presence of the restraining elastic forces,[12] whose action opposes the osmotic swelling force. The pressure observed in the osmotic measurement of a gel is the resulting swelling pressure

$$\omega = \Pi - G \tag{9}$$

The corresponding osmotic modulus is thus

$$K_{\mathrm{os}} = \left\langle c\frac{\partial \omega}{\partial c}\right\rangle$$

At swelling equilibrium $c = c_{\mathrm{e}}$ and $\omega = 0$, giving from eq 7 and 9

$$G_{\mathrm{e}} \propto \langle c_{\mathrm{e}}^{3\nu/(3\nu-1)}\rangle$$

It follows therefore that the longitudinal osmotic modulus at swelling equilibrium

$$M_{\mathrm{os}} \equiv c\frac{\partial \omega}{\partial c}\bigg|_{c_{\mathrm{e}}} + {}^{4}\!/_{3}G_{\mathrm{e}}$$

observed by macroscopic swelling pressure and mechanical techniques is

$$M_{\mathrm{os|macroscopic}} \propto \langle c^{3\nu/(3\nu-1)}\rangle$$

Turning now to the light-scattering technique, we note that the observed quantity is the intensity of the dynamically scattered light, i.e., from eq 3

$$I_{\mathrm{f}} \propto \left\langle \frac{c^2}{M_{\mathrm{os}}}\right\rangle \propto \langle c^{(3\nu-2)/(3\nu-1)}\rangle$$

The procedure used to obtain M_{os} requires a knowledge of the average gel concentration $\langle c\rangle$, from which the ratio $\langle c\rangle^2/I_{\mathrm{f}}$ can be calculated: this quantity, when suitably calibrated against a standard sample, yields the light-scattering longitudinal modulus. The longitudinal elastic modulus obtained in this way is therefore given by

$$M_{\mathrm{os|light}} \propto \frac{\langle c\rangle^2}{\langle c^{(3\nu-2)/(3\nu-1)}\rangle} \tag{10}$$

One may thus write for the ratio of the two longitudinal moduli

$$\frac{M_{\mathrm{os|macroscopic}}}{M_{\mathrm{os|light}}} = \frac{\langle c^{3\nu/(3\nu-1)}\rangle\langle c^{(3\nu-2)/(3\nu-1)}\rangle}{\langle c\rangle^2} \tag{11}$$

$$= \frac{\langle c^{2.25}\rangle\langle c^{-0.25}\rangle}{\langle c\rangle^2} \quad \text{when } \nu = 0.6 \tag{11$'$}$$

The averages appearing in eq 11′ are different moments of the Gaussian distribution function, eq 6, in which, as stated previously, $\langle\Delta c^2\rangle/\langle c\rangle^2 \ll 1$. The pth moment is

$$\mu_p = \frac{1}{(2\pi\langle\Delta c^2\rangle)^{1/2}}\int_{-\infty}^{\infty} c^p \exp[-(c - \langle c\rangle)^2/2\langle\Delta c^2\rangle]\,\mathrm{d}c$$
$$= \frac{\langle c\rangle^p}{\pi^{1/2}}\int_{-\infty}^{\infty}\left[1 + \frac{p(p-1)}{2!}\,\frac{2\langle\Delta c^2\rangle}{\langle c\rangle^2}\,x^2 + \ldots\right]\times \exp(-x^2)\,\mathrm{d}x$$

where $x = (c - \langle c\rangle)/(2\langle\Delta c^2\rangle)^{1/2}$. The symmetry requires that odd powers of x vanish, and the resultant expression for the pth moment is, to first order,

$$\mu_p = \langle c\rangle^p\left[1 + \frac{p(p-1)}{2}\,\frac{\langle\Delta c^2\rangle}{\langle c\rangle^2}\right]$$

