

Notes

Comparison between Neutral Gels and Neutralized Polyelectrolyte Gels in the Presence of Divalent Cations

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Introduction

In the past decade several investigations have been reported on various hydrogels,^{1–3} particularly neutral polymer gels [e.g., poly(acrylamide) or poly(vinyl alcohol)] and weakly charged polyelectrolytes [e.g., poly(acrylic acid) or poly(styrenesulfonate)]. Less attention has been paid to neutralized polyelectrolytes in the presence of added salt.

It is generally understood that fully neutralized polyelectrolyte gels in the presence of excess salt can be treated as neutral networks,⁴ because the Coulombic interactions are completely screened and the chains obey Gaussian statistics. Previous studies^{5–7} indicate that multivalent counterions are specifically bound to the polyelectrolyte chains and can act as additional cross-links. It is also known that the binding strength depends strongly on the nature of the particular polymer-counterion pair. However, the effect of such multivalent counterions on the thermodynamic and elastic properties of the network has not been fully elucidated.

In this note the effect of Ca^{2+} on the osmotic and scattering properties of fully neutralized sodium polyacrylate (PSA) gel is compared to that of changing the cross-link density in the corresponding neutral polyacrylamide (PAA) gel. In this comparison changes in the thermodynamic properties are investigated using complementary experimental techniques (light scattering, SANS, swelling pressure, and shear modulus measurements) to probe different characteristic length scales. Both kinds of gel are prepared by the same procedure with the same cross-linking agent [*N,N*-methylenebis(acrylamide)]. In the PAA gels the cross-link density was varied, while in the PSA gels, changes in the molecular interactions were induced by adding divalent cations. Both systems were investigated over a similar range of polymer volume fraction ($0.03 < \varphi < 0.25$).

Experimental Section

PAA and PSA gels were synthesized by free-radical copolymerization from their respective monomers and the cross-

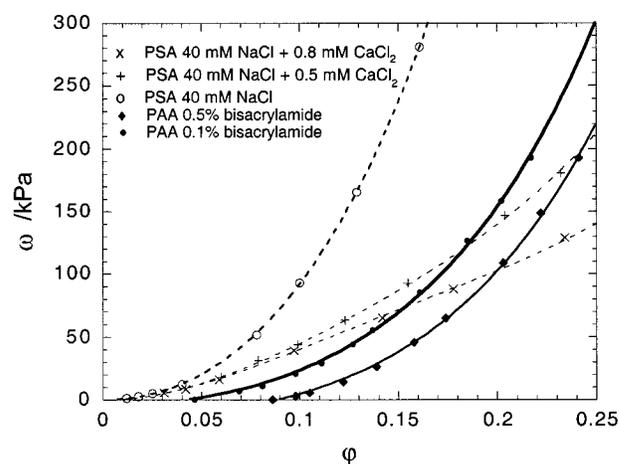


Figure 1. Variation of the swelling pressure with polymer volume fraction for PAA (filled symbols) and PSA hydrogels (open symbols). The curves through the data points are least-squares fits to eq 2 with the parameters displayed in Figure 2.

linker *N,N*-methylenebis(acrylamide) in aqueous solution as described previously.^{2,8} In the former, the concentration of cross-linker was varied from 0.1% to 0.5%, and the gels were swollen to equilibrium in pure water. These gels exhibit a change in appearance with increasing cross-linking density. At low bis(acrylamide) content, they are transparent, becoming opalescent at high cross-linking density.

In the polyacrylate gel the cross-linker concentration was 0.3%. The acrylic acid units were first neutralized in NaOH and equilibrated with aqueous solutions of 40 mM NaCl. The concentration of CaCl_2 in the surrounding solution was then increased gradually up to 0.8 mM CaCl_2 . At CaCl_2 concentrations higher than 1 mM a volume transition occurs in this system, probably due to associations induced by the Ca^{2+} ions.^{5,8} The present observations were made below this threshold.

Results and Discussion

The swelling pressure ω of a neutral network is given by

$$\omega = \Pi_{\text{mix}} - G \quad (1)$$

where Π_{mix} is the mixing pressure and G the shear modulus of the gel.⁹ Figure 1 shows the measured values of ω as a function of polymer volume fraction φ for two PAA gels with cross-linking density 0.1% and 0.5% (filled symbols), as well as the data from PSA gels in 40 mM NaCl solutions containing 0, 0.5, and 0.8 mM CaCl_2 , respectively. The curves through the experimental points are least-squares fits to the Flory-type expression⁴

$$\omega = -(RT/v_1)[\ln(1 - \varphi) + \varphi + \chi_0\varphi^2 + \chi_1\varphi^3] - G_0\varphi^{1/3} \quad (2)$$

