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Osmotic and Scattering Properties of Chemically Cross-Linked Poly(vinyl alcohol) Hydrogels[†]

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ABSTRACT: Swelling pressure and shear modulus measurements are reported for chemically cross-linked poly(vinyl alcohol) (PVA) hydrogels. An attempt is made to correlate the macroscopic results with data obtained by small-angle X-ray scattering (SAXS) measurements performed on the same gel samples. The swelling pressure of the PVA gels can be satisfactorily described by a two-term equation consisting of a separable elastic and mixing contribution. The concentration dependence of the elastic term differs slightly from the classical theoretical prediction. The mixing term follows a power law behavior with an exponent close to that predicted by scaling theory. Osmotic pressure results obtained for aqueous PVA solutions are used to normalize the SAXS spectra to yield absolute scattering intensities. The scattering spectra of the gels are resolved into a static and a dynamic (solution-like) component. The intensity of the latter is compared with values calculated from independent osmotic measurements. The second moments describing the static concentration fluctuations are found to increase strongly with the cross-linking density.

Introduction

Swollen polymer networks exhibit thermodynamic properties that are analogous to those of solutions, while retaining structural features, such as permanent accumulations of polymer around cross-links, that are reminiscent of solids. Various attempts have been made to describe either the microscopic structure of swollen gels or their thermodynamics,[1–11,35] but these two aspects have been compared directly in rather few cases.[12–16]

Hydrogels[2,5,6,8,10,13,35] usually contain more imperfections than nonpolar networks. Structural nonuniformities invariably develop, to a degree that depends on the method of preparation. Intermolecular interactions (e.g., hydrogen bonding) lead to the formation of physical junctions. The resulting rearrangement of the polymer segments is observable in small-angle X-ray or neutron scattering experiments.

In the present work the results of a series of elastic and swelling measurements performed on poly(vinyl alcohol) hydrogels cross-linked by glutaraldehyde are reported. The thermodynamic behavior of the swollen gels is compared with that of the solutions of the corresponding un-cross-linked polymer. The X-ray scattering spectra of both the gels and the polymer solutions are also measured. An attempt is made to correlate the thermodynamic data obtained from X-ray scattering and macroscopic osmotic measurements on the same samples.

Theoretical Background

Swelling Properties. In general, the swelling pressure of a gel, ω, is given by[17–19]

$$\omega = \Pi_g - G \tag{1}$$

where Π_g is the osmotic contribution (mixing pressure) of the cross-linked polymer and G is the elastic modulus. In equilibrium with a pure diluent $\omega = 0$; i.e., the mixing pressure is balanced by the elastic response of the network.

The first term of eq 1, describing mixing of polymer chains with solvent molecules, is given by the Flory–Huggins equation[19]

$$\Pi_g = -(RT/v_1)[\ln(1-\varphi) + \varphi(1 - 1/x) + \chi\varphi^2] \tag{2}$$

where φ is the volume fraction of the polymer, v_1 is the partial molar volume of the solvent, and x is the ratio of the molar volumes of the solute and the solvent. For a cross-linked polymer $x = \infty$. The polymer–solvent interaction parameter χ usually depends on the concentration.

According to more recent scaling theories,[20] the concentration dependence of the osmotic pressure of a polymer solution, Π, exhibits a simple power law behavior in the asymptotic semidilute regime (i.e., $x \rightarrow \infty$, $\varphi \ll 1$):

$$\Pi = A_0\varphi^n \tag{3}$$

where $n \approx 2.31$ in a good solvent and $n = 3$ in Θ conditions. The numerical constant A_0 depends on the particular polymer–solvent system.

The elastic modulus of the gel, G, is interpreted by using the statistical theory of rubber elasticity:[17–19]

$$G = G_0\varphi^m \tag{4}$$

where G_0 is a constant that depends on the given network and $m = {}^1/_3$.

Substituting eqs 3 and 4 into eq 1 yields[21,22]

$$\omega = A_0\varphi^n - G_0\varphi^m \tag{5}$$

Equation 5 implies that for fully swollen gels ($\omega = 0$) the elastic modulus G displays the same concentration dependence as the osmotic pressure of the solution of un-cross-linked polymer; i.e., the modulus of network homologues scales with the polymer volume fraction φ as φ^n.

