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Small Angle Neutron Scattering in Poly(vinyl alcohol) Hydrogels

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ABSTRACT: Neutron and light scattering observations are reported for chemically cross-linked poly(vinyl alcohol) hydrogels differing in cross-link density and for the corresponding semidilute polymer solution. The small angle neutron scattering spectra could be decomposed into a static and a dynamic component, the former being assumed to follow an Ornstein–Zernike form and the latter a stretched exponential. Macroscopic swelling pressure and shear modulus measurements were also performed on the same gels to provide an estimate of the scattering from dynamic concentration fluctuations in the zero wave vector limit. Introduction of cross-links increases the amplitude of the static concentration fluctuation component. The fluctuating part of the scattered intensity, independently determined by quasi-elastic and static light scattering measurements, is in close agreement with that estimated from the dynamic contribution of the neutron spectra.

Introduction

Several investigations have been reported recently on the structure of aqueous poly(vinyl alcohol) (PVA) solutions and their gels.[1–4] This system exhibits superstructures on variable length scales that depend on the conditions of preparation and storage of the sample. In aqueous solutions, clustering of the chains is caused primarily by association between the polar groups of the dissolved polymer. Such clusters tend to scatter radiation strongly, thereby complicating the analysis of the thermodynamic parameters of these systems.

In this paper we analyze the scattering spectra of a set of PVA hydrogels, differing only in their degree of cross-linking. An attempt is made to determine the thermodynamically active component of the scattering signal.

To obtain information from a wide range of characteristic length scales $1/Q$ (Q being the transfer wave vector), different scattering techniques are used: small angle neutron scattering and static and dynamic light scattering. In addition, the macroscopic osmotic properties of the gels are measured, in order to estimate the parameters that control the thermodynamic response of the system at large length scales.

Background

Scattering from Polymer Solutions and Gels. In a neutral polymer solution above the coil overlap concentration the intensity of scattered radiation is inversely proportional to the osmotic compression modulus $K_{os} = \varphi(\partial\Pi/\partial\varphi)$,[5]

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

where a is a constant, Q is the scattering wave vector, Π is the osmotic pressure, ξ is the density–density correlation length, and $(\rho_p - \rho_s)^2$ is the contrast factor between the polymer and solvent.

In a gel, because of its finite elasticity, the dynamics of the concentration fluctuations are governed no longer just by the osmotic compression modulus, but by the longitudinal osmotic modulus.[6]

$$M_{os} = \varphi\partial\omega/\partial\varphi + (4/3)G \qquad (2)$$

where ω is the swelling pressure and G the elastic modulus of the swollen network.

M_{os} can be estimated from measurements of the swelling pressure and of the elastic modulus as a function of concentration.

Experimental Section

Gel Preparation. Gels were prepared by cross-linking PVA in aqueous solutions with glutaraldehyde at pH = 1.5 using a method described elsewhere.[7] For the experiments a fractionated polymer sample was used ($M_w^{PVA} = 110\,000$). Cross-links were introduced at polymer concentrations $c = 5.5\%$ w/w. The molar ratio of monomer units to the molecules of cross-linker was 100, 200, and 400, corresponding to cross-link densities of 0.01, 0.005, and 0.0025, respectively.

For the calculation of the polymer volume fractions φ, the densities of the pure components ($\rho_{PVA} = 1.269$ g cm^{-3} and $\rho_{water} = 0.9971$ g cm^{-3}) were used.

Osmotic and Mechanical Measurements. The swelling pressure of the gels was measured as a function of the polymer concentration using a modified deswelling method.[8] The gels were equilibrated with aqueous solutions of poly(vinylpyrrolidone) ($M_n = 29\,000$) of known osmotic pressure.[9]

The additivity of the specific molar volumes of the solvent and the solute in the cross-linked polymer was checked both pycnometrically and optically (the dimensions of regularly shaped samples were measured at different stages of dilution by weighing and using a comparator). In the concentration range $0.02 < \varphi < 0.20$ no systematic deviation from additivity was observed.

The shear modulus measurements were performed on isometric cylindrical gel specimens. Swollen networks were uniaxially compressed (at constant volume) between two parallel flat plates.

