Osmotic Swelling of Poly(vinyl acetate) Gels at the Θ Temperature

Ferenc Horkay,[†] Erik Geissler,*[‡] Anne-Marie Hecht,[‡] and Miklós Zrinyi[†]

Department of Colloid Science, Loránd Eötvös University, H-1088 Budapest, Puskin utca 11-13, Hungary, and Laboratoire de Spectrométrie Physique,[§] Université de Grenoble I, B.P. 87, 38402 St Martin d'Hères Cedex, France. *Received November 19, 1987; Revised Manuscript Received February 23, 1988*

ABSTRACT: Three types of experiments are described in this paper to measure the osmotic swelling parameters of a series of poly(vinyl acetate) gels of different cross-link densities at the Θ temperature in isopropyl alcohol. These are (1) measurement of the swelling pressure, ω, during isotropic deswelling of the gel, using a semipermeable membrane and a polymer solution of known activity; (2) measurement of the macroscopic constant volume shear modulus, G; and (3) measurement of the gel concentration at equilibrium swelling with the pure solvent, when the samples are subjected to varying degrees of uniaxial compression. The results of all the observations are in agreement with a solvent chemical potential consisting of only two terms. The first, elastic term is proportional to $\phi^{1/3}$, where ϕ is the polymer volume fraction, and the second, mixing, term is proportional to ϕ^3, as expected at the Θ condition. The osmotic Poisson ratio, σ_{os}, is found to be equal to $^1/_3$.

Introduction

In recent years much consideration has been devoted to the swelling properties of gels in good solvents, particularly in connection with scaling theory.[1–5] In general, good agreement has been found between the exponents for the concentration dependence of the different osmotic moduli and those predicted from the scaling approach in the excluded-volume regime. Less attention has been paid to gels at the Θ temperature, at which the excluded-volume potential vanishes and the polymer chains are presumed to obey Gaussian statistics. One of the obstacles to such observations is the difficulty of preparing gels that remain at sufficiently low concentration at the Θ temperature. If they are prepared in a good solvent, deswelling at the Θ temperature can be large. If, alternatively, they are prepared at or near to the Θ temperature, inhomogeneous gels may result.

Measurements of the longitudinal osmotic modulus, M_{os}, by dynamic light scattering and of the shear modulus, G, of polyacrylamide gels in a mixed solvent (water/methanol) at the Θ temperature have been reported.[5,6] It has recently been pointed out, however, that inhomogeneities in these systems lead to a lower value for M_{os} from light scattering than its nominal equivalent, $K_{os} + {}^4/_3G$, where K_{os} is the isotropic osmotic modulus obtained by swelling pressure measurements. This difference arises from the different concentration averages that are observed in the two kinds of experiments and is analogous to the difference between the weight and number averages found in dilute polymer solutions by equivalent experiments. For a gel of mean polymer concentration $\langle c \rangle$ with a Gaussian distribution of static concentration fluctuations of mean-square amplitude $\langle \Delta c^2 \rangle$, it can be shown[7] that

$$R = \frac{K_{os} + 4G/3}{M_{os}} = 1 + \frac{1}{(3\nu - 1)^2}\frac{\langle \Delta c^2 \rangle}{\langle c \rangle^2} \qquad (1)$$

where ν, the excluded-volume exponent, is equal to $^1/_2$ in the Θ state. Values of $\langle \Delta c^2 \rangle / \langle c \rangle^2$ for this system (polyacrylamide–water/methanol) are not known but, judging from similar gels in good solvents,[8] could well be of the order of several percent. The ratio R in the Θ condition may thus be significantly different from 1, making comparisons between moduli from light scattering and mechanical methods an unreliable basis for further interpretation. It is important, for this reason, to examine the behavior of the osmotic and shear moduli by using only macroscopic techniques. Here, we investigate a series of gels of different cross-linking density, swollen to equilibrium in a Θ solvent. The gels were poly(vinyl acetate), cross-linked with glutyraldehyde and swollen in isopropyl alcohol at the Θ temperature, 52 °C.

We present measurements of the shear modulus, G, of the isotropic swelling pressure, ω, as well as measurements of uniaxial compression in equilibrium with the solvent.

