Phase transition in swollen gels

18. Effect of concentration of the crosslinker with a positive charge on the collapse of polyacrylamide networks

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Summary

The swelling and mechanical behaviour of networks of copolymers of acrylamide (AAm) with the ionic crosslinker (I) - N,N'-(1,4-phenylenedimethylene)bis(2-acrylamidoethyldimethylammonium chloride) - in water-ethanol mixtures was investigated. Two series of networks were prepared: a) AAm and ionic crosslinker (I) were copolymerized in series 1 (mole fraction $x_I = 0.005 - 0.1$); b) AAm, ionic crosslinker (I) and non-ionic crosslinker - methylenebisacrylamide (MBAAm) - were copolymerized in series 2 ($x_I + x_{MBAAm} = 0.1$, x_I was used in the same region as in series 1). In the range $x_I \geq 0.01$ the phase transition was observed for both series. While for networks of series 2 (constant total amount of crosslinkers) the extent of transition (jumpwise change in the gel volume) at the collapse increases with x_I, for samples of series 1 this extent is practically independent of x_I due to the compensation of the effect of the increasing crosslinking density and increasing charge concentration on the swelling. The critical concentration of ethanol in the mixture, at which collapse takes place, increases with x_I for both series. The jumpwise change in the gel volume is accompanied by a similar change in the shear modulus of the gel.

Introduction

First - order phase transition (collapse) was observed with lightly crosslinked polyacrylamide (PAAm) gels carrying a low number of charges on the chain ($\sim 1 - 10$ mol. %) in water-acetone mixtures (1–4). The charge was introduced into the chain by the copolymerization of AAm with sodium methacrylate (MNa) or sodium acrylate (ANa) (negative charge) (5,6). When AAm was copolymerized with MNa it was found that ~ 1 mol. % of charges on the chain were sufficient to bring about the collapse and experimental swelling data were in semiquantitative agreement with the theory of swelling equilibria of polyelectrolyte networks (5,7). In the case of PAAm networks with quarternary ammonium salts of the methacrylate type (attachment of the charge to the main chain through the ester group) the collapse required more than 3 mol. % of charges and the effect of positive charges on the jumpwise change in the gel volume (extent of transition) was from five to ten times weaker (6). On the other hand if the attachment of the positive charge to the main chain is through the amide bond the extent of the transition increases and the collapse is observed in the range ~ 1 mol. % of charges (8). This finding was interpreted
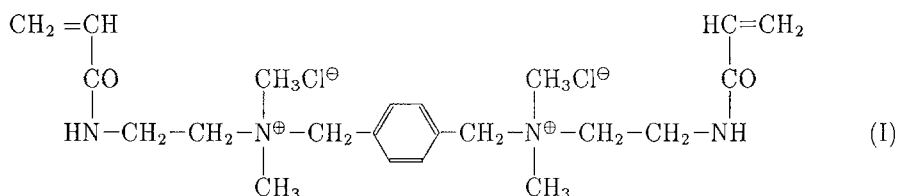
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by more favourable copolymerization parameters of AAm with salts containing a side chain of the amide type in comparison with salts of the methacrylate type (leading to the block character of the copolymer).

Also the effect of charge polarity in the side chain of a quarternary salt on the collapse of PAAm networks was studied (9). It was found that an exchange of the positive charge of the ammonium salt (e.g., $N^{\oplus}Cl^{\ominus}$) for the negative charge of the sodium salt (e.g., $COO^{\ominus}Na^{\oplus}$) in the side chain decreases the critical content of salt necessary for the collapse from 3 to 1 mol. %, increases the extent of the transition and the collapse takes place at lower concentration of acetone. In all studied systems the charged centres were placed in different positions in the side chain.

In this study we investigate the effect of the concentration of the positive charge in ionic crosslinker on the swelling and mechanical behaviour of polyacrylamide networks in water-ethanol mixtures. One can expect that with increasing concentration of ionic crosslinker the swelling degree will increase due the mixing of ions attached in network with the solvent (7). On the other hand, also the crosslinking density of network will increase and higher crosslinking will decrease swelling degree (7).
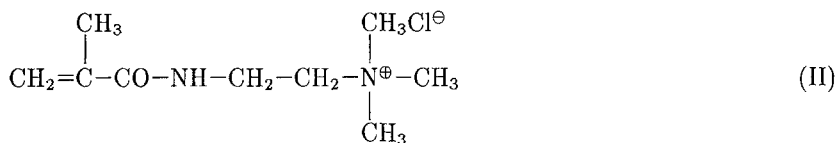
Experimental