According to scaling theory, the thermodynamic properties of a polymer–solvent system are governed by a correlation length ξ, which defines the range of the monomer–monomer pair correlation function.[20] For length scales shorter than ξ intramolecular interactions of excluded volume type dominate, while at greater distances the chains are ideal. For dilute solutions ξ is proportional to the size of the individual polymer coil. In the semidilute regime, where different coils overlap, ξ represents the mean distance between polymer segments (contact points), and the osmotic pressure is proportional to the density of contact points in the solution; i.e., $\Pi \propto kT/\xi^3$.

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From eq 3 it follows that

$$\xi \propto \varphi^{-n/3} \tag{6}$$

In principle, scaling theory can be directly applied to permanently cross-linked swollen networks. The analogy is based on the similarity between the structure of the gel and that of an entangled polymer solution.[20] In real systems the situation is usually more complicated. When cross-links are introduced the local segment density is enhanced in their immediate vicinity, while compensating solvent-rich regions appear elsewhere in the matrix. The rearrangement of the polymer segments due to the presence of cross-links causes appreciable differences between the physical properties of the gel and those of the corresponding polymer solution. A comparison between results obtained from macroscopic thermodynamic observations and those from techniques that probe the polymer system at the molecular level should yield information on the structure-property relationship in swollen networks.

Scattering Properties. The intensity of radiation scattered from a polymer solution, $I(Q)$, is governed by the mean square amplitude of the concentration fluctuations, $\langle\Delta\varphi^2\rangle$. This quantity is inversely proportional to the osmotic compressional modulus $K_{os} = \varphi(\partial\Pi/\partial\varphi)$.

$$I(Q) = a\frac{kT(\rho_p - \rho_s)^2\varphi^2}{K_{os}}S_S(Q) \tag{7}$$

where a is a constant that depends on the incident wavelength and on the scattering geometry used, ρ_p and ρ_s are the electron densities of the polymer and the solvent, respectively, $S_S(Q)$ is the structure factor of the solution, and $Q = (4\pi/\lambda)\sin(\theta/2)$ is the transfer wave vector for an incident wavelength λ at scattering angle θ.

At small values of Q in semidilute polymer solutions the structure factor can usually be satisfactorily described by an Ornstein-Zernicke (i.e., Lorentzian) lineshape function[20]

$$S_S(Q) = 1/(1 + Q^2\xi^2) \tag{8}$$

where ξ is the density-density correlation length.

In general, a polymer solution differs from the corresponding gel in several respects. One important difference is that the latter cannot be diluted indefinitely: swelling continues only until the chemical potential of the absorbed diluent reaches that of the pure solvent outside the swollen network. Connectivity of the chains reduces the number of configurations accessible to the cross-linked system. In the swollen network, regions of excess polymer content build up that appear as permanent departures from uniformity. The distribution of the polymer can then be deemed to be a static structure, with temporal fluctuations of limited magnitude. The mean square amplitude of the static excursions is denoted $\langle\delta\varphi^2\rangle$. The total amplitude of the concentration fluctuations is then the sum of two contributions, a static and a dynamic part:[11,13-15]

$$\langle\Delta\varphi^2\rangle = \langle\Delta\varphi^2\rangle_{dyn} + \langle\delta\varphi^2\rangle \tag{9}$$

The dynamic part, which exhibits solution-like behavior, is assumed to have a structure factor of the same form as eq 8. The static contribution $\langle\delta\varphi^2\rangle$, however, depends upon the size and distribution of the nonuniformities, and hence on the particular network system.