Theoretical Considerations

Several formulations exist for the swelling pressure of a gel, most of which are variants of the original James and Guth theory.[9] Unfortunately, none have so far secured a sound theoretical foundation, on account of our ignorance of the detailed mechanisms of the molecular interactions. In spite of its shortcomings, one of the most useful theories is that of Flory,[10] which, at a fixed temperature T, gives for the swelling pressure ω as a function of polymer volume fraction ϕ

$$\omega = \frac{RT}{\bar{V}_1}\{\ln(1 - \phi) + \phi + \chi_1\phi^2 + \chi_2\phi^3\} - B\left\{\lambda^{-1} - \frac{1}{2\lambda^3}\right\} \qquad (2)$$

where λ in the second, elastic, term represents the linear deformation of any coil in the network. In the first, mixing, term of eq 2, the interaction parameter, χ, has been taken to be concentration dependent:

$$\chi = \chi_1 + \chi_2\phi$$

A number of experimental investigations,[1–5] both on uncross-linked polymer solutions and on networks, have established beyond doubt that at and above the Θ temperature the mixing term in eq 2 is replaced with much improved precision by the scaling form[11]

$$A\phi^{9/4} + C\phi^3$$

where $A = RTv\tau/\bar{V}_1$ is the second virial coefficient, τ the reduced temperature $(T - \theta)/\theta$, and v the excluded-volume parameter. At the Θ temperature, $\tau = 0$. In this case, eq 2 reduces to

$$\omega = C\phi^3 - B\left\{\lambda^{-1} - \frac{1}{2\lambda^3}\right\} \qquad (2a)$$

[†] Loránd Eötvös University.
[‡] Université de Grenoble I.
[§] CNRS associate laboratory.

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Equations 2 and 2a are based on an analogy between a gel and an assembly of separate but linked polymer coils, in which the expansion factor, λ, of a given coil with respect to its reference state is affinely related to the polymer concentration

$$\lambda^{-3} = \phi/\phi_0 \tag{3}$$

ϕ_0 being the reference concentration of the coil (i.e., the Θ state). Just below the Θ temperature, the term $1/2\lambda^3$ gives rise to two solutions to eq 2a, an expanded and a condensed coil state.[12] Experimental evidence of a transition between two such states near the Θ point has so far eluded observation, along with evidence for the existence of the term $1/2\lambda^3$.

Neutron scattering experiments on polystyrene gels[13] have shown that at the Θ condition the polymer concentration may be 1 order of magnitude or more greater than that inside a single polymer chain in dilute Θ solution. Nonetheless the coil dimensions in both cases remain the same. Such behavior has a simple physical explanation in scaling theory[14,15] (Appendix A), according to which, in a gel the mean-square end-to-end length of a given polymer chain, R_t^2, varies nonaffinely with swelling as

$$R_t^2 \propto R_s^3/\xi \tag{4}$$

where R_s is the mean (spatial) separation between cross-links in the gel and ξ is the density–density correlation length. Upon swelling, R_s^3 varies affinely, i.e., as $1/\phi$, while in Θ conditions ξ also varies as $1/\phi$, so that according to eq 4 the dimensions of any given chain are unchanged. Such behavior is also observed experimentally.[13]

This nonaffine model of R_t has as a corollary that it is not the individual chains that are responsible for the bulk elasticity. The requisite affineness in eq 3, observed in macroscopic experiments, is obtained only by cooperative unfolding of a number of connected chains. The detailed mechanism of the unfolding must depend upon the local topology, which lies outside scaling theory.

An alternative approach to this problem has been proposed by Flory and Erman,[16,17] in which affine deformations of themean vector R_t are assumed, together with nonaffine instantaneous displacements of the junction points. The central argument of this approach is that different experiments yield different averages of the measured quantities and that by adjusting two experimental parameters, acceptable fits can be found for the macroscopic and microscopic response of a gel to external constraints. A major drawback in applying this theory is that no compelling physical argument emerges to select appropriate a priori values for the adjustable parameters, and, in addition, these are not concentration invariant, so that the theory remains nonpredictive. A general result of this theory seems, however, to be that at high swelling degrees the elastic term in eq 2 and 2a reduces to the simple form

$$B/\lambda = B(\phi_0/\phi)^{1/3} \tag{5}$$

the intricate correction term being in this case negligible. The evidence for a concentration dependence of the form of eq 5 in the elastic energy is now overwhelming,[18,2-5] so that no correction term is experimentally detectable in swollen gels.

