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Phase transition in swollen gels

15. The effect of the amide group in the side chain with a positive charge on the collapse of poly(acrylamide) networks

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SUMMARY

The swelling and mechanical behaviour of networks of copolymers of acrylamide, methylenebisacrylamide and of the quaternary salt - N′,N′,N′-trimethyl-N′-methacrylamido-2-ethylammonium chloride (mole fraction of salt x_s=0-0.17) in water-acetone mixtures was investigated. In the range $x_s > 0.01$ the phase transition was observed; with increasing concentration x_s both the extent of transition and the critical concentration of acetone in the mixture, at which the collapse takes place, increase. It was found that, compared with the ester group, the attachment of the positive charge to the main chain through the amide bond increases the extent of transition and decreases the critical acetone concentration. The jumpwise change in the gel volume accompanying the collapse is accompanied by a similar change in the shear modulus of the gel.

INTRODUCTION

Polyacrylamide (PAAm) networks prepared at high dilution at their formation (~ 95 vol.%) with a small number of charges on the chain undergo phase transition of the first order when passing from a good to a poor solvent (1-3); at the same time, the volume of the gel changes jumpwise from ten to a hundred times. The charge can be introduced in the chain either by a spontaneous hydrolysis of AAm groups (1,4) or by the copolymerization of AAm with a suitable monomer which may introduce either a negative (2) or a positive (5,6) charge. In the case of a negative charge, i.e. when AAm was copolymerized with sodium methacrylate (MNa) it was found that ~ 1 mol.% of charges on the chain were sufficient to produce the collapse; experimental data were in a semiquantitative agreement with the theory of swelling equilibria of polyelectrolyte networks (7). On the other hand, in the case of networks with positive charges obtained by copolymerizing AAm with quaternary salts (8) the collapse required more than 3 mole% of charges, and the effect of these charges on the extent of transition was also from five to ten times weaker. This finding was interpreted in the first place by the

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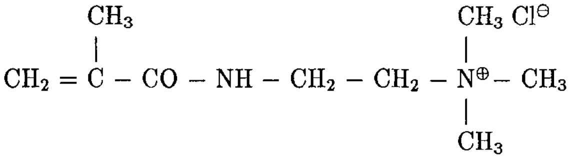
Dedicated to Dr. Karel Dušek on the occasion of his 60th birthday for his important contribution to polymer science

*To whom offprint requests should be sent greater distance of the positive charge from the main chain, and also by unfavourable copolymerization parameters of acrylamide with quaternary salts of the methacrylate type, which may favour the block character of the copolymer thus obtained (9).

In this study we investigate the effect of concentration of the positive charge on the swelling and mechanical equilibria of PAAm networks obtained by the copolymerization of AAm with a quaternary salt containing a side chain of the amide type. In addition to the degree of ionization being independent of pH, the system may also be expected (9) to have more favourable copolymerization parameters, which will lead to a more ideal random structure of the copolymer thus formed.

EXPERIMENTAL

Sample preparation: The samples were prepared from 100 ml of an aqueous solution which contained 5 g acrylamide (AAm), 0.135 g of the crosslinking agent - N,N′-methylenebisacrylamide, 0.02 g ammonium persulfate and 150 μl N,N′-tetramethylethylethylenediamine. N′,N′,N′,-trimethyl-N′ -methacrylamido-2-ethylammonium chloride



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CO-NH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3\ Cl^{\ominus}}{|}}{N^{\oplus}}}-CH_3 \qquad (1)$$

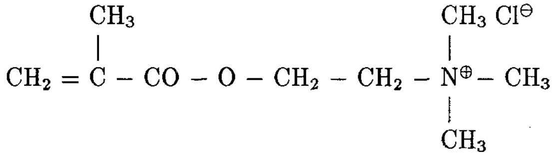
was used as the quaternary salt. Six series of networks were prepared with a varying mole fraction of the salt, x_s, ranging from 0 to 0.17 (Table 1). The polymerization proceeded at room temperature 5 h in ampoules, $D = 10$ or 20 mm in diameter. After the polymerization the samples were extracted in redistilled water for 7 days. The experimental data were compared with those on PAAm networks obtained by employing