This description of the gel is analogous to the approach of Pusey and van Megen,[23] who considered the spectrum of light scattered dynamically by nonergodic systems. In our case, the static structures, not being able to explore the whole of the sample volume, are ipso facto nonergodic. In a light scattering experiment they act as a local oscillator that heterodynes light scattered by the liquid-like component. The presence here of two components, liquid-like and static, respectively, having different degrees of freedom, produces more complex a situation than examined in ref 23: implications for light scattering are discussed elsewhere.[24]

To a good approximation, the cross-linking of polymer chains in the solution can be supposed to introduce only minor chemical modifications in the composition of the system. Consequently, although the shape of the scattering function $I(Q)$ is affected by rearrangements of the chains, the total second moment, namely

$$M_2 = \frac{1}{4\pi}\int_0^\infty I(Q)\exp(i\mathbf{Q}\cdot\mathbf{r})\,d\mathbf{Q}|_{r=0} = \int_0^\infty I(Q)Q^2\,dQ = 2\pi^2V\langle\Delta\rho^2\rangle \tag{10}$$

must remain invariant.[25] $\langle\Delta\rho^2\rangle$ is the mean square fluctuation in the electron density. This result is subject to two assumptions that are obviously fulfilled here: first, that the system is statistically isotropic, and, second, that there is no long-range order. In two-component systems, such as polymer solutions and the gels considered here (the cross-links causing negligible scattering[15])

$$\langle\Delta\rho^2\rangle = (\rho_p - \rho_s)^2\langle\Delta\varphi^2\rangle = (\rho_p - \rho_s)^2\varphi(1 - \varphi)$$

Thus the invariant[36] is

$$M_2 = 2\pi^2V(\rho_p - \rho_s)^2\varphi(1 - \varphi) \tag{10'}$$

According to eq 9, M_2 contains a static and a dynamic component, the latter arising from the solution-like part of the gel. In such a solution-like region the actual polymer concentration should be smaller than the average concentration of the swollen network, while around junction points the local polymer concentration is correspondingly higher.

The possibility of independently estimating $\langle\Delta\varphi^2\rangle_{dyn}$ affords an invaluable means of characterizing the gel: together with the second moment of the scattering spectrum, it allows the calculation of $\langle\delta\varphi^2\rangle$, i.e., the measure of the static nonuniformity of the network structure.

Experimental Section

Gel Preparation and Macroscopic Measurements. The PVA gels were made by cross-linking poly(vinyl alcohol) in aqueous solutions with glutaraldehyde at polymer concentration 6% w/w.[26,27] Gel samples were prepared with three different molar ratios of monomer units to the molecules of the cross-linking agent, 50, 100, and 200. The solutions of the polymer (pH = 1.5), the cross-linking agent, and the catalyst (2 N HCl solution) were mixed and poured into a demountable mold of the shape required for the experiments (cylinders or sheets). Gelation proceeded under isothermal conditions in a thermostat at 298.0 ± 0.1 K in about 2 h. After a day, the samples were placed in weighing bottles with ground-glass lids and left for 2 days for completion of the reaction. The solvent was then exchanged with distilled water, and the gels were stored until required at room temperature.

The swelling pressure was obtained by deswelling the swollen networks surrounded by aqueous poly(vinylpyrrolidone) solutions of known osmotic pressure.[28] To prevent penetration of the dissolved polymer molecules into the gel, the latter was separated from the polymer solution by a semipermeable membrane.[29] The swelling pressure of the gel was calculated from the osmotic pressure of the surrounding polymer solution. The time required to attain equilibrium was found to be between 2 and 4 weeks depending on the sample investigated.

The PVA/water solutions were made in the volume fraction range $0.025 < \varphi < 0.18$ by dissolving a fractionated PVA sample.

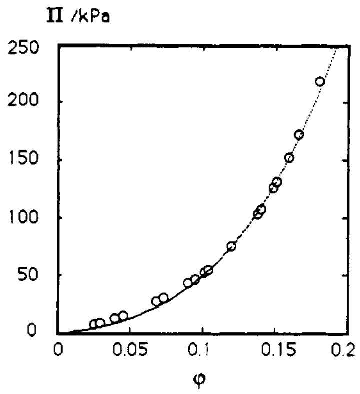

Figure 1. Double-logarithmic representation of the osmotic pressure, Π, as a function of polymer volume fraction for aqueous poly(vinyl alcohol) solutions. The curve through the data points is the least-squares fit to eq 11.

The molecular weight of this sample, measured by membrane osmometry, was M_n = 29 000 Da at 25 °C. In the semidilute regime the osmotic pressure of the solutions was obtained by equilibrating them with PVA gels whose swelling pressure had already been determined.