The term $1/2\lambda^3$ in the elastic term of eq 2a, although not detected, has nevertheless an important conceptual role when one considers the osmotic Poisson ratio, σ_{os}, of the polymer coils in the gel.[5] Under uniaxial stress, if this term were present, it would come from a free energy of the polymer coils of the form[12]

$$F = kT\left\{\frac{(R_\parallel^2 + 2R_\perp^2)}{2R_0^2} - \frac{1}{2}\ln(R_\parallel R_\perp^2)\right\} + AN\left(\frac{N}{R_\perp^2 R_\parallel}\right) + C\frac{N^3}{R_\perp^4 R_\parallel^2} \tag{6}$$

where $R_\parallel$, $R_\perp$, R_0 are the coil radii parallel and perpendicular to the constraint and in the unperturbed state, respectively. N is the polymerization index of the chains, and A and C are the second and third virial coefficients. At the Θ condition, $A = 0$, so that in the expanded state of the coil ($R \simeq R_0$), only the first two terms of eq 6 are important. Differentiating these with respect to $R_\perp$ while holding $R_\parallel$ constant gives

$$R_\perp = R_0/2^{1/2} = \text{constant}$$

It follows that the Poisson ratio

$$\sigma_{os} = -\partial R_\perp/\partial R_\parallel = 0 \tag{7}$$

If, on the contrary, the logarithmic term of eq 6 is absent, then one obtains at the Θ temperature, on differentiating with respect to $R_\perp$,

$$R_\perp^3 R_\parallel = \text{constant}$$

giving

$$\sigma_{os} = 1/3 \tag{8}$$

This solution corresponds formally to the condensed state of the coil. According to eq 4, however, the coil in this state has not collapsed on itself but is filled with other, neighboring coils (see Appendix A), so that its radius remains proportional to $N^{1/2}$ rather than $N^{1/3}$.

The osmotic Poisson ratio is related to the moduli of the gel at swelling equilibrium through the relation[5]

$$\frac{M_{os}}{G} = \frac{2(1 - \sigma_{os})}{1 - 2\sigma_{os}} \tag{9}$$

In view of the error discussed earlier connected with comparisons between moduli obtained by mechanical measurements and by light scattering from inhomogeneous gels, it is more appropriate to refer to the relation (derived from eq 9 and the definition of the longitudinal modulus, $M_{os} = K_{os} + {}^4/_3G$)

$$\frac{K_{os}}{G} = \frac{2}{3}\frac{1 + \sigma_{os}}{1 - 2\sigma_{os}} \tag{10}$$

obtained from osmotic and mechanical measurements alone.

The two possible values of σ_{os} in the Θ condition (eq 7 and 8) give respectively

$$K_{os}/G = 2/3 \qquad \text{(expanded coils)} \tag{11a}$$

$$K_{os}/G = 8/3 \qquad \text{(condensed coils)} \tag{11b}$$

Experimental Details

Poly(vinyl acetate) (PVAc) gels were prepared by acetylation of poly(vinyl alcohol) (PVA) networks. The PVA (Poval 420, Kuraray, Japan) was cross-linked with glutyraldehyde in aqueous solution at pH 1.5. The gels were then acetylated in a mixture of acetic acid and acetic anhydride–pyridine, at 90 °C for 8 h.[19,20]

The gels were washed in acetone, the presence of foreign matter in the wash being checked by interferometry.[21] The washing cycle involved no less than 30 solvent exchanges, and finally the acetone was slowly evaporated from the gels. The dry samples were reswollen in isopropyl alcohol at 52 °C (Θ temperature).

Unidirectional compression measurements were performed with a homemade apparatus.[19] The force versus deformation relation was determined for cylindrical gel samples at different stages of

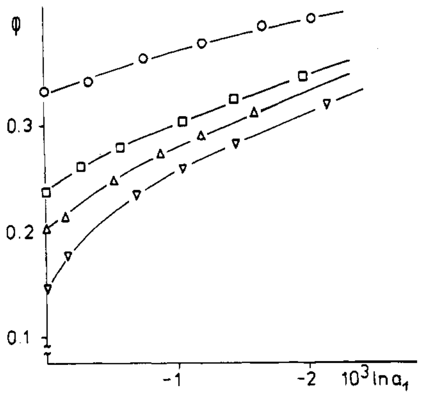

Figure 1. Dependence of polymer volume fraction ϕ on the activity of the diluent for PVAc gel homologues. Symbols: (○) 9/50; (□) 9/100; (△) 9/200; (▽) 9/400. The first number indicates the polymer mass fraction, in percent, at which the cross-links were introduced; the second is the molar ratio of monomers to cross-linking molecules.