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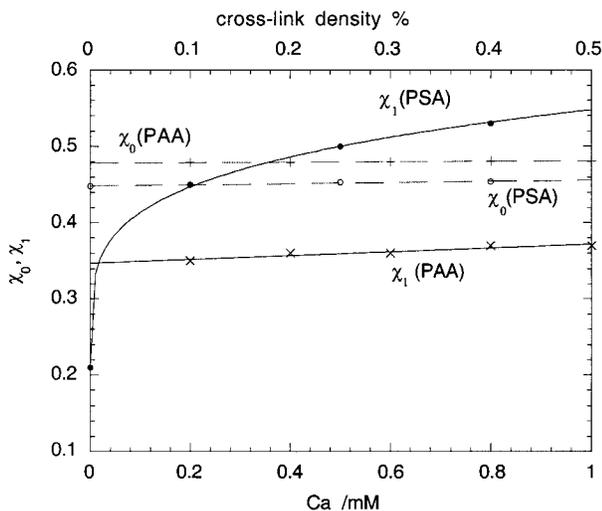


Figure 2. Interaction parameters χ_0 (dashed lines) and χ_1 (continuous lines) found from measurements of swelling pressure ω and eq 2. Horizontal axes: cross-link density, poly(acrylamide)–water; calcium concentration: poly(sodium acrylate) in 40 mM NaCl aqueous solution. Lines are guides for the eye.

where R is the gas constant, T is the absolute temperature, v_1 is the molar volume of the solvent, G_0 is the shear modulus of the unswollen network, and χ_0 and χ_1 are fitting parameters corresponding to second- and third-order interactions (Figure 2).

For the PAA gels both χ_0 and χ_1 (+ and × symbols, respectively, in Figure 2) display a very weak dependence on cross-linking density. It follows that changing the cross-link density in PAA modifies primarily the shear modulus, while the mixing term (first term in eq 2) for the gel remains essentially unchanged.

In the PSA gels, increasing the calcium concentration produces a slight enhancement in χ_0 . For χ_1 , however, a jumplike increase with respect to the calcium-free gel occurs at low calcium concentration, followed by a more gradual increase at higher calcium content. As reported previously,⁸ the value of the shear modulus in these gels is not significantly affected by the presence of calcium.

Small-angle neutron scattering (SANS) provides information on the local organization of the polymer in the network. The scattering intensity of a neutral gel can frequently be described as a sum of a dynamic (solution-like) and a static term,^{10–12}

$$I(q) = I_d(q) + I_s(q) = \Delta\rho^2 \left[\frac{kT\varphi^2}{(\varphi \partial\omega/\partial\varphi + 4G/3)} \frac{1}{1 + q^2\xi^2} + \frac{8\pi\Xi^3\langle\delta\varphi^2\rangle}{(1 + q^2\Xi^2)^2} \right] \quad (3)$$

where q is the transfer wave vector, $\Delta\rho^2$ is the contrast factor between polymer and solvent, k is the Boltzmann constant, ξ is the thermal correlation length, and Ξ is the characteristic dimension of frozen-in static concentration fluctuations, whose mean-square amplitude is $\langle\delta\varphi^2\rangle$. The calculated¹³ value of $\Delta\rho^2$ for the PAA–D₂O system is $4.7 \times 10^{20} \text{ cm}^{-4}$. For the PSA system, however, the contrast factor cannot be estimated with the same precision, since in the hydration shell that surrounds the polyelectrolyte chains the water is denser than in the bulk state.¹⁴ Calculation based on the tabulated chemical formula that neglects the hydration shell