Shear modulus data were obtained from uniaxial compression measurements performed on the gels at different swelling ratios.[26] The stress-deformation data were evaluated by using the Mooney-Rivlin equation. The C_2 term was found to be equal to zero. Absence of volume change and barrel distortion was carefully checked.

Small-Angle X-ray Scattering. The small-angle X-ray scattering measurements were performed on the D24 instrument on the DCI synchrotron at LURE, Orsay. The wavelength used here was 1.608 Å, and the beam cross-section was 3.0 × 0.5 mm². The Q range explored was $10^{-2} \leq Q \leq 0.12$ Å^{-1}.

Both gels and solutions were contained in stainless steel cells with thin mica windows to prevent evaporation of the solvent. The sample thickness was defined by a 1-mm-thick stainless steel spacer. Sample cells were lodged in a holder occupying 1.5 cm of air space in the X-ray beam and could be quickly replaced at the end of each run. A position-sensitive detector with a resolution of 256 points was located at the far end of a 120-cm-long evacuated tube. The beamstop was a 2-mm-thick tantalum rod of rectangular cross-section, placed just in front of the detector.

Sample blanks for background subtraction consisted of pure water contained in the same cell as for the sample measurement; this procedure ensured that sample and background had identical thickness. Each run lasting 2500 s was preceded and followed by a transmission measurement. For this, a thin sheet of amorphous carbon was placed in the beam downstream from the sample for a preset time (50 s); the strong scattering generated in this measurement yields the intensity of the incident beam transmitted by the sample, i.e., the product of the incident intensity I_0 and the sample transmission T. The corrected scattering signal from the sample is

$$I_{\mathrm{corr}}(Q) = I_{\mathrm{s}}(Q)/(I_{0\mathrm{s}}T_{\mathrm{s}}t_{\mathrm{s}}) - I_{\mathrm{b}}(Q)/(I_{0\mathrm{b}}T_{\mathrm{b}}t_{\mathrm{b}})$$

where s and b refer to the sample and background, respectively, and t is the duration of the experiment.

Results and Discussion

Macroscopic Measurements. In Figure 1 the osmotic pressure of the PVA solutions in the range $0.025 < \varphi < 0.18$ is plotted as a function of polymer volume fraction. The dotted line shows the least-squares fit of the experimental data to the equation

$$\Pi = (RT/v_1)[-\ln(1-\varphi) - \varphi + \varphi/x - \chi_1\varphi^2 - w\varphi^3] \qquad (11)$$

with parameters χ_1 = 0.485 and w = 0.241, taking RT/v_1 = 1.3764 × 10⁵ kPa and x = 840 (i.e., corresponding to M_n = 29 000). As described in the Experimental Section, the results shown in Figure 1 were obtained indirectly, by first measuring the swelling pressure of the gels against aqueous poly(vinylpyrrolidone) solutions and then measuring the osmotic pressure of the PVA solutions against the gels. Since this technique is more sensitive to errors at low osmotic pressures, in the fitting procedure for Figure 1 the molecular weight of the PVA was set equal to the value obtained directly by membrane osmometry.

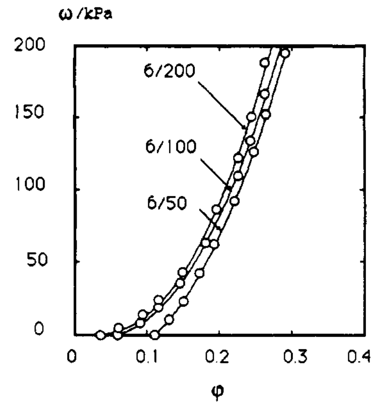

Figure 2. Variation of the swelling pressure, ω, as a function of polymer volume fraction for PVA/water gels. The continuous curves were calculated from eq 5 using the parameters listed in Table I.

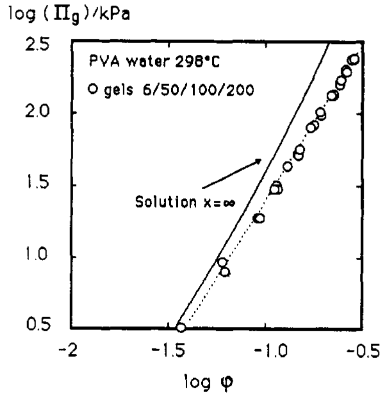

Figure 3. log-log plot of the mixing pressure, Π_g (=ω + G), calculated from swelling pressure and shear modulus data, as a function of polymer volume fraction for PVA/water gels (open circles). The slope of the dotted straight line is 2.15. The continuous line shows the concentration dependence of the osmotic pressure, Π, for a solution of the un-cross-linked polymer of infinite molecular weight ($x = \infty$).