Light Scattering Measurements. Static light scattering measurements were made in the angular range 30–150° using an ALV/SP-86 automatic goniometer (ALV, Langen, Germany) at 25 °C. The 647.1-nm wavelength light was supplied by a Spectra Physics 2020 Krypton ion laser working at 300 mW. Intensity correlation functions were measured by an ALV-3000 multibit correlator (ALV, Langen, FRG).

The solution and the gel samples were prepared in Hellma test tubes of inner diameter 8 mm. Dust was removed from the homogeneous solutions by filtering them through Teflon filters

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Table 1. Measured Shear Modulus G and Parameters of Eq 3 for PVA Hydrogels at $\varphi = 0.0434$ at Different Cross-Link Densities

cross-link density[a]	G/kPa	A/kPa	n	m	M_{os}/kPa[b]
0.01	3.57	3389	2.16	0.42	11.8
0.005	3.10	3384	2.25	0.33	9.6
0.0025	1.27	3656	2.16	0.28	10.1

[a] Ratio of the number of molecules of cross-link agent to the number of monomer units of polymer. [b] Calculated using $M_{os} = An\varphi^n + G$.

of 0.45-μm pore size. The absolute intensity was calibrated using pure toluene.

To ensure correct spatial averaging of the speckle pattern in the static light scattering measurements, the tubes were rotated slowly[10] (ca. 1 revolution/min). In the dynamic measurements both the intensity correlation function and the static scattered intensity were recorded simultaneously at various fixed positions of the sample.

The coherence factor of the optical detection, measured using a sample consisting of a dilute polystyrene latex,[11] was $\beta = 0.93 \pm 0.02$.

Small Angle Neutron Scattering Measurements. The SANS measurements were performed at the Institut Laue-Langevin, Grenoble, on the D11 instrument with an incident wavelength of 6 Å. The sample–detector distances used were 4 and 16.5 m, corresponding to an explored Q range of $0.003\ \text{Å}^{-1} \leq Q \leq 0.25\ \text{Å}^{-1}$. The ambient temperature during the experiments was 25 ± 1 °C.

Heavy water was used as the solvent. The sample cell consisted of 1-mm-thick quartz windows separated by a 1.8-mm-thick Viton O-ring. After radial averaging, corrections for incoherent background, detector response, and cell window scattering were applied.[12] The neutron scattering intensities were calibrated using the absolute intensity measurements of Ragnetti et al.[13]

Results and Discussion

Osmotic and Mechanical Measurements. In Table 1 are listed the measured values of the shear modulus G for the three gels of different cross-link densities.

To obtain the bulk osmotic compression modulus $\varphi(\partial\omega/\partial\varphi)$, the experimental data from measurements of the swelling pressure ω as a function of polymer volume fraction φ were fitted to an expression of the form[14]

$$\omega = A\varphi^n - B\varphi^m \qquad (3)$$

The first term of eq 3 is the pressure of mixing, while the second is the bulk elastic modulus of the network. From the condition of equilibrium with the pure solvent ($\omega = 0$, $\varphi = \varphi_e$), it follows that $B = A\varphi_e^{n-m}$. For gels that exhibit reversible swelling behavior, the theoretical expectation for the values of the exponents are[15] $m = {}^1/_3$ and, in semidilute excluded volume conditions,[5] $n \approx 2.25$.

In Figure 1 the curves of swelling pressure vs polymer volume fraction are shown for the PVA–water gels of highest and lowest cross-link density, together with the concentration dependence of the osmotic pressure of the solution of the un-cross-linked polymer of infinite molecular weight. The lines through the gel data points are the calculated least squares fits to eq 3. The corresponding values of the fitting parameters A, n, and m are also listed in Table 1. It can be seen that A is almost independent of cross-link density, indicating that it is a characteristic of the polymer–solvent pair.

