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Dielectric behaviour of swollen poly(acrylamide) gels in the collapse region

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Summary

The dielectrical behaviour (in the frequency range f=20 Hz - 200 kHz) of two networks - polyacrylamide (PAAm) network and a network obtained by the copolymerization of acrylamide with 3 mol.% sodium methacrylate (MNa) in a mixed solvent deionized water - acetone (acetone concentration a=0-80 vol.%) at T=298 K and pH ~ 7 was investigated. High values of complex permitivity $\varepsilon^{*}(=\varepsilon'+i\varepsilon'')$ were found for both networks. For the PAAm network the dependence of both components of ε^{*} on a is continuous. On the other hand, for the ionized network the jumpwise decrease in swelling at the phase transition is accompanied by a jumpwise increase in the values of both components of ε^{*} at all frequencies; the critical concentration of acetone a at the collapse is frequency independent. The high values of components of ε^{*} and their dependences on a observed with both networks can be explained qualitatively by the polarization of the space charge in the measured samples. While with the PAAm network the charge is given by the dissociation of water, in the case of the P(AAm-MNa) network ions arising by the dissociation of MNa also contribute to this charge. The collapse in the ionized network is accompanied by a jumpwise increase in the effective charge concentration in the gel. The fact that the extent of the jumpwise change of components of ε^{*} in the collapse is frequency dependent suggests that the dependence of ε^{*} on a is also affected by the mobility of charge carriers.

Introduction

With loosely crosslinked poly(acrylamide) (PAAm) networks containing a small number of charges on the chain (~ 1-5 mol.%), first-order phase transition (collapse) was observed when passing from a good to a poor solvent (1-4). The magnitude of the transition may be affected by molecular parameters of the network (network density (5) or dilution at network formation (6)), charge concentration (2,7), or concentration of the salt (8). It has been proved, both experimentally (1-8) and theoretically (9), that electrostatic interactions of charges on the chain have a decisive influence on the existence and extent of phase transition. The jumpwise change in volume is accompanied by a jumpwise change in the equilibrium modulus of the gel, which

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means that the equilibrium mechanical behaviour is determined by the network volume.

Measurement of the dielectrical behaviour of polar polymers offers the possibility of an investigation of motions of the dipole moments (orientational polarization). In the case of swollen PAAm networks, however, the dielectrical measurements are complicated by the conductivity of water. Since the absorption range of orientational motions of water molecules lies in the GHz frequency range (10), the results of the measurements are predominantly affected by polarization of the space charge of the solvent and by electrode phenomena.

This study deals with measurement of the dielectrical behaviour of the ionized and nonionized PAAm network in the mixture deionized water - acetone.

Experimental Part

Sample preparation: The networks were prepared from 100 ml of aqueous solution which contained 5 g acrylamide (AAm), 0.135 g N,N′-methylenebisacrylamide (MBAAm), 0.02 g ammonium persulfate and 150 μl N,N′-tetramethylethylenediamine (network N1); to the second network, sodium methacrylate (MNa) was added so as to make the mole fraction of MNa on the chain (i.e. per monomer AAm and crosslinking agent MBAAm) $x_{MNa}=0.03$ (network N2). The polymerization proceeded at room temperature 5 h in ampoules having the diameter 10 or 20 mm. After the polymerization the samples were extracted in deionized water. After the extraction, the samples were swollen in mixtures acetone - deionized water (pH ~ 7) at room temperature for at least four weeks. Cylindrical samples swollen to equilibrium (diameter 10-20 mm, height ~ 3 mm) in the corresponding mixtures were used in the measurements.

Dielectrical measurements: The measurements were carried out in a plate capacitor with a mobile upper electrode. The accuracy of reading of the distance between the electrodes was 0.02 mm. Frequency dependences of complex permittivity (relative) $\varepsilon^{*} = \varepsilon' + i\varepsilon''$ (ε' and ε'' being its real and imaginary component, respectively) were measured in the frequency range f=20 Hz - 200 kHz at 25°C. The measurements were performed with a Tesla BM 507 measuring apparatus, which allows both impedancy and phase shift to be measured. The ε' and ε'' values were calculated from a parallel combination of resistance and capacity obtained by measurements with three samples; the accuracy of determination was better than 10%.

Refractive index and degree of swelling: The refractive index of the gel, n_g, was measured with a Pulfrich PR2 (Carl Zeiss Jena) refractometer using a VoF2 prism (accuracy of determination of n_g was 0.5%). Swelling of the samples in water - acetone mixtures was characterized by the ratio X determined from a change in the diameters of cylindrical samples by means of the relation

$$X = V/V^{+} = (D/D^{+})^{3}$$

in which D and D^+ are diameters of the sample after swelling and after its preparation, respectively, V and V^+ are the respective gel volumes. The diameters were measured in a microscope with an accuracy of 0.02 mm. Using the known X, it is easy to determine the degree of swelling related to the dry state of the network, $q = V/V_d = Xq^o$, where V_d is the dry volume, q^o is the degree of swelling at network formation (q^o=25).