When substituted into eq 11, this gives in the same approximation

$$\frac{M_{\mathrm{os|macroscopic}}}{M_{\mathrm{os|light}}} = 1 + \left(\frac{1}{3\nu-1}\right)^2\frac{\langle\Delta c^2\rangle}{\langle c\rangle^2} \tag{12}$$

which reduces to

$$\frac{M_{\mathrm{os|macroscopic}}}{M_{\mathrm{os|light}}} = 1 + \frac{25}{16}\,\frac{\langle\Delta c^2\rangle}{\langle c\rangle^2} \tag{12$'$}$$

in the case of a good solvent. Values of the quantity $\langle\Delta c^2\rangle/\langle c\rangle^2$ for the polyacrylamide gels used here are not known, but an indication of the expected size of this effect can be obtained from measurements of the excess second moment of the intensity $I(Q)$ of the X-ray or neutron scattering curves[13]

$$\int_0^q Q^2\, I(Q)\,\mathrm{d}Q \propto \tilde{M}_2 = \langle\Delta c^2\rangle \tag{13}$$

where Q has the same meaning as in eq 2. The upper integration limit q is taken as the wave vector limit beyond which static and dynamic concentration fluctuations become indistinguishable, i.e., $q \approx 1/\xi$, where ξ is the density–density correlation length in the gel.

In ref 13 measurements were made of $\tilde{M}_2$ in several polyacrylamide gels, which were not, however, at swelling equilibrium and are thus not directly comparable with the present samples. It was found for cross-linking densities similar to those used here that for $\langle c\rangle \simeq 0.08$ g cm^{-3}

$$\langle\Delta c^2\rangle \sim 10^{-4}\ \mathrm{g^2\ cm^{-6}}$$

so that $\langle\Delta c^2\rangle/\langle c\rangle^2 \simeq 1.5 \times 10^{-2}$. At swelling equilibrium in the pure solvent this value is probably somewhat greater, so that $M_{\mathrm{os|macroscopic}}$ could exceed the theoretical value of $M_{\mathrm{os|light}}$ by several percent.

An accurate knowledge of both $M_{\mathrm{os|macroscopic}}$ and $M_{\mathrm{os|light}}$ could thus, in principle, be a means of measuring the degree of heterogeneities in gels without having recourse to small-angle X-ray or neutron-scattering techniques.

Experimental Section

Five sets of poly(acrylamide–bisacrylamide) water gels were prepared in 1 cm^2 × 4 cm glass optical cells at room temperature, 23 °C, with starting acrylamide concentrations of 0.03, 0.06, 0.09, 0.12, and 0.15 g cm^{-3} and a weight ratio of acrylamide to bisacrylamide of 75. The gelation was initiated with 0.7 g/L ammonium persulfate and 3×10^{-4} volume fraction of tetramethylethylenediamine. Gelation occurred in about 20 min, and the reaction was allowed to go to completion for several hours. The gels were then removed from their rectangular moulds and steeped in water containing a small amount of sodium azide. The water was renewed several times in the following month. This washing procedure allowed the gels to swell to equilibrium and at the same time removed any un-cross-linked polymer or unreacted monomers still present in the networks.

The measurements of swelling pressure and shear modulus were performed at the Loránd Eötvös University in Budapest. The technique used for the swelling pressure, described elsewhere,[6,14] consisted of placing the gels in dialysis bags surrounded by a polymer solution of known activity at 25 °C. The polymer used was poly(vinylpyrrolidone) (Fluka K-30) purified and dialyzed, having M_{n} = 28 000 daltons.

As the gels deswelled, the samples were weighed at each equilibrium point. This gave the isotropic swelling pressure, ω, derived from the solution activity, as a function of the gel concentration, up to a maximum concentration of 0.25 g cm^{-3} (Figure 1).

The shear modulus measurements were made by using a balance technique to transmit pressure to the surface of the gels, working at the zero displacement point of the balance.[15] Barreling of the samples was not observed. For the measurements of the weakest gel, which could not support its own weight in air, the sample was surrounded by water.