Sample preparation: Two series of networks were prepared: a) In series 1 the samples were prepared from 100 ml of an aqueous solution which contained 5 g acrylamide (AAm), 0.02 g ammonium persulfate, 150 μl N,N,N',N'-tetramethylethylenediamine (TEMED) and various amount of ionic crosslinker - N,N'-(1,4-phenylenedimethylene)bis(2-acrylamidoethyl-dimethylammonium chloride) (I),

$$
\begin{array}{cccc}
CH_2 =CH & & & HC=CH_2 \\
| & & & | \\
CO & CH_3Cl^{\ominus} & CH_3Cl^{\ominus} & CO \\
| & | & | & | \\
HN-CH_2-CH_2-N^{\oplus}-CH_2-\!\!\!\bigcirc\!\!\!-CH_2-N^{\oplus}-CH_2-CH_2-NH & \quad\quad (I)\\
| & & | & \\
CH_3 & & CH_3 &
\end{array}
$$

Six series of networks were prepared with a varying mole fraction of the crosslinker x_I ranging from 0.005 to 0.1 (Table 1).

  b) In series 2 the samples were prepared from the same solutions as in series 1; in addition to each solution non-ionic crosslinker, N,N'-methylenebisacrylamide (MBAAm), was added in such amount, that $x_I+x_{MBAAm} = 0.1$. Six series of networks with $x_I = 0.005-0.1$ and $x_{MBAAm} = 0.095-0$ (constant total amount of crosslinkers) were prepared (Table 1).

The polymerization proceeded at room temperature for 5 h in ampoules with diameter D=10 mm. After polymerization the gels were cut to the pieces of height from 10 to 20 mm a extracted in redistilled water for 7 days. The experimental data were compared with those obtained on PAAm networks which contained a quarternary salt - 2-methacrylamidoethyl-trimethylammonium chloride ($x_s = 0 - 0.164$) (8),

$$
\begin{array}{ccccccc}
& \overset{\displaystyle CH_3}{|} & & & & \overset{\displaystyle CH_3Cl^{\ominus}}{|} & \\
CH_2{=}C{-}CO{-}NH{-}CH_2{-}CH_2{-}\overset{\oplus}{N}{-}CH_3 & & & & & & \\
& & & & & \underset{\displaystyle CH_3}{|} &
\end{array}
\tag{II}
$$

Swelling and mechanical measurements: The samples were swollen in water-ethanol mixtures in the range 0-95 vol.% of ethanol. Swelling proceeded for 28 days to reach the equilibrium. After that the swelling ratio X, related to the state of network formation, was determined from

$$
X = (D^*/D)^3 = V^*/V \tag{1}
$$

where D^* and D are the sample diameters after the preparation and after equilibrium swelling in the ethanol-water mixtures respectively, V^* and V are the corresponding sample volumes. The diameters D were measured by means of Abbe's comparator (accuracy 0.002 mm); values of swelling ratios X in Fig. 1 and 2 are averages from at least two samples. From X values it is easy to calculate the volume fraction of the polymer in swollen state $v_2{=}v^0 X$, where v^0 is the volume fraction of the polymer at network formation ($v^0 = 0.037$).

Deformation measurements on swollen cylindrical samples in water-ethanol mixtures were carried out in unidirectional compression using earlier described apparatus (5). The specimen, 10-20 mm high, was compressed to the compression ratio $\lambda({=}l/l_0$, l and l_0 being the compressed and the initial height of the sample) and the force f was determined after 30 s relaxation; 10 values of λ and f in the range $0.7 < \lambda < 1$ were determined. The equilibrium shear modulus G was obtained from relation

$$
G = f/S_0(\lambda^2 - \lambda^{-1}) \tag{2}
$$

Table 1: Basic network characteristics and the collapse parameters

x_I	x_{MBAAm}	G_1 gcm^{-2}	$10^5 \nu_d$ mole cm^{-3}	$\Delta \log X$	$\Delta \log G$	e_c vol%
			Serie S1			
0.005	0	11.5	0.91	–	–	–
0.010	0	18.1	1.43	1.20	0.4	45
0.020	0	22.9	1.81	1.55	0.5	55
0.050	0	40.0	3.16	1.60	0.5	62
0.075	0	45.2	3.57	1.50	0.5	67
0.100	0	57.5	4.55	1.60	0.6	70
			Series 2			
0.005	0.095	49.5	3.92	–	–	–
0.010	0.090	52.5	4.15	0.70	0.2	40
0.020	0.080	51.0	4.03	1.00	0.3	45
0.050	0.050	57.0	4.51	1.30	0.4	60
0.075	0.025	54.5	4.31	1.50	0.5	67
0.100	0	57.5	4.55	1.60	0.6	70