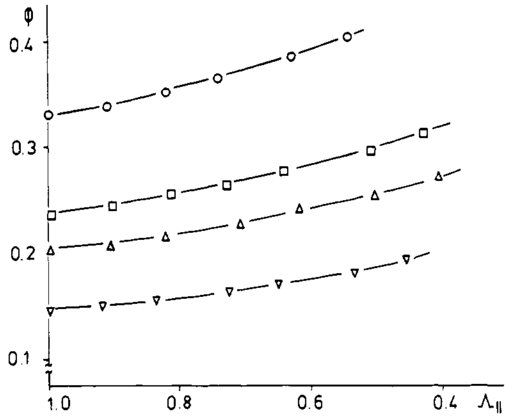

Figure 2. Dependence of the equilibrium polymer volume fraction on the deformation ratio, $\Lambda_{\parallel}$. Symbols as in Figure 1.

dilution. The measurements were performed in the range $0.6 < \Lambda < 1.0$, where Λ is the macroscopic deformation ratio at constant volume. The data were evaluated by using the relation

$$f = C_1(\Lambda - \Lambda^{-2}) + C_2(\Lambda - \Lambda^{-2})/\Lambda \qquad (12)$$

where f is the nominal stress and C_1 and C_2 are constants. It was found that $C_2 = 0$ independently of the deformation ratio, and accordingly the constant C_1 was identified with the shear modulus of the gel. The absence of volume change and barrel distortion was also checked.

Deswelling was achieved by two methods. The equilibrium deswelling method reduces the activity of the diluent when a polymer (PVAc, Mowilith M40, Hoechst) is dissolved in the liquid phase in equilibrium with the gel but separated from it by a semipermeable membrane.[22] The concentration of the gel as well as that of the solution can readily be determined, as the gel is not in direct contact with the viscous polymer solution. The activity of the diluent in the equilibrated phases can be calculated from the activity–concentration dependence of the polymer solution, known either from osmotic pressure or from vapor pressure measurements.[23]

The second method of deswelling consisted of applying uniaxial compressional stress on the gel in equilibrium with the pure diluent.[24] Cylindrical gel samples were compressed along their symmetry axis between two parallel flat plates whose distance of separation could be adjusted to produce the desired uniaxial deformation ratio $\Lambda_{\parallel}$ in the range $0.5 < \Lambda_{\parallel} < 1$, where $\Lambda_{\parallel}$ describes the ratio of the deformed cylinder length to the length of the unconstrained fully swollen sample. In this arrangement, the deswelling is caused by the hydrostatic component of the stress.

Table I
Fitting Parameters of Isotropic Swelling Measurements to Swelling Pressure Curve $\omega = C(\phi^n - \phi_e^{n-m}\phi^m)$

sample[a]	ϕ_e	n	m	K_{os}/kPa[b]	G_{os}/kPa
9/400	0.146	2.86	0.375	23.0	9.26
6/200	0.149	2.61	0.413	26.6	12.1
9/200	0.201	2.85	0.321	56.5	22.4
12/200	0.219	2.44	0.349	75.7	36.2
9/100	0.237	3.00	0.331	88.5	33.2
6/50	0.253	2.78	0.326	103.7	42.2
9/50	0.330	3.70	0.252	248.0	72.0
12/50[c]	0.365	(3)	(0.333)	380.0	142.3

[a] Designation of samples: polymer weight fraction at which cross-links were introduced/number of monomer units beween two neighboring cross-link points. [b] $K_{os} = \phi(\partial\omega/\partial\phi)|_{\phi=\phi_e}$, $G_{os} = C\phi_e^{\,n}$. [c] As this sample had insufficient data to allow a free determination of m and n, a forced fit to eq 14 was used.

