Osmotic and scattering properties of polymer gels containing free chains

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Measurements are made of the osmotic swelling pressure and small angle X-ray scattering from lightly crosslinked poly(vinyl acetate) (PVAc) gels swollen in toluene and containing known amounts of free PVAc chains. Gels with different amounts of free chains, but with identical total polymer concentration, exhibit similar behaviour. The differences observed between the thermodynamic properties of the gels and the solutions are consistent with a reduction in the fraction of polymer participating in the dynamic concentration fluctuations.

Introduction

A few investigations have been reported into the effect of free polymer chains on the thermodynamics of swollen polymer networks (semi-interpenetrating networks)[1-4]. It has been found that the penetration of polymer chains in a chemically identical host matrix can be appreciable. Bastide et al.[5] derived an expression for the partition coefficient of the mobile chains on the basis of a scaling argument.

In general, the interpretation of the experimental results from such ternary systems (crosslinked polymer/mobile chains/solvent) is based on the Flory-Rehner theory of network swelling[6]. The assumptions of this theory have, however, been questioned by several authors[7-10]. It has been found that the Flory-Huggins interaction parameter for the pure swollen network is usually significantly higher than in the corresponding uncrosslinked system, i.e. the osmotic pressure of mixing of the network chains is smaller than that of a solution of the same polymer at identical concentration.

The intensity of radiation scattered at small angles by thermodynamic concentration fluctuations is governed by the osmotic properties. By combining osmotic and scattering measurements, complementary information is obtained on the thermodynamics of ternary systems both on a macroscopic and on a molecular level.

Here we report measurements of the swelling pressure and elastic modulus of poly(vinyl acetate) (PVAc) gels swollen in toluene and containing varying amounts of linear PVAc chains. The dynamic component of the concentration fluctuations was determined from small angle X-ray scattering (SAXS) measurements. Comparisons of the osmotic properties obtained by these two techniques are made: (i) between the gel and the solution, and (ii) among gels with different free polymer chain content.

Theoretical background

In the framework of the Flory-Rehner theory[6], the swelling pressure of a polymer gel may be expressed as

$$\omega = -\{(RT/v)[\ln(1-\varphi)+\varphi+\chi\varphi^2+w\varphi^3]+G\} \quad (1)$$

where G is the elastic modulus of the swollen network, v is the molar volume of the solvent, φ is the volume fraction of the polymer, and χ and w are the second- and third-order interaction parameters, respectively.

The scattering intensity from a polymer solution is governed by the amplitude of the concentration fluctuations, $\langle\Delta\varphi^2\rangle$, which is inversely proportional to the osmotic compressional modulus $K_{os}(=\varphi\ \partial\Pi/\partial\varphi$, where Π is the osmotic pressure). The resulting X-ray scattering intensity $I(Q)$ is given by[11]:

$$I(Q)=a\frac{kT(\rho_p-\rho_s)^2\varphi^2}{K_{os}}\frac{1}{1+Q^2\xi^2} \quad (2)$$

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, ξ is the polymer correlation length and $Q=(4\pi/\lambda)\sin(\theta/2)$ is the transfer wave-vector at incident wavelength λ and scattering angle θ.

For swollen networks, the osmotic compressional modulus in equation (2) should be replaced by the longitudinal osmotic modulus[12]:

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

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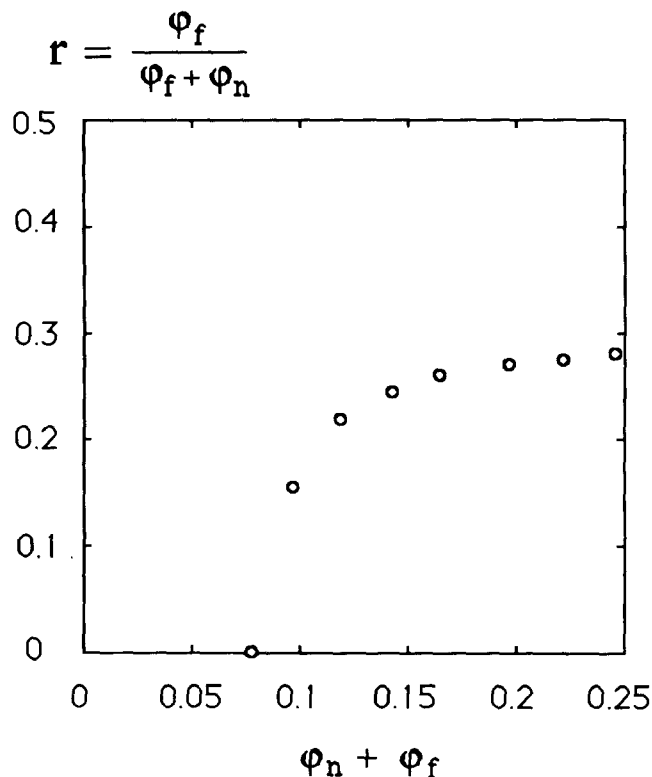
$$r = \frac{\varphi_f}{\varphi_f + \varphi_n}$$