At high polymer concentrations, eq 11 may be expected to describe the osmotic properties of a polymer solution somewhat better than the simple scaling relation (3). For the correlation length, however, which exhibits no singularity at $\varphi = 1$, and for which no mean field description exists, the scaling form is preferred in the interpolation procedures below. In principle, this apparent inconsistency could be removed with the approach of Muthukumar,[30] but the additional complication does not justify its use here.

In Figure 2 the variation of swelling pressure of three gel samples differing in cross-linking densities is displayed as a function of polymer volume fraction. In the classical picture of swelling, the osmotic component of the swelling pressure Π_g is identified with the osmotic pressure of a solution of the corresponding un-cross-linked polymer of infinite molecular weight. In Figure 3 the values of Π_g (=ω + G), obtained from swelling pressure and modulus measurements performed on the same PVA gel samples, are shown together with the calculated concentration

Table I
Swelling and Elastic Parameters of Poly(vinyl alcohol)/Water Gels at 25 °C

sample	φ_e	n	m	A_0/kPa	K_{os}/kPa[a]
6/50	0.1120	2.19	0.416	3561	52.3
6/100	0.0607	2.32	0.391	3738	10.8
6/200	0.0373	2.30	0.316	3573	3.7

[a] $K_{os}(\text{gel}) = \varphi(\partial\omega/\partial\varphi) = A_0\,(n - m)\varphi^n$.

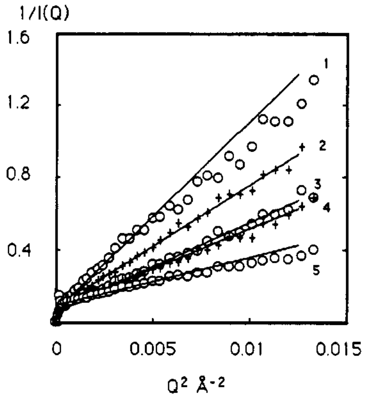

Figure 4. Zimm representation of corrected scattering spectra for five PVA/water solutions. Volume fractions: (1) 0.0246, (2) 0.0421, (3) 0.0673, (4) 0.0850, (5) 0.1314. To improve signal to noise ratio, the original data points have been averaged in sets of 5.

Table II
Scattering Parameters of Poly(vinyl alcohol)/Water Solutions

soln	vol fract φ	ξ/Å	$I(0)/10^3$
1	0.0246	50 ± 10	$20._5 \pm 3$
2	0.0421	$34._2 \pm 4$	$15._9 \pm 3$
3	0.0673	$26._5 \pm 3$	$14._5 \pm 3$
4	0.0850	$22._2 \pm 2$	$11._9 \pm 1$
5	0.1314	$13._7 \pm 3$	$8._8 \pm 3$

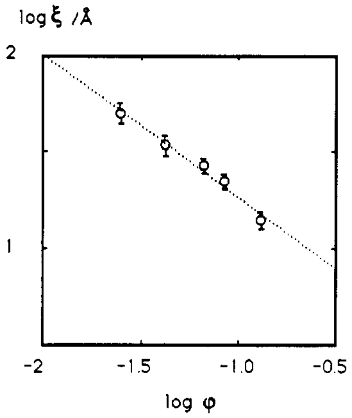

Figure 5. Double-logarithmic representation of the correlation length ξ as a function of polymer volume fraction φ for PVA/water solutions. The straight line represents the least-squares fit through the experimental points.

dependence of the osmotic pressure (eq 11), taking $x = \infty$. In the double-logarithmic plot of this figure, the values of Π_g scatter around a single straight line that is independent of the degree of cross-linking. Linear regression of these data yields a slope ($n = 2.15$) close to that predicted by scaling theory for good-solvent conditions. The two curves in the figure do not coincide, the solution data systematically lying above those of the gel. It is also apparent that the solution curve is steeper than that of the gel.