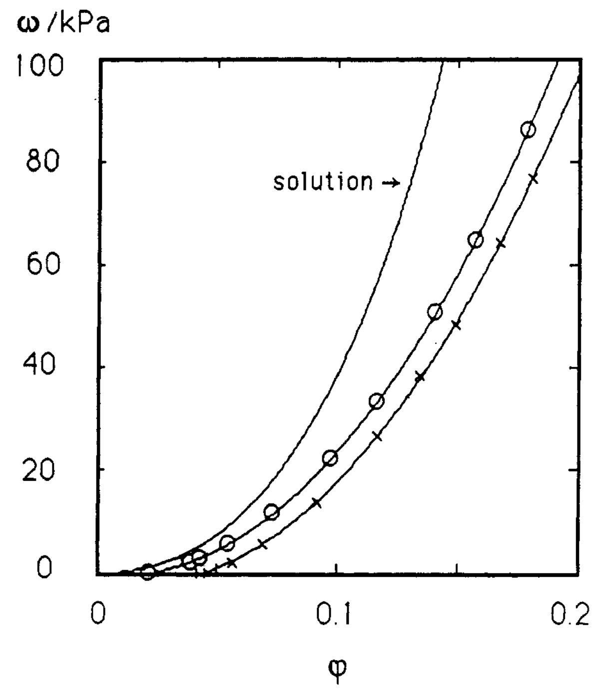

Figure 1. Measured swelling pressure ω as a function of polymer volume fraction φ for two PVA hydrogels: (○) cross-link density 0.0025; (×) cross-link density 0.01. The continuous lines through the experimental points are the least squares fits to eq 3, with the parameters listed in Table 1. The solution curve, which shows the concentration dependence of the osmotic pressure of the infinite molecular weight PVA, is taken from ref 3.

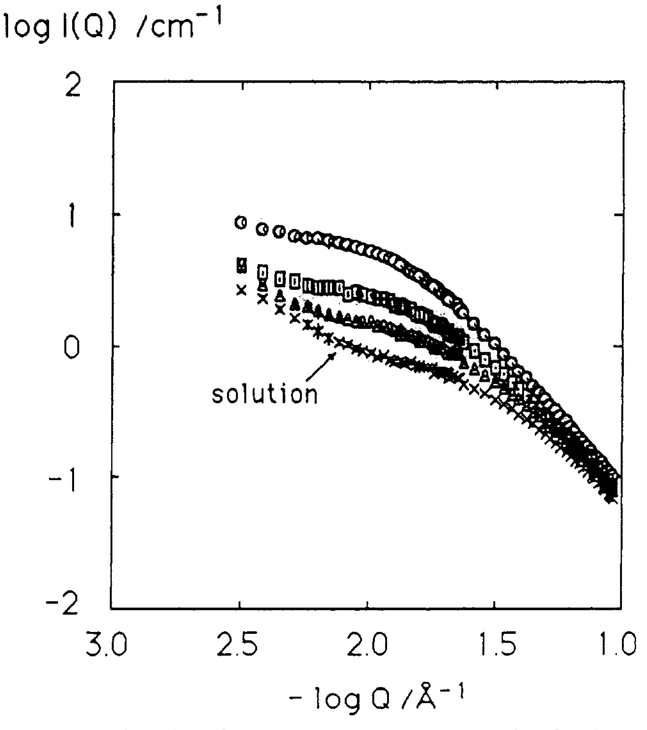

Figure 2. Small angle neutron scattering curves for the three PVA water gels at $\varphi = 0.0434$ and for the corresponding solution of molecular weight M_w = 110 000 (crosses). Cross-linking density: (triangles) 0.0025; (squares) 0.005; (circles) 0.01.

In Figure 2 the neutron scattering spectra of the three PVA gels are shown as a function of Q as is the spectrum of the solution at the same concentration. The scattering intensity at small Q increases systematically with increasing cross-link density; i.e. cross-linking of the chains is accompanied by large-scale nonuniformities. A similar behavior has been reported for other systems.[16–18] It is apparent even for the solution spectrum that the spatial distribution of the segments is not uniform in the low **Q** region: this phenomenon has been observed by several authors[1–3,19–21] and is attributed to supermolecular structures (clusters, associations) that form primarily owing to hydrogen bonding between PVA chains. It is interesting to note in Figure 2 that, unlike poly(vinyl acetate) gels swollen in acetone[2] (excellent solvent conditions), the gel spectra and the solution spectra do not cross each other in the Q range explored here.