Figure 1 Variation of the fraction $r = \varphi_f/(\varphi_f + \varphi_n)$ of free chains in a PVAc–toluene gel as a function of total polymer content $(\varphi_n + \varphi_f)$. φ_f is the volume fraction of free polymer chains and φ_n that of the network polymer

Experimental

The preparation of the PVAc gels used in the present investigation has been described previously[3]. The ratio of the number of monomer units to crosslinker was 200, yielding $\varphi = 0.078$ for the polymer volume fraction in equilibrium with pure toluene at 25°C.

The swelling pressure of the gels was measured as a function of φ. Gel samples were allowed to come to equilibrium with PVAc–toluene solutions $(M_w = 130\,000)$ of known osmotic pressure[13]. Two types of deswelling measurements were performed: (i) with gels separated from the polymer solution by a semipermeable membrane, thus preventing diffusion of the polymer molecules into the swollen network; and (ii) with gels placed directly in contact with the polymer solutions.

Shear modulus measurements were carried out on cylindrical gel specimens at different stages of dilution. The samples were uniaxially compressed (at constant volume) between two parallel flat plates. The stress–strain data were determined in the range of deformation ratio $0.7 < \Lambda < 1$. Neither volume change nor barrel distortion was detected.

The X-ray scattering measurements were made on the D24 instrument on the DCI synchrotron at LURE, Orsay. The wavelength used was 1.608 Å. In the present experiments, the beam size at the sample was 3 mm × 0.5 mm. The samples were contained between thin mica windows sealed in an air-tight holder that minimized solvent evaporation. The separation between the windows was 1 mm. An 18 cm linear gas-filled detector with 512 channels was used. Spectra were accumulated in 1800 s, and pure toluene was used as the blank for background subtraction. Transmissions were measured by inserting a thin sheet of amorphous carbon in the beam behind the sample[14].

The sample temperature for all measurements was 25°C.

Results and discussion

In *Figure 1* the ratio $r = \varphi_f/(\varphi_n + \varphi_f)$ (where φ_n is the volume fraction of the network polymer and φ_f that of the free chains in the gel) is shown as a function of the total polymer volume fraction, $(\varphi_n + \varphi_f)$. The ratio r increases with increasing total polymer concentration and, at the highest concentration investigated, r reaches almost 0.3.

Figure 2 shows the variation of the swelling pressure ω as a function of total polymer volume fraction $\varphi = \varphi_n + \varphi_f$ of a PVAc gel in direct contact with the surrounding polymer solution. The curve through the experimental points is the least-squares fit to equation (1), where $\chi = 0.4468$ and $w = 0.3706$. Also displayed is the concentration dependence of the swelling pressure of the same PVAc gel, without free chains present. It is apparent that, within experimental uncertainty, these two sets of data coincide. This finding implies that the free chains in the gel adopt the same interaction parameter as the crosslinked polymer.

In the same figure, the concentration dependence of the sum

$$\Pi_{gel} = \omega + G \qquad (4)$$

for the gel is compared with that of the osmotic pressure of the solution (in the limit of infinite molecular weight), Π. It can be seen that $\Pi_{gel} < \Pi$, i.e. the apparent value