The dynamic light-scattering measurements were performed at the University of Grenoble by using gels made from the same

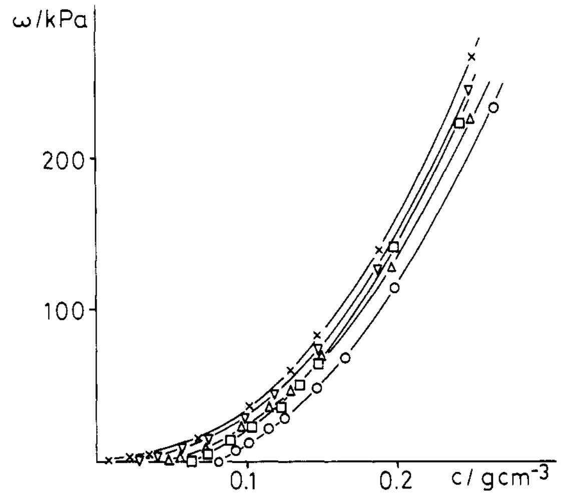

Figure 1. Swelling pressure of polyacrylamide/water gels as a function of gel concentration, c (×) $c_e = 0.009$ g cm^{-3}; (▽) $c_e = 0.03$ g cm^{-3}; (△) $c_e = 0.048$ g cm^{-3}; (□) $c_e = 0.064$ g cm^{-3}; (○) $c_e = 0.081$ g cm^{-3}.

Table I
Least-Squares Fits of Eq 14 to Swelling Pressure Measurements of Figure 1[a]

c_e, g cm^{-3}	n	m	A, kPa	$K_{os} = c(\partial\omega/\partial c)\|_{c=c_e}$, kPa
0.009	2.23	0.321	5804	0.287
0.030	2.23	0.340	5583	4.21
0.048	2.22	0.313	5157	12.0
0.064	2.23	0.335	5832	22.8
0.081	2.25	0.334	5246	38.6

[a] At swelling equilibrium, $K_{os} = (1.05 \times 10^4)c^{2.23}$ kPa.

batch. The technique was the photon correlation method summarized in the Theory section and described fully elsewhere.[3,7] A standard polystyrene cyclohexene solution at 45 °C was used as the reference sample.[16] The reference sample is probably the principal systematic source of error in the light-scattering measurements, since, because of the relative scarcity of dust in it to act as a local oscillator, additional light had to be introduced into the photomultiplier in order to achieve correct heterodyning. This procedure can cause loss of heterodyne efficiency for the reference sample and thus lead to an underestimate of the value of M_{os} in the samples under study. This effect is difficult to correct for, and highlights the desirability of calibrated reference samples with local oscillator inclusions, analogous to the benzene reference samples used in static light scattering.

Results and Discussion

In Figure 1 are shown the results of the deswelling measurements, with the swelling pressure ω plotted as a function of gel polymer concentration c. Each of these curves can be expressed as

$$\omega = Ac^n - B(c_e)c^m \tag{14}$$

in which the first term represents the osmotic pressure causing expansion of the network and the second is the restraining pressure exerted by the elastic modulus. At swelling equilibrium, $c = c_e$, and according $B(c_e) = Ac_e^{n-m}$. It follows from eq 9 that the elastic modulus G is given by

$$G = Ac_e^{n-m}c^m$$

Usually,[5] the concentration dependence of the elastic modulus is given by $m = {}^1/_3$, and in a semidilute system with a good solvent, one expects[11] $n = {}^9/_4$. In the present case the data were fitted to curves of the form (eq 14) in which the values of n and m were adjusted and the error iteratively calculated until the point of minimum variance was reached. The results of this fit are shown in Table I. As has been found for other systems,[2] the agreement between the theoretical values of n and m and those measured is excellent.