Table II
Uniaxial Deswelling: Least-Squares Fit to $\Lambda_{\parallel} = K(\phi_e/\phi)^p$

sample	K	p	sample	K	p
3/50	0.998	2.99	9/100	1.005	3.03
6/200	1.008	3.04	9/50	0.994	2.95
6/50	0.994	2.98	12/200	0.998	2.98
9/400	1.001	3.01	12/50	1.001	3.01
9/200	1.000	3.00			

In Figures 1 and 2 are shown the variation of gel concentration for PVAc gel homologues differing in cross-linking densities, as a function of the activity of the diluent and of the deformation ratio $\Lambda_{\parallel}$, respectively. In both cases considerable deswelling occurs, the effect being more pronounced for the loosely cross-linked networks.

Results and Discussion

Isotropic Deswelling. The results of these experiments are most conveniently analyzed in terms of eq 2a, in the absence of the elastic volume term, $1/2\lambda^3$, i.e.,

$$\omega = C\phi^3 - B/\lambda \qquad (13)$$

which, in the case of isotropic swelling, becomes (cf. eq 3)

$$\omega = C\phi^3 - B(\phi/\phi_e)^{1/3} \qquad (14)$$

The isotropic swelling experiments were analyzed by allowing the exponents in eq 14 to vary freely, with the condition that $\omega = 0$ at the equilibrium polymer volume fraction ϕ_e. Thus

$$\omega = C(\phi^n - \phi_e^{\,n-m}\phi^m) \qquad (14a)$$

where n and m were found by a nonlinear least-square method. The results are listed in Table I. This experimental technique gives a higher scatter in the values obtained for n (2.9 ± 0.4) and for m (0.34 ± 0.05) than is found in the intrinsically more straightforward and simple uniaxial deswelling experiments that are described below, but the results are in agreement with those theoretically expected, namely, 3 and $^1/_3$, respectively.

The shear modulus at swelling equilibrium, G_{os}, deduced from these osmotic pressure measurements, is given by the second term on the right-hand side of eq 14 and 14a, i.e.,

$$G_{os} = C\phi_e^{\,3} \qquad (15)$$

Uniaxial Deswelling. For uniaxial deswelling the relevant relation is eq 13, in which, because of the equilibrium with the pure diluent, $\omega = 0$. Thus at the Θ condition, one expects that

$$\Lambda_{\parallel} = (\phi_e/\phi)^p \qquad (16)$$

with $p = 3$, and where ϕ_e, as before, represents the equilibrium swelling polymer volume fraction in the unconstrained gel. In Table II are listed the values of the parameters of the least-squares fits to the data for each gel. The observed agreement with eq 16 is excellent, the mean value of the experimental exponent p being

$$p = 3.00 \pm 0.03$$

Table III
Shear Modulus Measurements $G = G_e(\phi/\phi_e)^m$

sample	m	G_e/kPa	sample	m	G_e/kPa
6/200	0.331	8.81	9/100	0.328	37.0
6/50	0.333	44.3	9/50	0.333	89.5
9/400	0.326	8.14	12/200	0.334	29.1
9/200	0.330	22.7	12/50	0.331	126.3

Table IV
Summary of Isotropic Moduli K_{os} and Shear Moduli G_e at Swelling Equilibrium[a]

equilibrium vol frctn	K_{os}/ kPa	G_{os}/ kPa	G_e/ kPa	K_{os}/ G_e	osmotic Poisson ratio σ_{os}
0.365	380.0	142.3	126.3	3.00	0.350
0.330	248.0	72.0	89.5	2.77	0.339
0.253	103.7	42.2	44.3	2.34	0.313
0.237	88.5	33.2	37.0	2.39	0.316
0.219	75.7	36.2	29.1	2.60	0.330
0.201	56.5	22.4	22.7	2.49	0.323
0.149	26.6	12.1	8.81	3.02	0.351
0.146	23.0	9.26	8.14	2.82	0.341

[a] $\bar{\sigma}_{os} = 0.333 \pm 0.014$; $\overline{K_{os}/G_e} = 2.68 \pm 0.25$.