The above behavior is consistent with what has so far been observed for other network systems: in general, Π_g is lower in the gel than in the solution.[31-34] The decrease in the mixing contribution due to the cross-links is generally attributed to structural differences between the gel and the solution. In gels the mobility of the polymer segments is hindered by cross-links, and consequently the degree of freedom of the network chains is lower. In addition, in PVA/water solutions, aggregation of the dissolved PVA molecules is known to occur due to hydrogen bonding.[10] The relatively high value found here for the interaction parameter ($\chi = 0.484 + 0.241\varphi$) suggests that polymer–polymer contacts may be favored in aqueous PVA solutions. For the gels, it is reasonable to assume that the cross-links, which act like large side groups, hinder sterically the formation of aggregates.

To check the validity of eq 5 for the PVA hydrogels, a nonlinear least-squares fitting procedure with free variables A_0, n, and m was applied. Listed in Table I are the coefficients obtained from the best fit through the data points in the range $\varphi_e \leq \varphi < 0.2$ for each gel sample, where φ_e is the value of φ at swelling equilibrium. The continuous curves in Figure 2 are the resulting fits of $\omega(\varphi)$. The theoretical curves describe satisfactorily the experimentally determined values of ω over the whole concentration range. The exponent m slightly exceeds the value predicted by rubber elasticity theory ($m = {}^1/_3$).

Small-Angle X-ray Investigations. Figure 4 shows the Zimm plots of PVA/water solutions measured at five different concentrations. At small angles strong excess scattering is observed, causing the Zimm plots to be nonlinear. In the region $Q \geq 0.02$ Å^{-1}, however, straight-line behavior is recovered (Figure 4). The correlation lengths ξ and intensities $I(0)$ estimated from linear least-squares fits through the experimental points in the region $Q\xi \leq 1$ are displayed in Table II.

In Figure 5 ξ vs φ is shown in a double-logarithmic representation. Within experimental error the correlation length follows a power law behavior. The least-squares fit through the data points yields the equation

$$\log \xi = 0.530 \pm 0.08 - (0.74 \pm 0.06) \log \varphi \qquad (12)$$

i.e.

$$\xi = (3.39 \pm 0.07)\varphi^{-0.74\pm0.06}\ \text{Å} \qquad (12')$$

The exponent determined from the slope of the resulting straight line is close to the value (−0.77) expected from scaling theory, although the uncertainty, due to the small number of samples investigated, is somewhat large.

According to eq 7 the concentration dependence of the scattering intensity of a polymer solution is governed by the quantity φ^2/K_{os}. The compressional modulus of the polymer solution, $K_{os} = \varphi(\partial\Pi/\partial\varphi)$, is known from the concentration dependence of the osmotic pressure. At fixed scattering conditions, for a given polymer–solvent system the factor $a(\rho_p - \rho_s)^2$ is constant. A comparison between the calculated and the measured intensities thus yields this constant factor. In Figure 6, the dependence of φ^2/K_{os} calculated from eq 11 is plotted as a function of φ (continuous curve) in a double-logarithmic representation. The measured intensities $I(0)$ shown (crosses) have been shifted down the vertical logarithmic scale of this figure to give coincidence with the calculated curve. The best fit was obtained by applying a shift factor of −4.95 with respect to our experimental SAXS intensity scale. It can be seen that both $I(0)$ and φ^2/K_{os} display the same dependence on polymer concentration.

In Figure 7 the scattering spectra of three fully swollen PVA gels (6/50, 6/100, and 6/200) are shown together with the spectrum of a solution ($\varphi_{sol} = 0.1314$). This

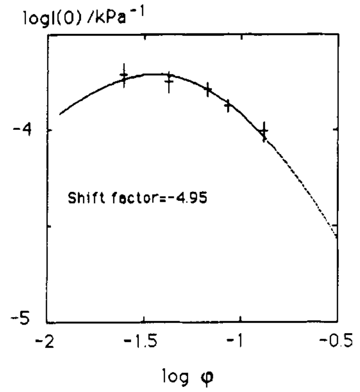

Figure 6. Double-logarithmic representation of $\varphi/(\partial\Pi/\partial\varphi)$ (kPa^{-1}) calculated from the osmotic pressure data shown in Figure 1 (continuous line) vs polymer volume fraction φ. Crosses: observed SAXS intensity data for PVA/water solutions, shifted down the vertical axis by a constant logarithmic factor −4.95.