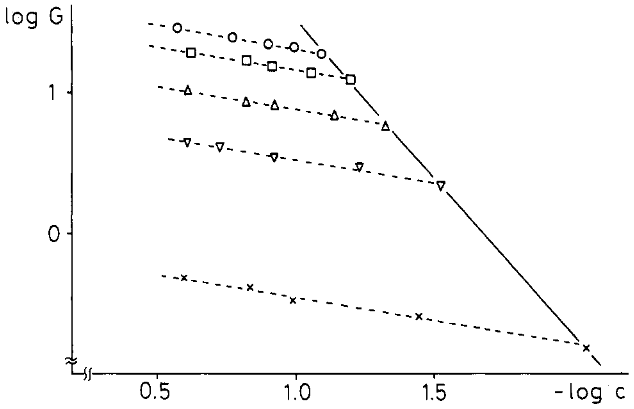

Figure 2. Double logarithmic plot of shear modulus G (kPa) vs concentration c as a function of deswelling. The mean slope of the dotted lines describing the deswelling of each sample is 0.334, and that of the line through the equilibrium swelling point is 2.19. The symbols have the same meaning as in Figure 1.

Table II
Parameters of Least-Squares Fits to Shear Moduli of Deswelling Gels[a]

sample	c_e,[b] g cm^{-3}	m'	B', kPa	G_e,[c] kPa	G_e,[d] kPa
1	0.009	0.335	0.766	0.158	0.149
2	0.030	0.333	7.20	2.24	2.31
3	0.048	0.333	16.6	6.03	5.73
4	0.064	0.337	31.8	12.6	12.6
5	0.081	0.334	43.6	18.9	18.6

[a] Data fitted to $G = B'c^{m'}$. [b] Equilibrium concentration. [c] Equilibrium swelling value of G (measured). G_e(measured) = $(4.88 \times 10^3)c_e^{2.19}$ kPa. Calculated by using $B = Ac_e^{n-m}$ from Table I, with $G_e = Bc_e^{m'}$. Average G(measured)/G(osmotic pressure) = 1.02 ± 0.03. [d] Equilibrium shear modulus calculated from swelling pressure.

Table III
Values of M_{os} from Light-Scattering Measurements

sample	measured concn, g cm^{-3}	M_{os}, kPa light scattering	$K_{os} + (4/3)G$, kPa osmotic deswelling
1	0.0114	0.436 ± 0.075	0.498
2	0.034	5.10 ± 1.5	7.19
3	0.054	16.0 ± 2.3	20.1
4	0.0755	31.1 ± 3.6	39.6
5	0.085	40.1 ± 5.6	63.7

In Figure 2 are shown the values of the shear modulus G observed for each gel at different stages of deswelling, plotted in a double logarithmic representation. The characteristic parameters of the least-squares fit to these data points for each gel are listed in Table II, and within experimental error these are in agreement with the values of m found independently by the osmotic deswelling measurements in Table I. It is noteworthy that the numerical values of G obtained by these two different methods are also in mutual agreement, their average ratio being equal to 1.02 ± 0.03. This comparison between the values of G obtained by direct deformation and from the swelling pressure measurements provides information about the original Flory[12] expression for the swelling pressure of a gel, in the case of a good solvent, namely,

$$\omega = -\frac{RT}{\bar{v}_1}[\log(1-\Phi) + \Phi + \chi\Phi^2] - G_0\left[\left(\frac{\Phi}{\Phi_0}\right)^{1/3} - \frac{\Phi}{2\Phi_0}\right] \tag{15}$$

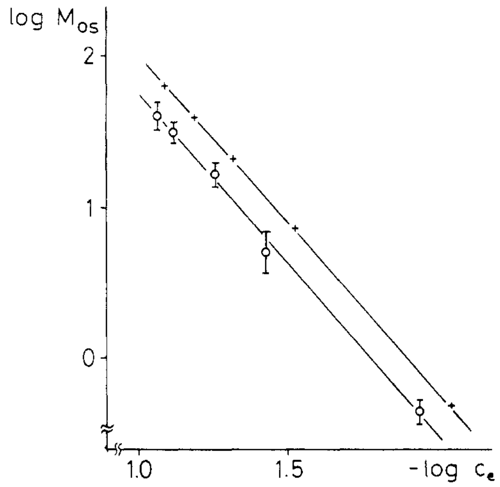

Figure 3. Double logarithmic plot of the longitudinal osmotic modulus M_{os} (kPa) (solid circles) as a function of equilibrium swelling concentration c_e, obtained by quasi-elastic light scattering from polyacrylamide/water samples. Slope of straight line through these points is 2.27 ± 0.03. Crosses denote $K_{os} + (4/3)G$ obtained by swelling pressure and shear modulus measurements, whose least-squares fit has slope 2.22. The vertical separation between the two lines corresponds to a multiplying factor of about 1.80.