In general, the intensity scattered by the inhomogeneities can greatly exceed that from the thermodynamic concentration fluctuations. Consequently, it becomes unreliable to extract thermodynamic information in these systems from the total static scattering response alone. Below, we apply a procedure to separate out the static component of the neutron scattering spectra of the gels in order to estimate the dynamic component. The latter will be compared with the results of independent osmotic and quasi-elastic light scattering observations on the same system.

In many gel systems the total scattered intensity can be treated as the sum of a static and a dynamic component,[18,22-24]

$$I_{\mathrm{tot}}(Q) = I_{\mathrm{S}}(Q) + I_{\mathrm{D}}(Q) \tag{4}$$

As proposed previously,[22,23] the dynamic contribution is here assumed to adopt a liquidlike structure factor, given by the Ornstein–Zernike form of eq 1. For the static component, it has been found in several gel systems that $I_{\mathrm{S}}(Q)$ is reasonably described over the available range of neutron scattering vectors by the stretched exponential

$$I_{\mathrm{S}}(Q) = 2\pi^2 s(\rho_{\mathrm{p}} - \rho_{\mathrm{s}})^2\{\langle\delta\varphi^2\rangle/\Gamma(3/s)\}\Xi^3 \exp[-(Q\Xi)^s] \tag{5}$$

where $\langle\delta\varphi^2\rangle$ is the mean square amplitude of the static concentration fluctuations, Ξ is their average radius, and $\Gamma(x)$ is the gamma function. The exponent s depends on the particular distribution of the network nonuniformities: in the case of randomly cross-linked poly(vinyl acetate) networks,[23] it was found that $s \approx 0.7$.

In Figure 3 the neutron scattering spectrum of the gel 5.5/200 (i.e. a gel prepared at the polymer concentration 5.5 g/g with an average of 1 molecule of cross-linker/200 monomer units) is displayed (open circles). The line through the neutron data points is the least squares fit to eq 4. The lower line is the dynamic component $I_{\mathrm{D}}(Q)$ belonging to this fit. Table 2 lists the values of the parameters obtained for this fitting procedure for the gels as well as for the un-cross-linked PVA solution. Inspection shows that the intensity of the dynamic component varies rather weakly with the cross-link density; i.e. cross-linking makes its influence felt primarily in the static scattering intensity. It is also apparent that the thermodynamic correlation length ξ increases with the cross-link density. This effect has already been observed in other gel systems and attributed to the redistribution of the polymer into more and less concentrated regions in the gel.[16,25] Further inspection of Tables 1 and 2 reveals that the pure osmotic compressibility K_{os} (where $K_{\mathrm{os}} = \varphi(\partial\omega/\partial\varphi) + G/3 = M_{\mathrm{os}} - G$) is lower in the gels than in the solution of the same concentration; this result is consistent with Figure 1.

An independent estimate of the fluctuating intensity can be made using quasi-elastic light scattering.[26,27] The initial amplitude of the time correlation function yields the fraction of the dynamic component in the total scattered light. In a system containing large stationary nonuniformities acting as a local oscillator, the heterodyned intensity correlation function is given by[27]

$$G(Q,\tau) = 1 + \beta[2X(1 - X)g(Q,\tau) + X^2 g(Q,\tau)^2] \tag{6}$$

where $g(Q,\tau)$ is the normalized field correlation function, β is the coherence factor (see Experimental Section), τ is the delay time, and X is the ratio of the time-averaged intensity of the fluctuating component to that of the total scattered intensity.