ω, Π /kPa
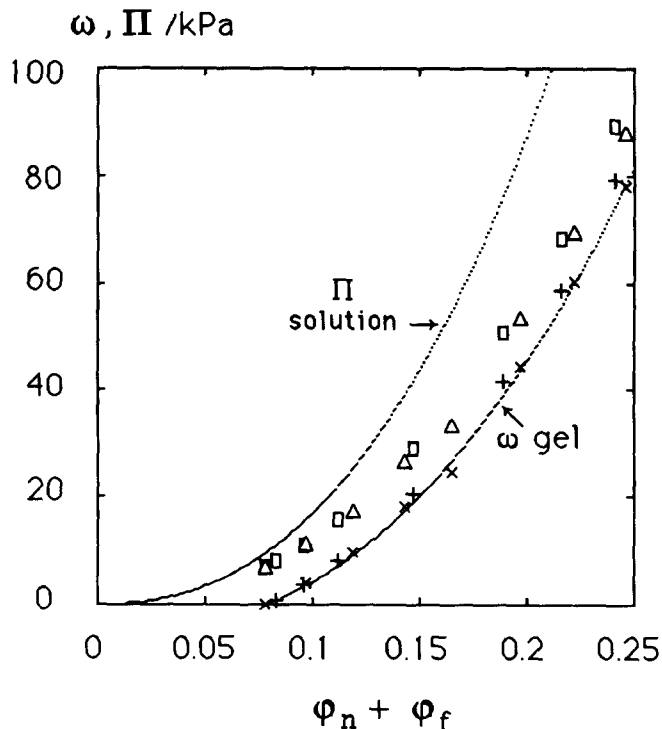
Figure 2 Swelling pressure of the PVAc–toluene gel as a function of total polymer content $(\varphi_f + \varphi_n)$. +, Gel without free chains $(\varphi_f = 0)$; ×, gel containing free chains, with φ_f as shown in *Figure 1*. Lower curve, least-squares fit to equation (1) through the ternary gel data points. Upper curve, variation of the osmotic pressure of the PVAc–toluene solution at infinite molecular weight, from ref. 13. □, $\omega + G$ for gels without free chains; △, $\omega + G$ for gels containing free chains

log I(Q) /kPa^{-1}

log I(Q) /kPa^{-1}
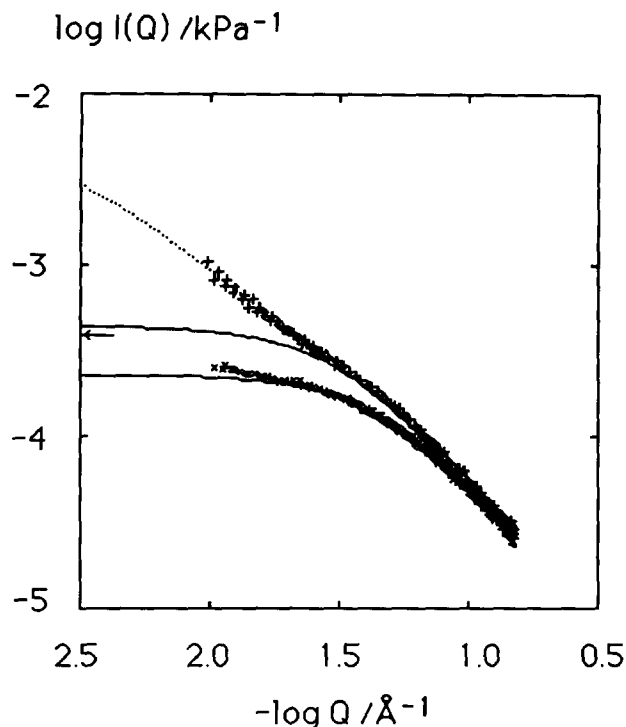
Figure 3 SAXS spectra for a PVAc–toluene gel ($\varphi_f = 0$) at polymer volume fraction $\varphi_n = 0.137$ (+), and for a solution at $\varphi = 0.117$ (×). The dotted line is the best fit of equation (5) to the gel data points, and the upper continuous curve shows the contribution from the dynamic concentration fluctuations, $I_d(Q)$. The arrow at the origin indicates the intensity $\varphi^2/(\varphi\, \partial\omega/\partial\varphi + 4G/3)$ calculated from the osmotic and mechanical measurements. The lower continuous curve is the fit of equation (2) to the solution spectrum

Figure 4 Comparison between SAXS spectra of a PVAc–toluene gel at the same overall concentration $\varphi_f + \varphi_n = 0.204$, with different free chain fractions, $r = 0$ (×) and $r = 0.24$ (+). The continuous line is the dynamic contribution of the scattering intensity $I_d(Q)$ obtained from the fit of equation (5) to the scattering spectra. For these two samples, $I_d(Q)$ is indistinguishable
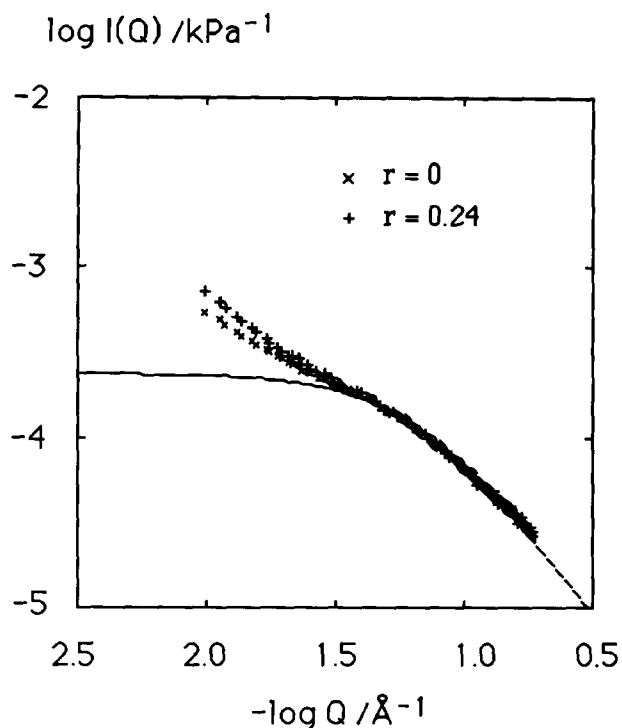
of the interaction parameter $\chi + w\varphi$ is larger in the gel than in the solution. This finding is surprising in view of the fact that the swelling pressure of the ternary gel (i.e. containing free chains) is indistinguishable from that of the corresponding binary gel.