Table 1: Basic network characteristics and parameters of collapse

x_s	G_1 (g cm^{-2})	$10^5\nu_d$ mole cm^{-3}	$\Delta \log X$	$\Delta \log G$	a_c vol%	ϕ
–	30.1	3.22	–	–	–	–
0.012	34.2	3.66	0.90	0.35	45	0.25
0.024	40.0	4.28	1.25	0.45	50	0.35
0.050	32.2	3.44	1.60	0.60	55	0.23
0.090	33.3	3.56	1.90	0.60	60	0.18
0.164	31.2	3.34	1.95	0.60	66	0.18

x_s is the mole fraction of salt, G_1 is the shear modulus measured after network formation, ν_d is the network density, $\Delta \log X$ is the extent of collapse, $\Delta \log G$ is the jumpwise change in the modulus at collapse, a_c is the critical value of acetone at collapse and ϕ is the correction factor ($\alpha = x_s\phi$)

the same procedure, but contained a quaternary salt with a different structure of the side chain, i.e., N′,N′,N′-trimethyl-N′-2-methacryloyloxyethylammonium chloride



$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CO - O - CH_2 - CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3\ Cl^{\ominus}}{|}}{N^{\oplus}}} - CH_3 \qquad (2)$$

Swelling and mechanical measurement: After extraction the samples were swollen in water-acetone mixtures in the range 0-90 vol.% acetone. Swelling proceeded for ~ 28 days, after which the swelling ratio X related to the state at network formation was determined:

$$X = (D^*/D)^3 = V^*/V \qquad (3)$$

in which D^* and D respectively are the sample diameters after the preparation and swelling, V^* and V respectively are the corresponding sample volumes after the preparation and swelling to equilibrium. The diameters D were measured with an Abbé comparator (Zeiss Jena, accuracy ± 0.002 mm); values of the swelling diameter X in Fig. 1 are averages from at least three samples. From the X values it is easy to calculate the volume fraction of the polymer in the swollen state v_2 ($= v^o X$, where v^o is the volume fraction of polymers at network formation, $v^o = 0.037$).

Deformation measurements were carried out using cylindrical specimens in a uniaxial compression in an apparatus described earlier (2). The specimen, ~ 1-2 cm high, was compressed to a ratio λ ($= l/l_o$, where l, l_o respectively are the deformed and the initial specimen height) and the force f was determined after 30 sec of relaxation. Usually, ten λ_i and f_i values were measured in the range $0.7 < \lambda < 1$, and from these values the equilibirium shear modulus G was determined using the relation

$$G = f/S_o(\lambda^2 - \lambda^{-1}) \qquad (4)$$

in which S_o is the initial cross-section of the specimen (Fig. 1).

RESULTS AND DISCUSSION

Swelling and mechanical characteristics

It can be seen in Fig. 1 that already at the lowest salt concentration $x_s = 0.012$ PAAm networks undergo phase transition; only for the PAAm network alone the dependence of the swelling ratio X on the acetone concentration is continuous. A characteristic feature of the phase transition is a jumpwise change in the swelling ratio X (characterized by the extent of transition $\Delta \log X$). Fig. 1 shows that the extent of the collapse $\Delta \log X$ increases with increasing salt concentration; a similar behaviour is also observed