where G_0 is the shear modulus at the concentration of preparation, Φ_0. Taking $\chi = 0.45$, and force fitting the osmotic term in eq 15 to a scaling form Φ^p, one finds for the concentration range investigated $p = 2.18$, which is not greatly different from that found from the nonlinear fit to the scaling relation to eq 14 (2.23 ± 0.01). The difference between the two approaches becomes more marked at the lowest concentration, where, in the earliest stages of deswelling (Figure 1), the observed slope remains equal to 2.23, while that predicted from eq 15 falls to 2.1. Secondly, for the elastic term in eq 15, the observed agreement of the experimental data with a simple power law of the type Φ^m with $m = {}^1/_3$ leaves no room for the much discussed logarithmic term $\Phi/2\Phi_0$ that was present in the early Flory theory.[12] If this term had the values indicated by eq 15, then, in the present case, it would lead to an error in G_0 of some 50%. The experimental ratio between the values of the shear modulus obtained by the mechanical and osmotic methods, namely, 1.02 ± 0.03, is additional proof that this term is much smaller than indicated in eq 15. The last refuge for this term, namely, that it is included into the first quadratic term, is untenable, since the sum of the two leads to a power dependence in the concentration of less than 2, and not 2.23, as observed.

The light-scattering measurements of M_{os} from photon correlation spectroscopy are plotted in Figure 3, together with the values of $K_{os} + {}^4/_3G$ from the osmotic and mechanical observations. The error bars shown are those arising from the scatter in the experimental measurements, and the least-squares fit through the points gives

$$M_{os} = (1.11 \times 10^4)c_e^{2.27} \text{ kPa}$$

This value is consistent, within experimental error, with earlier light-scattering measurements on this system, using the same technique.[3]

In Figure 3 a minor discrepancy can be seen concerning the equilibrium gel concentrations. This difference is probably due to different drying techniques in the two laboratories. In Budapest the gels were baked at 80 °C in a vacuum for 4 days, while in Grenoble they were dried in an air-filled oven at 40 °C for 10 days: it is probable that the latter procedure was not enough to drive all the residual water away.

It can be seen that the two techniques give curves of very similar slope, consistent with the scaling value of 2.25. The values of M_{os} obtained by light scattering are, however, lower, by a factor of about 1.8, than $K_{os} + {}^4/_3G$. According to the arguments developed in the theoretical section, that these two distinct measurement techniques should yield different values of the same nominal quantity is not entirely surprising, but in the present case the systematic difference is greater than might reasonably be expected from the concentration heterogeneities present in these gels. The indirectness of the light-scattering technique makes it more vulnerable to systematic errors of which almost certainly the most crucial is the signal from the reference sample. It is essential that the heterodyning conditions for the unknown sample and the reference should be identical. Hitherto, this has not been the case, because the polystyrene cyclohexane reference samples of low molecular weight require additional heterodyning, as dust particles do not stay in suspension. The comparison that has been carried out in this paper thus provides a more reliable calibration for M_{os} than has hitherto been available.

Finally, these measurements give information on the osmotic Poisson ratio σ_{os} of the polymer coils composing the gel, where[3b]

$$\frac{K_{os} + {}^4/_3G}{G} = \frac{2(1 - \sigma_{os})}{1 - 2\sigma_{os}}$$

In view of the above discussion on the systematic differences between light scattering and direct osmotic swelling measurements, this ratio should be evaluated by using the results of one or other technique, i.e., either only light scattering, which can in principle be done as a function of deswelling, or only swelling pressure and macroscopic shear modulus measurements. In practice, light-scattering measurements from a deswelling gel are complicated by the appearance of nonexponential decays associated with high degrees of coil overlap and so were not performed here. The following discussion is thus based only on the measurements of K_{os} and G.