Results and discussion

It can be seen from Figs 1 and 2 that for a charge-free network N1, the swelling ratio X and the refractive index n_g ($n_g^2 \sim \varepsilon_\infty$, ε_∞ being permittivity at very high frequencies) depend continuously on the acetone concentration a in the water - acetone mixture. On the other hand, in the case of the network N2 with MNa, both X and n_g change jumpwise in the range a ~ 48 vol.%. While in the collapsed state the dependence of X and n_g on a is virtually the same for both networks, in the expanded state (a < 40 vol.%) swelling of the ionized network N2 is much higher than swelling of the network without MNa. In the expanded state the refractive index of networks swollen in water approaches that of water (n=1.33). Similar results for swollen PAAm networks have been obtained earlier (2,11).

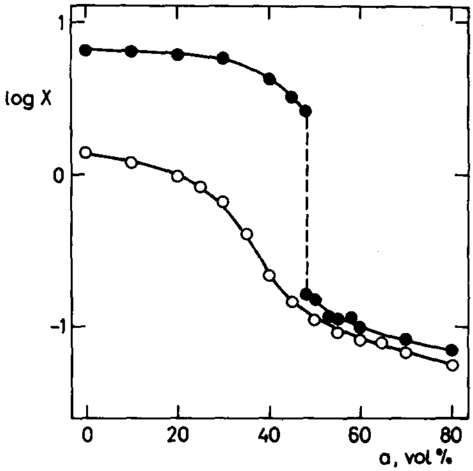

Figure 1. Dependence of swelling ratio X on acetone concentration in mixed solvent a. ○ - nonionized network N1, ● - ionized network N2

Figs 3a,3b show that, with increasing frequency f, there is a great decrease in both ε' and ε" in all samples of both networks. The permittivity ε' of nonionized samples (N1) decreases monotonically by several orders of magnitude with increasing a; the decrease becomes less pronounced at high frequencies (Fig. 3a). The high absolute ε' values along with a similar dependence

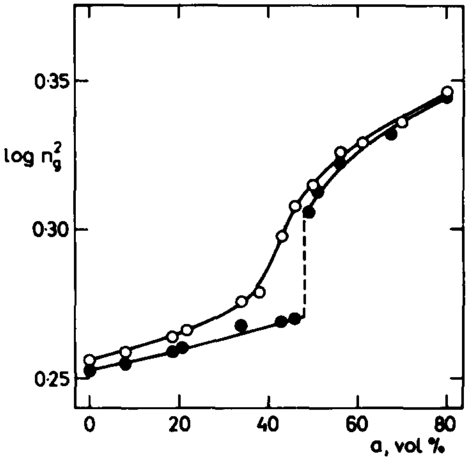

Figure 2. Dependence of refractive index of swollen gels n_g on acetone concentration in mixed solvent a. ○ - nonionized network N1, ● - ionized network N2

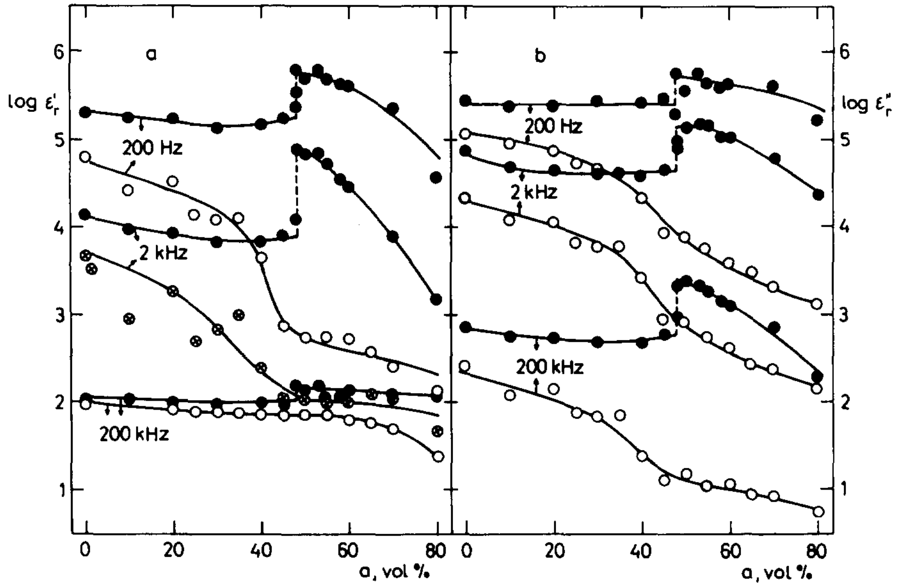

Figure 3. Dependence of real ε' and imaginary ε'' permittivity component of swollen gels on acetone concentration in mixed solvent a. ○, ⊗ - nonionized network N1, ● - ionized network N2; numbers denote frequency of measurement