The exponent p is directly related to the osmotic Poisson ratio of the gel, σ_{os}, which, for the macroscopic deformations $\Lambda_\parallel$ and $\Lambda_\perp$ parallel and perpendicular to the uniaxial constraint, can be expressed (cf. eq 7) as

$$\sigma_{os} = -\partial\Lambda_\perp/\partial\Lambda_\parallel$$

The sample volume is defined by

$$\Lambda_\parallel\Lambda_\perp^2 = \phi_e/\phi \tag{17}$$

Combining eq 16 and 17, one obtains

$$\Lambda_\parallel^{p-1}\Lambda_\perp^{2p} = \text{constant}$$

and hence

$$\begin{aligned}\sigma_{os} &= (p-1)/2p \\ &= 0.333 \pm 0.001\end{aligned} \tag{18}$$

This result is in agreement with the condensed state value of the osmotic Poisson ratio ($\sigma_{os} = {}^1/_3$) discussed in the theoretical section and completely at odds with the dilute Θ solution value ($\sigma_{os} = 0$).

Shear Modulus. The last set of experimental data to be obtained from these gels is the shear modulus, G, measured by uniaxial compression under constant volume conditions. These results are shown in Figure 3 in a double-logarithmic representation as a function of the polymer volume fraction ϕ. The slopes, m, of the mean lines through each set of data points, listed in Table III, have an average value of 0.331 ± 0.003, also in satisfactory agreement with the theoretical value of ${}^1/_3$.

Table IV contains a summary of the swelling equilibrium values for K_{os}, G_{os}, and G_e, where G_{os} is the shear modulus deduced from the swelling pressure measurements alone (eq 14) and G_e is that obtained by direct mechanical measurement. The ratio K_{os}/G_e, equal to ${}^2/_3$ if the coils are in the "expanded" Θ state and ${}^8/_3$ in the "condensed" state, is found experimentally to have a mean value of 2.68 ± 0.25. For these samples, therefore, the evidence is thus clearly in favor of the coils at the Θ temperature being in the condensed state.

From Table IV can also be obtained the concentration dependence of the equilibrium values of the osmotic moduli, namely,

$$K_{os} = [(6.53 \pm 0.98) \times 10^3]\phi_e^{2.94\pm0.09}\ \text{kPa}$$

and

$$G_e = [(2.52 \pm 0.19) \times 10^3]\phi_e^{2.96\pm0.05}\ \text{kPa}$$

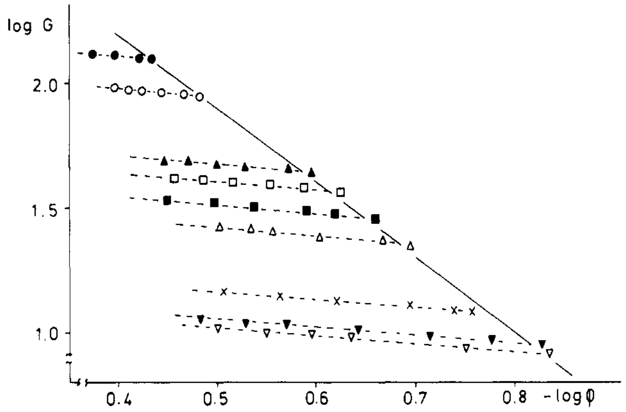

Figure 3. Double-logarithmic representation of the variation with polymer volume fraction ϕ of the shear modulus, G, measured mechanically. Symbols: (●) 12/50; (■) 12/200; (○) 9/50; (□) 9/100; (△) 9/200; (▽) 9/400; (▲) 6/50; (▼) 6/200; (×) 3/50. The continuous straight line refers to PVAc gel homologues swollen in pure isopropyl alcohol (T = 52 °C); the dashed lines show the variation of log G versus log ϕ for each gel sample.

These experiments display independent agreement with the theoretical exponent of 3.