We examine two theoretical possibilities corresponding to a gel in a good solvent.

(1) The gel at swelling equilibrium consists of an assembly of contiguous space-filling coils that do not overlap. The total osmotic Poisson ratio is that of each component coil[17]

$$\sigma_{os} = {}^1/_4; \qquad (K_{os} + {}^4/_3G)/G = 3$$

(2) The swelling pressure is given by the scaling form (eq 14), with $n = {}^9/_4$ and $m = {}^1/_3$. The osmotic modulus is thus

$$K_{os} = A(n - m)c_e^{\,n}$$

and the shear modulus at equilibrium swelling

$$G_e = Ac_e^{\,n}$$

Thus

$$\left.\frac{K_{os} + {}^4/_3G}{G}\right|_{c=c_e} = 3.25; \quad \sigma_{os} = 0.278$$

Since we have already eliminated the Flory logarithmic term, we shall not consider its effects further. It is sufficient to add that inclusion of this term leads to a value of σ_{os} lower than 0.25. In Table IV are shown the experimental values of $(K_{os} + 4G/3)/G|_{c=c_e}$ obtained from the swelling pressure and shear modulus measurements and the corresponding values of σ_{os}. It is clear that σ_{os} is in

Table IV
Osmotic Poisson Ratio σ_{os} of Swollen Polyacrylamide Gels

sample	equilibrium concn, g cm^{-3}	$(K_{os} + (4/3)G)/G$	σ_{os}[a]
1	0.009	3.09	0.261
2	0.030	3.21	0.274
3	0.048	3.32	0.285
4	0.064	3.14	0.267
5	0.081	3.38	0.290

[a] Average $\sigma_{os} = 0.275 \pm 0.011$.

better agreement with the scaling form of eq 14 than with the simple assembly of swollen coils.

Conclusions

In swollen polymer networks, the osmotic properties are described by two independent moduli, the isotropic osmotic modulus K_{os} and the shear modulus G (or any linear combination of these). K_{os} varies with concentration c as $c^{9/4}$, while in gels that are deswollen from their equilibrium swelling concentration c_e G varies as $c^{1/3}$. In this paper, measurements of both of these quantities are reported, determined by using osmotic swelling experiments. Dynamic light scattering, which is governed by the longitudinal osmotic modulus $M_{os} = K_{os} + 4G/3$, shows that this parameter also varies as $c_e^{9/4}$ in gels swollen to equilibrium in a good solvent.

We also show that significant differences may exist between the values of the longitudinal modulus M_{os} measured by dynamic light scattering from polymer gels and the nominally equivalent parameter obtained by macroscopic measurements of the swelling pressure and the shear modulus. The differences are caused by the different way in which the averages over the concentration contribute to the result in the two experiments. Discrepancies between such averages arise in samples that display concentration heterogeneities.

In the present case of polyacrylamide/bisacrylamide gels, a further discrepancy of an experimental nature is noted, whose origin lies in the conditions of observation of the reference sample. The present results in effect provide a new reference point for future light-scattering measurements of M_{os} in other gel systems.

The osmotic and shear modulus measurements show that for such static properties good solvent scaling behavior is observed up to polymer concentrations of 0.25 g cm^{-3}. Furthermore, the osmotic Poisson ratio, σ_{os}, obtained from these measurements takes a value of 0.275 ± 0.011, in acceptable agreement with that deduced from scaling theory for gels, namely, 0.278.

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Registry No. (Acrylamide)(*N,N'*-methylenebisacrylamide) (copolymer), 25034-58-6.

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(18) The factor 2 appearing in eq 5 and the equivalent term of eq 4 replace an incorrect form in ref 7. This correction is, however, of no consequence for relative measurements of the scattered intensity.