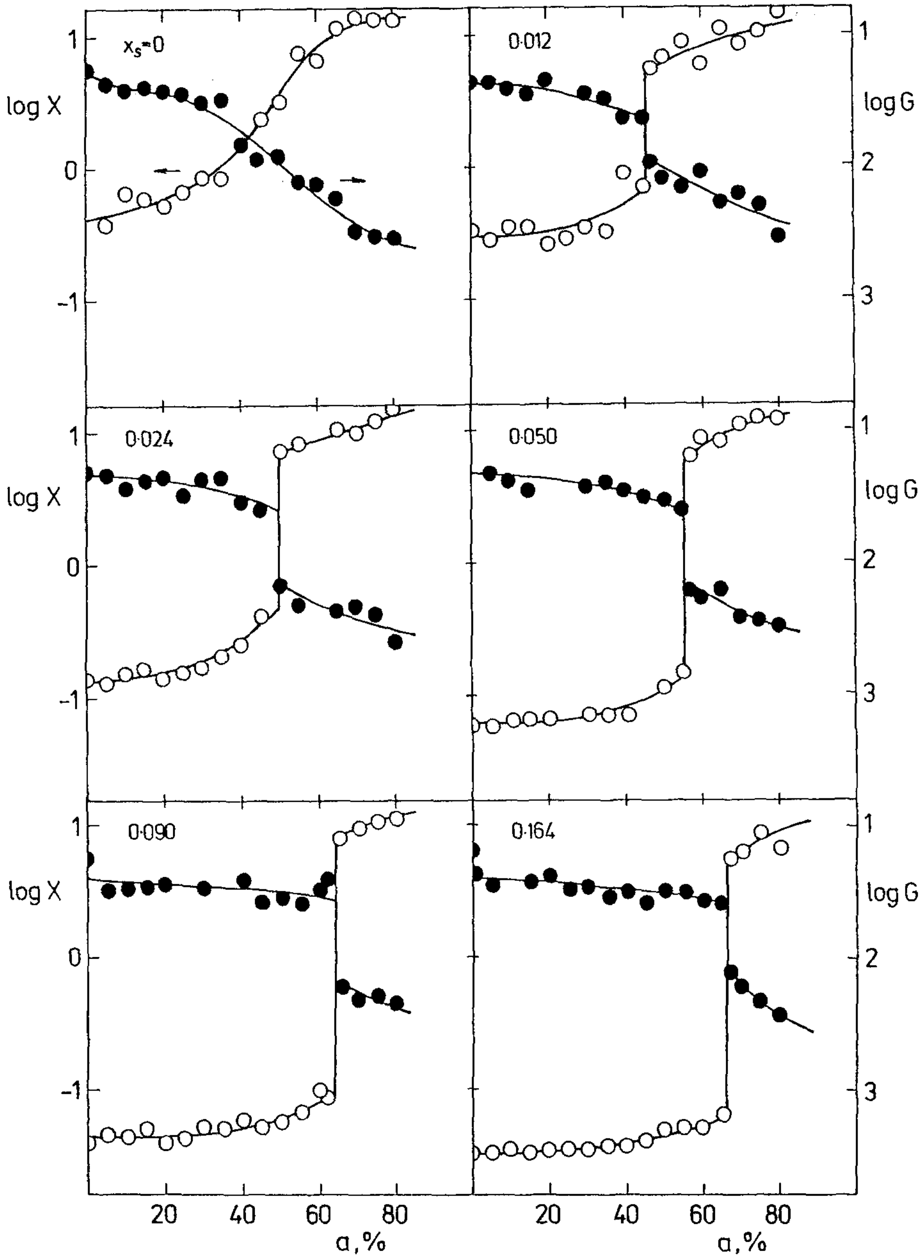


Figure 1: The dependence of the swelling ratio X and modulus G (g cm^{-2}) on the concentration of acetone a (vol%).
○ – X, ● – G. The numbers correspond to the mole fraction of salt x_s

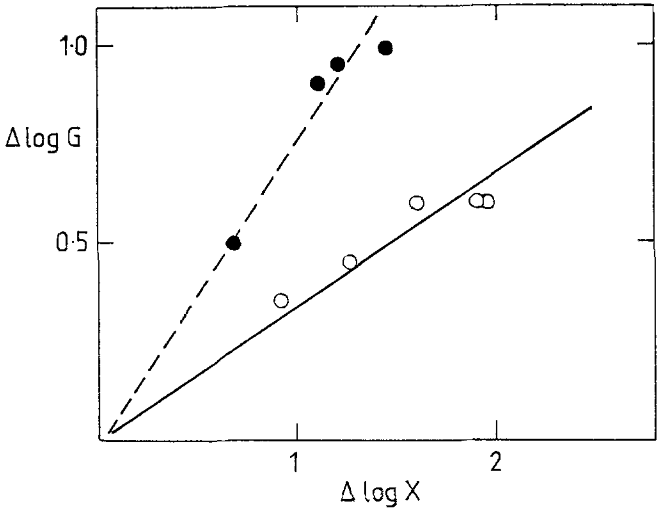


Figure 2: The dependence of the jumpwise change in the modulus $\Delta \log G$ on the change in the swelling ratio $\Delta \log X$.
Quaternary salt: ○ -Eq.(1), ● -Eq.(2)

in the critical acetone concentration in the mixture a_c at which the collapse takes place.

As expected, for the PAAm network alone also the dependence of the modulus G on acetone concentration is continuous. With all further networks containing a quaternary salt $x_s > 0$, however, a jumpwise change in the modulus G can be observed, which may be characterized by the value of $\Delta \log G$. According to Fig. 2, the jumpwise change in the modulus $\Delta \log G$ adequately correlates with the jumpwise change in the swelling ratio (and hence, in volume) of the gel $\Delta \log X$ ($\Delta \log G = 0.35 \Delta \log X$). The slope of this dependence, 0.35, adequately fits in with the value predicted by the kinetic theory of rubberlike elasticity, being in agreement with the slope found for PAAm-MNa networks bearing a negative charge (2). It is, however, half as high as the slope value found for AAm containing quaternary salts ($s = 0.7$) with ester group in the side chain (8) (cf.Eq.(2)).

Using the modulus G_1 values measured after preparation of the networks the concentration of elastically active chains related to the dry state $\nu_d = G_1/RTv^o$ can be calculated, R being the gas constant, T being temperature (Table 1). The low ν_d values indicate the low efficiency of the crosslinking reaction at the high dilution used, and thus large cyclization of the system.