Last, the degree of consistency between the values of G obtained by the two methods can be seen from inspection of Table IV, where the average ratio of the moduli is

$$G_{os}/G_e = 1.07 \pm 0.18$$

A more complete verification, using all the data points from the uniaxial deswelling measurements instead of only the equilibrium swelling values for each sample, can be procured by comparing the activity of the solvent in the gel as a function of concentration with that obtained from uniaxial deswelling. The procedure is as follows. In the isotropic deswelling experiments, the gel concentration ϕ is measured as a function of the known activity

$$\Delta\mu_1 = -\omega\bar{V}_1 \tag{19}$$

of the solution outside the semipermeable membrane, where $\bar{V}_1$ is the solvent molar volume. In the uniaxial deswelling measurements, the difference in chemical potential between the free solvent and the strained gel is, from eq 14a and 15,

$$\Delta\mu_1 = -G_{os}\bar{V}_1\{(\phi/\phi_e)^3 - (\phi/\phi_e)^{1/3}\} \tag{20}$$

The two chemical potentials of eq 19 and 20 are theoretically identical. The comparison of interest here is obtained by replacing G_{os} in eq 20 by G_e found from the mechanical measurements. In Figure 4 are shown the experimental points $\omega(\phi)\bar{V}_1$ plotted against $G_e\bar{V}_1\{(\phi/\phi_e)^3 - (\phi/\phi_e)^{1/3}\}$. The straight line, of slope unity, represents the relation

$$\omega(\phi)\bar{V}_1 = G_{os}\bar{V}_1\{(\phi/\phi_e)^3 - (\phi/\phi_e)^{1/3}\} \tag{20'}$$

It is clear that the experimental and the theoretical values of the chemical potential are in good numerical agreement.

Conclusions

In this paper three types of experiments are undertaken to measure the osmotic swelling parameters of a series of gels at the Θ temperature. These are (1) measurement of the swelling pressure, ω, during isotropic deswelling of the gels by a polymer solution of known activity, using a semipermeable membrane; (2) measurement of the constant volume shear modulus, G, in each sample as a function of deswelling, by mechanical methods; and (3) measurement of the gel concentration at equilibrium

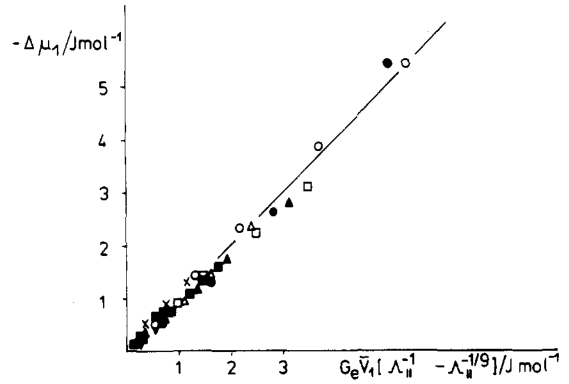

Figure 4. Plot of $-\Delta\mu_1 = \omega\bar{V}_1$ versus $G_e\bar{V}_1(\Lambda_\parallel{}^{-1} - \Lambda_\parallel{}^{-1/9})$ for PVAc–isopropyl alcohol gels, where $\Lambda_\parallel = (\phi_e/\phi)^{1/3}$ is the observed deformation ratio of the gel at equilibrium swelling under uniaxial stress. Symbols as in Figure 3. $\Delta\mu_1$ is the chemical potential of the sovlent and ω the swelling pressure.

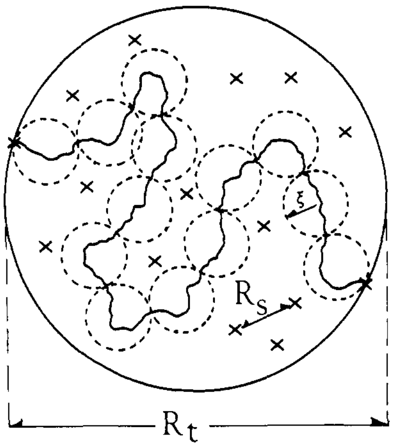

Figure 5. Model used for the description of the nonaffine swelling of individual polymer chains within the polymer gel. The continuous line represents a given chain, the distance between whose end points is R_t. The chain is subdivided into correlation spheres of radius ξ (dashed circles). The crosses represent other cross-link points lying in the volume defined by R_t, each connected to other polymer chains (not shown). The mean separation between the crosses is R_s.

swelling in the pure solvent, while the gels are subjected to uniaxial compression.

The results of all these experiments are compatible with a solvent chemical potential containing only two terms. The first consists of an elastic term, proportional to $\phi^{1/3}$, where ϕ is the polymer volume fraction, and the second, mixing, term is proportional to ϕ^3. The osmotic Poisson ratio, σ_{os}, is found to be equal to $^1/_3$, as is to be expected when the logarithmic term of Flory's earlier theory is absent, and corresponds to a condensed state of the polymer coils. For comparison, had the logarithmic term the form suggested by Flory, then $\sigma_{os} = 0$ and the coils would adopt an "expanded" configuration, of mean concentration similar to that found inside polymer coils in dilute Θ solutions.