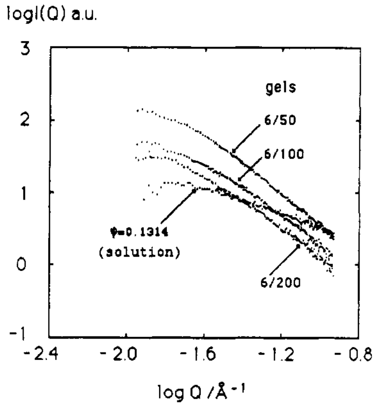

Figure 7. Small-angle X-ray scattering (SAXS) spectra of three fully swollen PVA/water gels and that of a PVA/water solution (φ = 0.1314).

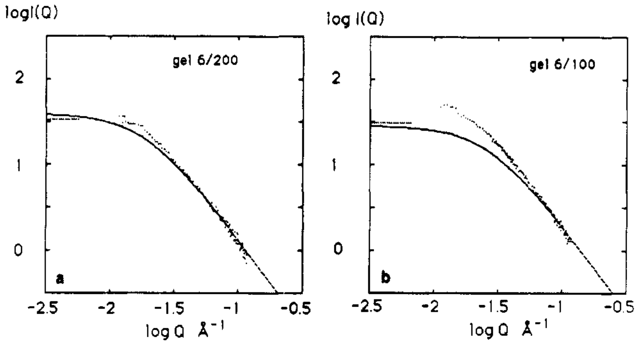

Figure 8. Spectra of PVA hydrogels 6/200 (a) and 6/100 (b) (experimental points). Continuous lines: spectra of solutions with φ chosen so that the high-Q region of the spectra matches the gel. Dotted bars at left on vertical axis correspond to the values of φ^2/K_{os} calculated from the swelling pressure data of each gel, taking $K_{os}(\text{gel}) = \varphi(\partial\omega/\partial\varphi)$.

solution line crosses all three gel curves: at low Q values the solution intensity falls below the gel curve, while at higher Q values the solution signal exceeds that of the gel. Although the data do not extend to large enough Q vectors to observe a complete crossing of the spectra of gel 6/50 and solution 5, such behavior is common for gels and solutions of the same concentration.[11,14-16] The excess scattering from the gels at small Q betrays the presence of large static scatterers in the system. As noted above, introduction of cross-links causes the polymer segments to rearrange: polymer-rich and polymer-depleted regions develop. As the distribution of the polymer in the gel differs from that of the solution, simple correspondence between their respective scattering spectra is not expected: only a certain fraction of the network polymer is likely to exhibit solution-like behavior. This view implies that the effective concentration φ_{eff} that controls the thermodynamic properties of the gel will be smaller than the overall polymer concentration. The purpose of the rest of this analysis is to estimate the solution-like component of the gel spectra.

Table III
Characteristics of Poly(vinyl alcohol)/Water Gels Measured by SAXS

sample	vol fract φ	$I(0)/10^3$	ξ/Å	equiv vol fract φ_{eff}	$\langle\delta\varphi^2\rangle \times 10^3$
6/200	0.0373	39	53	0.023	0.08
6/100	0.0607	28	37	0.039	0.53
6/50	0.1120	16	21	0.084	3.87

The method adopted here to resolve this component is to require that the solution and the gel spectra coincide in the high-Q region, i.e., where the intensity scattered by the static nonuniformities in the gel is expected to become negligibly small. Combining eqs 7, 8, and 11 yields the Ornstein–Zernicke scattering function

$$I(Q) = a(\rho_p - \rho_s)^2 \frac{v_1}{N_A}\left(\frac{1}{\frac{1}{1-\varphi} - 2\chi_1 - 3w\varphi}\right)\left(\frac{1}{1 + Q^2\xi^2(\varphi)}\right) \quad (13)$$

where N_A is Avogadro's number. χ_1 and w are given their values found in solution, and x has been set equal to ∞; ξ is given by eq 12. By varying φ, this solution-like signal is adjusted until the required coincidence is obtained. This procedure yields φ_{eff}, the effective solution concentration. Figure 8 shows the resulting solution-like parts of the scattering signals for gel samples 6/200 (Figure 8a) and 6/100 (Figure 8b). The continuous curves are the solution spectra for interpolated concentrations φ_{eff} = 0.023 and φ_{eff} = 0.039, respectively. The data listed in Table III confirm the expectation that the effective concentration is lower than the mean polymer concentration in the fully swollen networks.