The dependence of the extent of collapse $\Delta \log X$ and of the critical acetone value a_c on the molar salt concentration x_s can be seen in Figure 3. The Fig. 3 also shows earlier results obtained for P(AAm-MNa) networks and for networks obtained by the

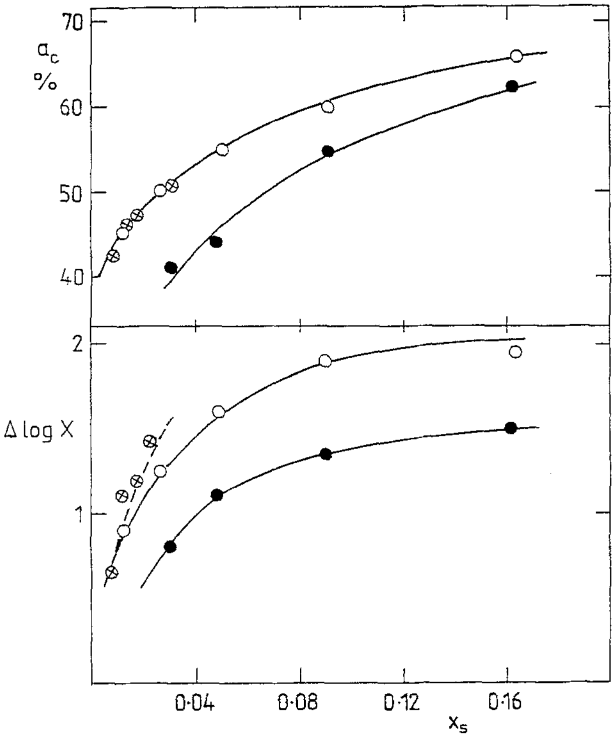


Figure 3: The dependence of the extent of the collapse $\Delta \log X$ and of the critical acetone concentration at collapse a_c on the molar concentration of salt x_s.
○ - salt Eq.(1), ● - salt Eq.(2), ⊗ -networks with sodium methacrylate

copolymerization of AAm with N′,N′,N′-trimethyl-N′-2-methacryloyloxyethylammonium chloride (Eq.(2) – the same structure as that given in Eq.(1), but with an ester group instead of the amide group in the side chain). It is quite obvious that the existing data both for the critical concentration a_c and for the extent of the collapse correspond to those found for P(AAm-MNa) bearing a negative charge. This means that the introduction of a hydrophilic amide (NH) group into the side chain eliminates the effect of hydrophobic side group of the salt given in Eq.(2).

A comparison between the theory of swelling equilibria of polyelectrolyte networks and experiment

The introduction of the effect of electrostatic interaction of charges into the theory of rubber elasticity (7) has led to the prediction of the swelling pressure P in the form

$$P = P_m + P_{el} + P_{os} + P_{els} \tag{5}$$

where P_m corresponds to the mixing of chain segments with the solvent characterized by the Flory-Huggins interaction parameter χ, P_{el} is given by a change in the free elastic energy of the chain with swelling, P_{os} is given by the mixing of network ions with the solvent, P_{els} is determined by a change in the free energy of electrostatic interactions with swelling. In a theory published earlier the individual terms P_i were expressed in both molecular parameters characterizing the network structure (network density ν_d, molar volume of the water-acetone mixture, degree of ionization of the network α, dry network density $d = 1.35$ g cm^{-3}) and experimental values of the volume fraction of the swollen network v_2. Using Eq.(5), the dependence of the interaction parameter χ on v_2 was calculated from experimental v_2 values (the data were obtained for the free swelling, i.e. $P = 0$) by employing a similar procedure described in detail for networks carrying a negative charge (2).

The use of Eq.(5) without the quaternary salt ($x_s = 0$) swollen in water alone led to the expected value of the parameter $\chi = 0.48$. Similarly as before (2,8), for ionized networks with the salt concentration $x_s > 0$, Eq.(5) gave high unrealistic values of the χ parameters. Since χ is a measure of the polymer-solvent interaction when all charges are screened (the effect of charges in Eq.(5) is considered in the contributions P_{os} and P_{els}), $\chi = 0.48$ may be required also for ionized networks in pure water. This requirement may be met by assuming that the effective degree of ionization α is lower than the salt concentration x_s, i.e. $\alpha = x_s\phi$, where ϕ is the empirical correlation factor (Table 1). The ϕ values thus calculated lie in the range 0.2-0.35 and are higher than the ϕ values measured for the quaternary salt of the methacrylate type.

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