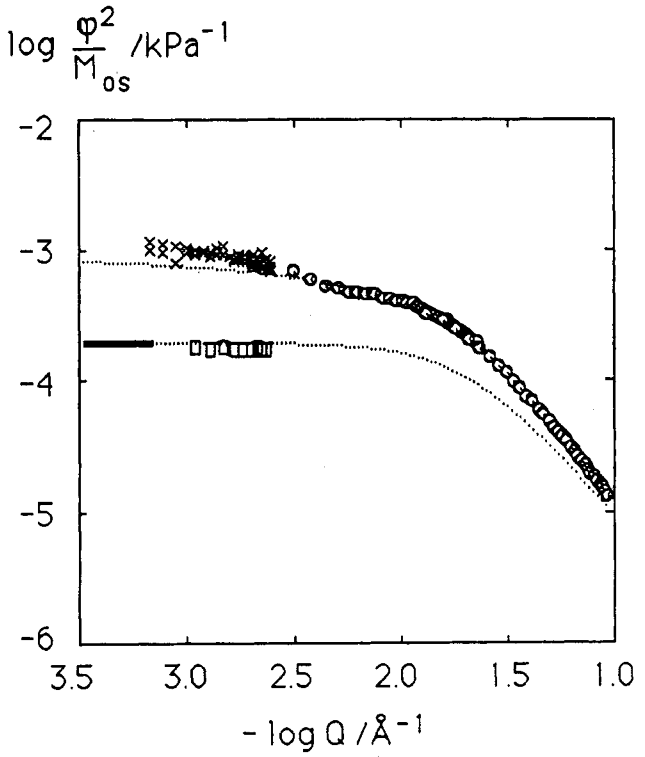

Figure 3. Scattering intensity, expressed as $\varphi^2/M_{\mathrm{os}}$, for a PVA gel with cross-link density 0.005, in a double logarithmic plot as a function of transfer wave vector Q: neutron scattering (○); static light scattering (×); dynamic light scattering (□). The lower curve is the calculated dynamic component of the neutron spectrum; the upper curve is the best fit of the neutron data to eq 5. The bold horizontal line on the left hand side is the intensity corresponding to the thermodynamic limit calculated from the swelling pressure and elastic modulus data in Table 2.

Table 2. Scattering Parameters for Fit of Neutron Spectra to Eq 5 with s = 0.7

cross-link density[a]	$I_{\mathrm{D}}(0)$/cm^{-1}	$I_{\mathrm{S}}(0)$/cm^{-1}	ξ/Å	Ξ/Å	$10^3\langle\delta\varphi^2\rangle$
0.01	0.95	12.7	48	117	3.2
0.005	1.18	4.3	47	117	1.1
0.0025	1.07	3.4	40	218	0.14
solution	0.96		38		

[a] Ratio of the number of molecules of cross-link agent to the number of monomer units of polymer.

In Figure 3 the square symbols show the absolute intensities of the dynamically scattered light for the gel 5.5/200. The crosses represent the corresponding absolute intensities of the total scattered light. The three sets of results from neutron and static and dynamic light scattering shown in Figure 3 are independent and are expressed in the same units, using for the neutron contrast factor the calculated value[28] for this system, $(\rho_{\mathrm{p}} - \rho_{\mathrm{s}})^2 = 1.49 \times 10^{21}$ cm^{-4}. No adjustable scale factor has been used. The neutron and static light scattering spectra match reasonably, although it is apparent that in the very low Q region the experimental spectrum deviates from the simple phenomenological function of eq 5. For the thermodynamic component, the intensity of the quasi-elastically scattered light lies close to that estimated from the decomposition of the neutron scattering signal.

According to general fluctuation theory, the scattering intensity arising from thermodynamic fluctuations is inversely proportional to the longitudinal osmotic modulus (eq 1). The latter quantity can be deduced from the concentration dependence of the macroscopic swelling pressure (cf. Table 1). The thick horizontal line on the left hand side of the Figure 3 shows the value of φ^2/M_{os} calculated in this way for this sample. The numerical value agrees satisfactorily with that obtained both from the quasi-elastic light scattering and from decomposition of the neutron spectrum.

Conclusions

The results of small angle neutron scattering and static light scattering measurements in the gels indicate that, as has been seen in other systems, the scattering intensity at low Q values increases significantly with increasing cross-link density. The presence of cross-links does not, however, profoundly affect the dynamic component of the total scattered intensity.

The values estimated from the neutron spectra for the dynamic scattering intensity are in agreement with the results of the quasi-elastic light scattering observations. In addition, reasonable agreement is found between the latter and the zero Q intensity limit obtained from macroscopic osmotic and mechanical measurements.

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