With this estimate of the solution-like part of the spectrum, the permanent concentration deviations, described by the static part of the gel spectra, can in turn be evaluated. The quantity $\langle\delta\varphi^2\rangle$ may be determined by numerical integration of the difference in scattering intensities between the gel signal and that of the effective solution; i.e.

$$2\pi^2 a(\rho_p - \rho_s)^2\langle\delta\varphi^2\rangle = \int_0^\infty (I_g(Q) - I_s(Q))Q^2\,dQ \quad (14)$$

where I_g and I_s are the scattering intensities of the gel and solution-like spectrum, respectively, and the factor $a(\rho_p - \rho_s)^2$ is accounted for in the normalization procedure in Figure 6. The values obtained for $\langle\delta\varphi^2\rangle$ are shown in the last column of Table III. According to these data, the relative mean square amplitude of the static concentration fluctuations $\langle\delta\varphi^2\rangle/\langle\varphi\rangle^2$ varies from 6% for sample 6/200 to 31% for sample 6/50. The contribution from static inhomogeneities is thus seen to increase strongly with cross-linking density. These values of $\langle\delta\varphi^2\rangle/\langle\varphi\rangle^2$, although somewhat higher than found in end-linked poly(dimethylsiloxane) gels swollen in toluene,[14] are comparable with measurements made in homologues of the present gels (poly(vinyl acetate) swollen in toluene[15] and in acetone[16]). The latter, prepared by cross-linking PVA gels and then acetylating the resulting gel,[26] should have closely similar topological properties. In principle, because $\langle\delta\varphi^2\rangle$ depends on the details of the cross-linking, such similarities between gel homologues are to be expected.

The swelling pressure data, obtained independently, allow a comparison between the osmotic properties of the gels and the osmotic modulus governing the scattering intensity of the solutions. In Figure 8 the values of $\varphi^2/K_{os}(\text{gel})$, calculated from the parameters listed in Table I, are shown as broken horizontal lines intersecting the vertical axis. In view of the indirectness of the measurements employed in this investigation, the agreement between the calculated and the estimated values is quite satisfactory.

Conclusions

The osmotic and SAXS behaviors of chemically cross-linked poly(vinyl alcohol) hydrogels are investigated and compared with those of the corresponding polymer solutions.

The swelling pressure of the PVA gels in the lower range of concentration is satisfactorily described by a two-term equation consisting of an elastic and a mixing contribution. The mixing term for the cross-linked polymer differs from that of the solution and seems to be consistent with the concentration dependence predicted by scaling theory.

Absolute scattering intensities were obtained by normalizing the SAXS spectra by means of osmotic pressure data obtained for PVA solutions. The correlation length in the polymer solution displays a simple power law dependence on concentration, the exponent lying close to the value expected theoretically for excluded volume conditions.

The gel scattering spectra are decomposed into a solution-like part and a static part. The zero-angle scattering intensity of the solution-like component is in satisfactory agreement with that estimated from macroscopic swelling pressure measurements. The second moment of the gel scattering spectra reveals that the amount of static nonuniformities strongly increases with the cross-linking density.

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(36) For polymer solutions it is often found that $I(Q)/\varphi$ is independent of concentration in the region $Q\xi > 1$, since in scaling theories of semidilute solutions,[20] $I(Q)$ is proportional to $\varphi Q^{-1/\nu}$, where ν is the excluded volume exponent. Although ν is a function of the scaling regime, it is sometimes concluded that $I(Q)/\varphi$ is an alternative invariant. This is not a general result: swollen gels that exhibit excess scattering at small values of Q will, by virtue of relation 10′, scatter less strongly at high Q than a polymer solution of the same composition.