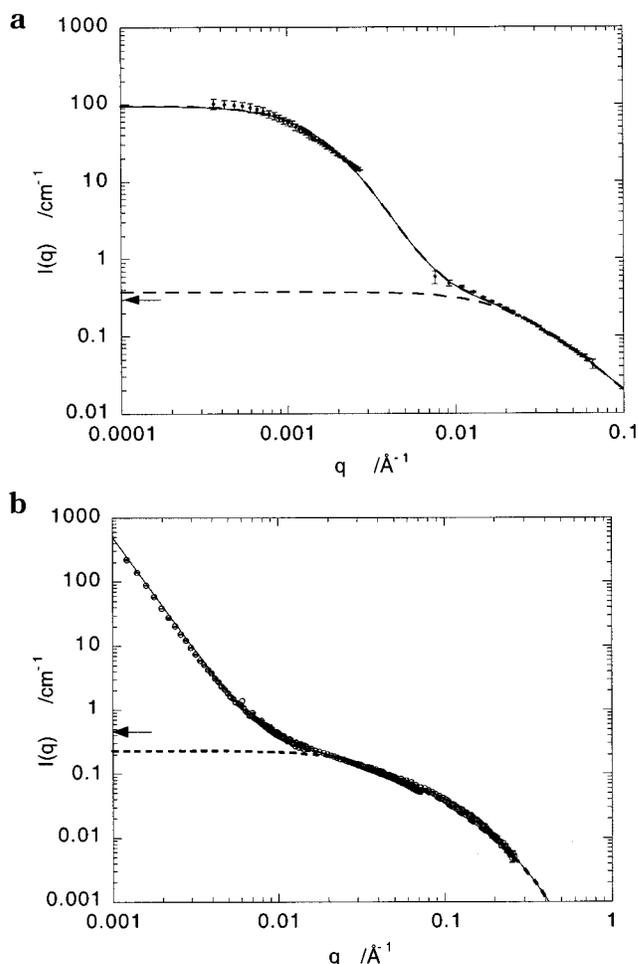


Figure 3. (a) SLS and SANS spectra from a PAA gel at cross-link density 0.3%. These two data sets are expressed in absolute units and have been normalized to the neutron scattering contrast. The continuous curve through the data points is the least-squares fit to eq 3, while the dashed curve is the dynamic component (first term). The horizontal arrow is the intensity of the dynamic fluctuations calculated from swelling pressure measurements. (b) SANS spectrum of PSA gel equilibrated with a solution containing 40 mM NaCl and 0.85 mM CaCl₂. Continuous line: least-squares fit to eq 4; dashed line: solution-like term of eq 4; arrow on left-hand axis: theoretical dynamic intensity from swelling pressure measurements.

yields for the PSA–D₂O system the value $\Delta\rho^2 = 1.7 \times 10^{21} \text{ cm}^{-4}$.

Figure 3a shows the scattering response for a PAA gel with cross-linking density 0.3 wt %. The data in this figure, obtained from static light scattering (SLS) and SANS, are expressed in terms of the same SANS absolute units. For these neutral gels,² increasing the cross-link density (i) leaves the dynamic component at high q virtually unchanged, while (ii) enhancing the static concentration fluctuations. The continuous curve in this figure is the fit of eq 3 through all the data points, the dashed curve being the dynamic component of the fit. The arrow at the left axis of this figure indicates the intensity calculated from the swelling pressure measurements and the corresponding neutron contrast factor for this system. The latter value is some 25% smaller than that deduced from SANS, a discrepancy that lies within the experimental uncertainties of these independent techniques. The correlation lengths ξ and Ξ estimated from the fit to eq 3 take the values 43 Å

and 390 Å, respectively, while the relative amplitude of the static concentration fluctuations is $\langle \delta\varphi^2 \rangle^{1/2}/\varphi \approx 0.1$.

Figure 3b shows the SANS spectra of a PSA gel at equilibrium with an aqueous solution containing 40 mM NaCl with 0.85 mM CaCl₂, i.e., just below the volume transition where the solution-like scattering is most intense. In the low- q region the intensity displays an extensive region of straight-line behavior with a slope of about -3.6 , characteristic of surface scattering.¹⁵ This feature, which is independent of the calcium content and of the degree of swelling, is distinctive of these polyelectrolyte gels¹⁶ and may reflect a starlike internal structure.¹⁷ To obtain a satisfactory fit to the data, the second term in eq 3 was replaced by a simple power law, while the dynamic term was assumed to remain valid.

$$I(q) = \Delta\rho^2 \left[\frac{kT\varphi^2}{\varphi \partial\omega/\partial\varphi + 4C/3} \frac{1}{1 + q^2\xi^2} + Bq^{-3.6} \right] \quad (4)$$

The continuous curve in Figure 3b shows the fit of eq 4 to the data, which yields for the dynamic correlation length $\xi = 26$ Å. Absence of a plateau behavior in the power law at low q makes it impossible here to estimate the value of $\langle \delta\varphi^2 \rangle$. The first term in eq 4 is displayed as a dashed line. It is clear from the figure that the intensity obtained from the neutron fit is notably smaller than that calculated from macroscopic osmotic measurements. The observed discrepancy may be caused by the uncertainty in the value of the contrast factor due to the hydration shell. Another possible explanation, however, is that the thermodynamic response of the polyacrylate gel is not adequately described by a single correlation length. The latter explanation is probably the correct one, since at conditions far from the volume transition eq 4 provides a somewhat less satisfactory fit to the data in the intermediate and higher q regime.

Conclusions

The present results indicate that the analogy between neutral gels and neutralized polyelectrolyte gels in the presence of added salt is an oversimplification. Although the osmotic properties of both systems can be described by the Flory–Huggins formalism, substantial differences arise in their thermodynamic response and in their static superstructure. In the PAA gel, the third-order interaction parameter χ_1 is virtually independent of the cross-link density. In the neutralized PSA gel, however, the Ca²⁺ has a pronounced effect on χ_1 . This result may be related to an increase in chain flexibility upon replacing monovalent by divalent counterions.¹⁸ The value of χ_0 is also substantially lower in the PSA system (i.e., at low concentrations the mixing pressure is higher than with PAA), a fact that may be attributed to incompletely shielded electrostatic interactions, which in the presence of added salt do not contribute explicitly

to the thermodynamics but influence the local organization of the polymer segments. Differences in the structure are also reflected in the scattering response. Both systems display liquidlike and static components. For the PSA system, however, the intensity of the liquidlike component calculated from the macroscopic swelling pressure is significantly greater than that obtained from the decomposition of the SANS spectrum (Figure 3b). This shortfall in the observed intensity of the thermodynamic fluctuations is too large and of the wrong sign to be explained by a faulty decomposition of the SANS spectrum. The static scattering features also differ from those of the neutral gel: the spectrum is more consistent with starlike structures.

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