To investigate this apparent discrepancy, SAXS measurements were made in a series of gel samples at fixed total polymer concentration, but with a variable ratio of free chains, r.

A comparison was made between a free solution and a binary gel at a similar concentration. *Figure 3* shows the SAXS spectra for a PVAc–toluene solution at volume fraction $\varphi = 0.117$ with that of a gel containing no free chains at a similar concentration ($\varphi = 0.137$). The difference in the shapes of the two curves is clear. The spectrum of the solution closely follows equation (2) and yields a value for the correlation length $\xi = 19.0$ Å, with an extrapolated intensity $I(0) = 2.28 \times 10^{-4}\,\text{kPa}^{-1}$. To evaluate the gel spectra, the following equation was used[15]:

$$I(Q) = I_d(0)(1 + Q^2\xi^2)^{-1} + I_s(0)\exp[-(Q\Xi)^p] \quad (5)$$

Equation (5) is based on the fact that scattering from gels contains a static component $I_s(Q)$ due to permanent constraints, and a dynamic component $I_d(Q)$ associated with the dynamic concentration fluctuations. The length Ξ is the characteristic size of the permanent non-uniformities. For the present PVAc system[15] it is found that $p = 0.7$. The dynamic component, displayed as a continuous curve in *Figure 3*, yields $\xi = 24.6$ Å and $I_d(0) = 3.71 \times 10^{-4}\,\text{kPa}^{-1}$. These values are higher than those of the solution.

The above results demonstrate the extent to which the crosslinks affect the concentration fluctuations in the gel. The scattering behaviour is consistent with the increase in the apparent interaction parameter noted above. In *Figure 3* the arrow indicates the value of $\varphi^2/(\varphi\, \partial\omega/\partial\varphi + 4G/3)$ calculated from the macroscopic measurements of swelling pressure. The agreement between the results of the two techniques is satisfactory.

Figure 4 shows two spectra from a gel at the same total polymer concentration $\varphi = 0.204$, containing free polymer ratios $r = 0$ and $r = 0.24$, respectively. Apart from a small difference in the low Q region, the two curves practically coincide*.

The above result, together with the observations of the macroscopic swelling pressure, is in agreement with a picture in which the free polymer chains in the gel behave like network chains, rather than like those in an uncrosslinked solution. In the swollen network, only a fraction of the crosslinked polymer participates actively in the dynamics of the concentration fluctuations.

For the present gels, this result can be interpreted in the following way. Swelling of the gel causes a reduction in the proportion of network chains that are free to fluctuate. The observed increase in the apparent values of the interaction parameters χ and w in the gel can thus be attributed to a reduction in the active fraction of the polymer, rather than to a modification of the effective

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*In the swelling pressure experiment, the mobile polymer is at liberty to enter and leave the gel, while SAXS measures concentration fluctuations at fixed composition. In general, therefore, these two conditions are not equivalent. In the present case, however, the corresponding thermodynamic responses of the binary and ternary gels are indistinguishable

pair interactions. When, at a fixed total polymer volume fraction, free polymer chains are introduced into the network, the latter must swell correspondingly. The resulting loss in freedom of the network chains due to the swelling is compensated by the free polymer.

Conclusions

Measurements were made of osmotic swelling pressure and small angle X-ray scattering from lightly crosslinked PVAc gels swollen in toluene and containing known amounts of free PVAc chains. A clear difference both in the swelling behaviour and in the scattering spectra between solutions and gels was observed, but swollen networks containing different amounts of free chains exhibited similar behaviour.

The observed differences between the osmotic properties of networks and the corresponding solutions can be understood in terms of a reduction in the fraction of the polymer participating in the dynamic concentration fluctuations, owing to network constraints. In the ternary PVAc–toluene gels, the reduction in the fluctuating component, due to the network expansion, is compensated by the free chains.

Acknowledgements

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