of both ε' and X on a suggest that the ε' values of nonionized samples are predominantly determined by the polarization of the space charge of water, i.e. by H+ and OH^- ions formed by dissociation. Since both the concentration of water in the mixed solvent and the degree of swelling decrease continuously with increasing a, the charge concentration also decreases continuously with a. This decrease leads to the observed continuous decrease of ε' with a. The decrease in the degree of swelling may also cause a decrease in the mobility of charge carriers due to the increase in the concentration of polymer chains. It can be seen in Fig.3a that the rate of decrease in ε' with a depends on the frequency f. At high frequencies the contribution of the space charge to ε' is small, and therefore at a=0 for f=200 kHz ε' approaches the static permittivity of water.

Qualitatively different dependences of ε' on a have been observed with samples of the ionized network N2 (Fig.3a). In the expanded state ($a < 40$ vol.%) the ε' values of ionized networks are three times higher for all frequencies than the ε' values of samples of the network N1 and decrease slightly with increasing a. In the collapse region for $a \sim 48$ vol.% the ε' value increases jumpwise at all frequencies, and the critical a value at the collapse is independent of f. The relative change in the ε' values (the maximal to minimal value ratio) during the collapse passes through a pronounced maximum depending on frequency. In the collapsed state ($a > 50$ vol.%) the ε' of the ionized network rapidly decrease with a.

The dependences of ε' on a of the ionized network can also be explained qualitatively by the polarization of the space charge (12). In the network N2, ions due to the dissociation of MNa also contribute to the space charge, along with the H^+ and OH^- ions. This causes a rise in the total charge concentration, which raises the ε' value of samples of the ionized network, compared with the ε' value of samples of the nonionized network in the whole range of a. The jumpwise increase in ε' at the collapse of the ionized network is then due to the jumpwise increase in the charge concentration of the gel in the collapsed state (consequence of the jumpwise decrease in the sample volume), even if the charge concentration from water - acetone solvent has decreased. The fact that the magnitude of the jumpwise change in ε' during the collapse is markedly dependent on frequency means that the mobility of charge carriers also plays an important role. Both the decrease in the charge concentration from solvent and the decrease in the total charge mobility contribute to the total rapid decrease in ε' with a in the ionized nework in the collapsed state ($a > 50$ vol.%).

It can be clearly seen in Fig.3b that the dependences of ε'' on a and frequency are similar to those of ε'. The ε'' value of networks N1 decreases with a continuously and monotonically, while ε'' of ionized network N2 in the collapse region increases jumpwise. The rate of decrease of ε'' with a in N1 network becomes somewhat slower with increasing frequency. The fact that the relative change in ε'' with a in network N2 at the collapse slightly increases even at high frequencies (unlike ε') suggests that losses in the gel are not affected by a change in the charge mobility too much (cf. Figs.3a,3b). This may be due to the increased interaction of charges with polymer chains, when due to the increased polymer density the frequency of their collisions increases.

It may be said, in conclusion, that the dielectrical method of measurement is sufficiently sensitive to the investigation of phase transition in swollen polymer gels. The dependence of ε' on a shows that the relative change in the ε' values at the collapse is frequency dependent.

References

1. Tanaka, T., Fillmore, D.J., Sun, S.-T., Nishio, I., Swislow, G., Shah, A., Phys. Rev. Letters 45, 1636 (1980)
2. Stejskal, J., Gordon, M., Torkington, J.A., Polym. Bull. 3, 621 (1980)
3. Ilavský, M., Macromolecules 15, 782 (1982)
4. Janas, V.F., Rodriquez, F., Cohen, C., Macromolecules 13, 977 (1980)
5. Ilavský, M., Hrouz, J., Polym. Bull. 8, 387 (1982)
6. Ilavský, M., Hrouz, J., Polym. Bull. 9, 159 (1983)
7. Nicoli, D., Young, C., Tanaka, T., Pollak, A., Whitesides, G., Macromolecules 16, 887 (1983)
8. Ohmine, I., Tanaka, T., J. Chem. Phys. 77, 5725 (1982)
9. Ilavský, M., Polymer 22, 1687 (1981)
10. Smyth, C.P., Dielectric behavior and structure, McGraw Hill, New York 1955
11. Hrouz, J., Ilavský, M., Polym. Bull. 12, 515 (1984)
12. Macdonald, J.R., Phys. Rev. 92, 4 (1953)

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