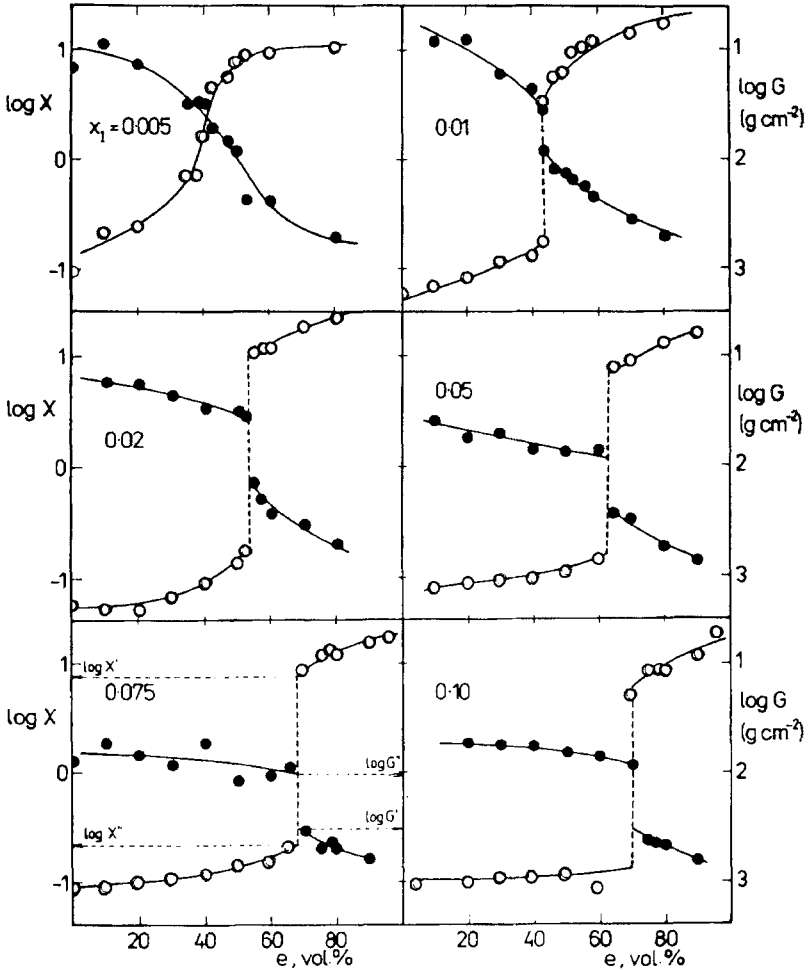Figure 1: The dependence of the swelling ratio X and modulus G (g cm^{-2}) on the concentration of ethanol, e, (vol.%) of networks of series 1; $\circ$ X, $\bullet$ G; the numbers correspond to the mole fraction of ionic crosslinker, x_I

in which S_0 is the initial cross-section of the specimen. Also the deformation measurements on samples just after polymerization (X=1) were carried out and the value of the shear modulus G_1 was determined. The concentration of elastically active network chains (EANC) related to the dry volume of network ν_d was determined (10)