The present results, taken in conjunction with scaling arguments concerning the nonaffine swelling process, imply that the gel cannot be considered simply as a superposition of a set of separate coils swollen at the Θ condition. On the contrary, each coil contains, in addition to the solvent, many other coils, and the overall affine elastic behavior of the gel is the result of a cooperative unfolding process in which the deformation of any individual coil is small or vanishing. The "condensed" state is thus one in which the coils are swollen to their Θ dimensions both by the solvent molecules and by adjacent coils, in such a way that the polymer concentration inside each coil is much greater than for a single coil in dilute Θ solution.

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Appendix A

Scaling Analysis of Coil Dimensions in Swelling Gels.[14,15] Let the mean spatial distance of separation between cross-link points in the gel be R_s, each having functionality f. Each cross-link point is attached to f chains, all of which are assumed to have molecular weight Nm, N being the polymerization index and m the mass of the monomer. As each cross-link point is connected only indirectly to its nearest spatial neighbor, their relative motion on gel swelling is taken to be affine, i.e., the concentration c is given by

$$c = \frac{fNm}{(4\pi/3)2R_s{}^3} \tag{A1}$$

For a given polymer chain, the mean-square separation between its topologically connected ends is $R_t{}^2$. Along the chain contour (Figure 5), the excluded-volume effect causes a repulsive interaction between a given segment and its neighbors over a characteristic radius, ξ, the correlation length. Beyond ξ the repulsion is screened out, so that the chain can be considered as a Gaussian sequence of n correlation spheres of radius ξ, such that

$$R_t{}^2 = n(2\xi)^2 \tag{A2}$$

Now each correlation sphere (cf. Figure 5) contains g monomers, such that the concentration is

$$c = \frac{gm}{(4\pi/3)\xi^3} \tag{A3}$$

Conservation of mass requires that

$$N = gn \tag{A4}$$

Combining eq A1–A4 gives

$$R_t{}^2 = \frac{8R_s{}^3}{f\xi} \tag{A5}$$

Denoting the step length of the chain monomer as b, one obtains for the radius of gyration R_G of the coil[25]

$$R_G{}^2 = \frac{1}{12}(Nb^2 + R_t{}^2)$$

In good solvents,[11] $\xi \propto c^{-0.75} \propto q^{0.75}$, where q is the swelling ratio. $R_s{}^3$, from eq A1, varies as q. It follows that compared to the dry gel, where $R_t{}^2 = Nb^2$ and $\xi \simeq b$,

$$R_G{}^2 = \frac{R_0{}^2}{2}(1 + q^{0.25}) \tag{A6}$$

where $R_0{}^2 = Nb^2/6$. Equation A6 is in good agreement with the experimental observations of neutron scattering from gels in good solvents.[15,26]

For gels in a Θ solvent, in which $\xi \propto q$, $R_t{}^2$ is not expected to vary on swelling. This result has also been observed experimentally.[13]

The transition between these two states can be described in this model by taking into account the temperature dependence of the correlation length ξ. On the basis of the phase diagram proposed by Daoud and Jannink[27]

$$\xi = \xi_0 c^{\nu/1-3\nu} \tau^{(2\nu-1)/(1-3\nu)} \tag{A7}$$

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

Erik Geissler,[*,†] Anne-Marie Hecht,[†] Ferenc Horkay,[‡] and Miklôs Zrinyi[‡]

Laboratoire de Spectrométrie Physique,[§] Université de Grenoble I, B.P. 87, 38402 St Martin d'Hères Cedex, France, and Department of Colloid Science, Lorând Eötvös University, H-1088 Budapest, Puskin utca 11-13, Hungary.

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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 $K_{os} + {}^4/_3 G > M_{os}$. 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]

$$M_{os} = K_{os} + {}^4\!/_3 G \qquad (1)$$

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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[†] Laboratoire de Spectrométrie Physique, Université de Grenoble I.

[‡] Department of Colloid Science, Lorând Eötvös University.

[§] CNRS associate laboratory.