$$\nu_d = G_1/RTv^0 \tag{3}$$

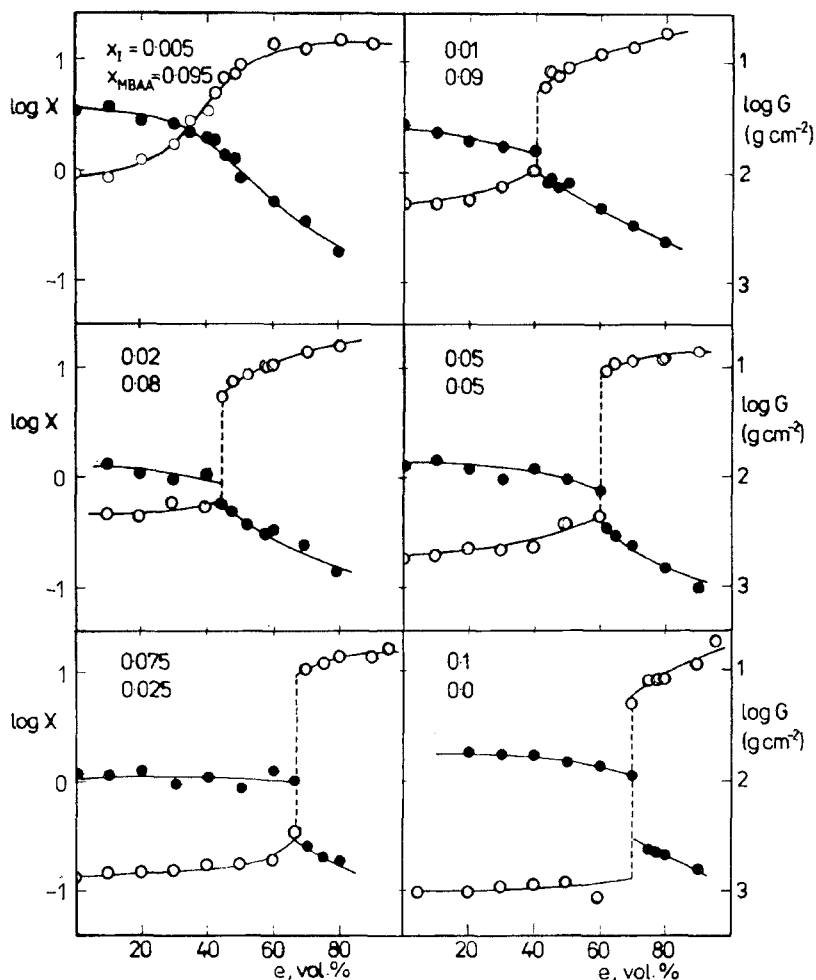where R is the gas constant and T is the temperature (Table 1).

Figure 2: The dependence of the swelling ratio X and modulus G (g cm^{-2}) on the concentration of ethanol, e, (vol.%) of networks of series 2; $\bigcirc$ X, $\bullet$ G; the numbers correspond to the mole fractions of ionic ,x_I , and non-ionic, x_{MBAAm}, crosslinkers

Results and Discussion

Swelling and mechanical characteristics

As expected, with increasing concentration of ionic crosslinker in networks of series 1 the value of equilibrium shear modulus measured after polymerization, G_1, increases together with the concentration of EANC, ν_d, (Table 1). On the other hand, the G_1 and ν_d values of networks of series 2 are roughly independent of the composition; this is due to the constant total ammount of crosslinkers in the system. The low ν_d values in both

series indicate the low efficiency of the crosslinking reaction at the high dilutions used, and thus large cyclization in the system.

It can be seen from Fig. 1 and 2, that with the lowest concentration of ionic crosslinker $x_I = 0.005$, the dependence of the swelling ratio X on the ethanol content, e, is continuous. On the other hand, the networks with $x_I \geq 0.01$ undergo phase transition reflected in a jumwise change in X (gel volume) in both series 1 and 2 from the expanded state (low values of e) to the collapsed state (high e values) of network. Fig. 2 shows that the extent, of the collapse, $\Delta \log X = \log X' - \log X''$ (Fig. 1) increases for samples of series 2 with increasing ionic crosslinker concentration; a similar behaviour is also observed in the critical ethanol concentration in the water-ethanol mixture, e_c, at which collapse takes place (Table 1). With the exception of network with $x_I = 0.01$, the $\Delta \log X$ values of networks of series 1 are independent of composition (Fig. 1, Table 1).

As expected, at constant crosslinking density ν_d, the swelling degree in the expanded state increases (the value X decreases) with increasing charge concentration, x_I, for networks series 2 (Fig. 2). On the other hand, the swelling degree in the expanded state is roughly independent of the composition of networks of series 1 (Fig. 1). In this case the increase in swelling due to the increasing charge concentration is compensated by the decrease in swelling due to the increasing network density. In the collapsed state the swelling is almost composition independent and roughly the same for both series (Fig. 1 and 2).

The phase transition of networks of both series with $x_I \geq 0.01$ is reflected also in a jumpwise change in the shear modulus (Fig. 1 and 2). This jump can be characterized by the value of $\Delta \log G = \log G'' - \log G'$ (Fig. 1). As in the case of the jump in the swelling ratio $\Delta \log X$, the $\Delta \log G$ values increase with x_I in networks of series 2 and are independent of composition in networks of series 1 (Table 1).

According to Fig. 3, 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 $\Delta \log X$ ($\Delta \log G = 0.33 \Delta \log X$). This means, that mechanical behaviour at the collapse is predominantly determined by the degree of swelling. The slope s=0.33 fits in with
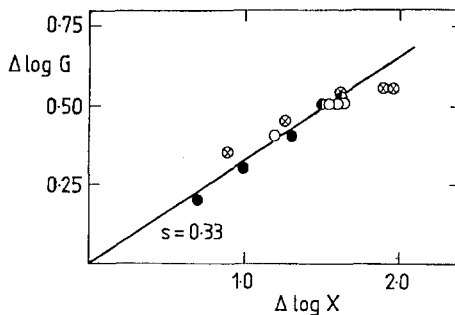

Figure 3: The dependence of the jumpwise change in the modulus $\Delta \log G$ on the change in the swelling ratio $\Delta \log X$ at the collapse; $\bigcirc$ series 1, $\bullet$ series 2, $\otimes$ networks with salt (II) from (8)

the value predicted by the kinetic theory of rubberlike elasticity, being in agreement with the slope found for networks copolymerized with salt (II) (8) and also found for P(AAm/MNa) networks (5). This slope is, however, half of the slope found for AAm containing quaternary salts with ester group in the side chain (6).

The dependence of the extent of collapse $\Delta \log X$ and of the critical ethanol e_c (Table 1) or acetone a_c (data for salt (II) are taken from (8)) concentration on the molar concentration of a positive charge $x_{N\oplus}$ ($x_{N\oplus} = 2x_I$ for networks of series 1 and 2, $x_{N\oplus} = x_s$ for networks with salt (II)) can be seen in Fig. 4. While for series 2 (constant ν_d) the $\Delta \log X$ values increase with $x_{N\oplus}$, for samples of series 1, the $\Delta \log X$ values are independent of $x_{N\oplus}$ (with the exception of network with $x_{N\oplus} = 0.02$). This independence of $\Delta \log X$ on $x_{N\oplus}$ is due to the compensation of the effect of the increasing crosslinking density ν_d and increasing charge concentration $x_{N\oplus}$ on the swelling in the networks of series 1. Similar behaviour was observed also for the degree of swelling in water and in low ethanol concentrations (Fig. 1). From comparison of the $\Delta \log X$ values of series 1 and 2 with those of salt (II) it follows that the increase in the crosslinking density cause the decrease in the $\Delta \log X$ values.

The critical ethanol, e_c, or acetone, a_c, concentrations at which the collapse takes place increase with increasing charge concentration $x_{N\oplus}$ (Fig. 4). While the dependences of e_c or a_c on $x_{N\oplus}$ are identical for series 1 and networks with salt (II), the e_c values of series 2 are lower at low $x_{N\oplus}$. Lower e_c values of series 2 are given by higher crosslinking and this is in accord with previous results on P(AAm/MNa) networks with different concentrations of MBAAm crosslinker (11).
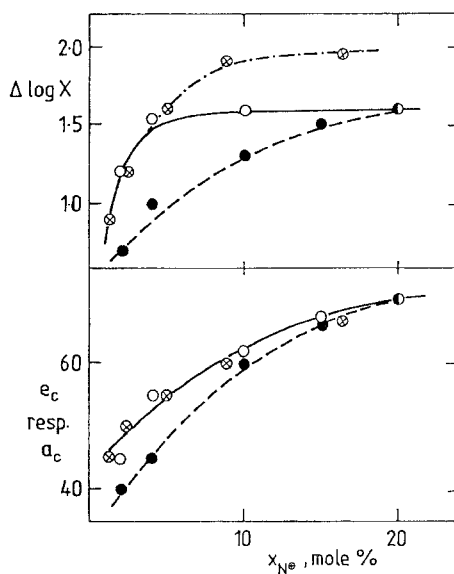

Figure 4: The dependence of the extent of the collapse $\Delta \log X$ and of the critical ethanol, e_c, (series 1 and 2) or acetone, a_c, concentrations at the collapse on the molar concentration of positive charge $x_{N\oplus}$; $\bigcirc$ series 1, $\bullet$ series 2, $\otimes$ networks with salt (II) from (8)

Therefore one can conlude, that the effect of the charge in ionic crosslinker on the appearance and the extent of the collapse is comparable with the effect of the similar charge placed in the side chain. The change in the crosslinking density has only minor effect on observed phenomena.

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