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Phase transition in swollen gels

19. Effect of the crosslinker with a negative charge on the collapse of polyacrylamide networks

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Summary

The swelling and equilibrium mechanical behaviour of networks of copolymers of acrylamide (AAm) with a ionic crosslinker – sodium salt of 2,2–bisacrylamidopropionic acid (I) in water-ethanol mixtures was investigated. Two series of networks were prepared. While in series 1 AAm and ionic crosslinker were copolymerized (mole fraction x_I = 0.005 to 0.1), in series 2, AAm, ionic crosslinker and non-ionic crosslinker – methylenebisacrylamide (MBAAm) – were copolymerized in such way that $x_I + x_{MBAAm} = 0.05$ (x_I varied from 0 to 0.05). In the region $x_I \geq 0.01$ the phase transition was observed for both series. As expected, for networks of series 2 with constant crosslinker concentration the extent of transition (jumpwise change of the volume of the gel) increases with increasing charge concentration, x_I. On the other hand, for samples of series 1 this extent slightly decreases with x_I which means that the effect of increasing crosslinking density on the swelling is greater than that of increasing charge concentration. The critical ethanol concentration at which collapse takes place, e_c, increases with x_I in both series. The jumpwise change in the gel volume is accompanied by a similar change in the equilibrium modulus of the gel.

Introduction

During a transition from a good to a poor solvent a first-order phase transition (collapse) has been observed in lightly charged polyacrylamide (PAAm) hydrogels (1–4), reflected in a jumpwise change of the volume of the gel. The extent and appearance of the jump is influenced by changes in either the structural parameters of network (dilution at network formation, the concentration of charges or the crosslinking density) or the position and the polarity of the charge. In all studied systems the negatively or positively charged centres were placed in different positions in the side chains. Experimental swelling behaviour of PAAm gels at the collapse could be described by the theory of the swelling equilibria in polyelectrolyte networks if the correction factor for the effective degree of ionization was introduced (5,6).

In our previous paper we investigated the effect of the positive charge in ionic crosslinker (7) on the appearance and the extent of the collapse in polyacrylamide gels in water-ethanol mixtures. It was found that with increasing concentration of crosslinker the compensation effect of the increasing crosslinking density and increasing charge concentration on the swelling degree is operative. In this study we investigate the effect of the concentration of the negative charge in ionic crosslinker on the swelling and mechanical

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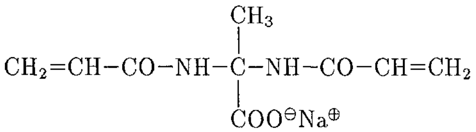
behaviour of PAAm gels in water-ethanol mixtures and compare the results with those obtained for positively charged crosslinker. To separate the effect of the increasing charge and increasing crosslinking density concentration, also the networks with a constant total amount of ionic and non-ionic crosslinker are studied.

Experimental

Sample preparation: The sodium salt of 2,2-bisacrylamidopropionic acid (I),



$$CH_2{=}CH{-}CO{-}NH{-}\overset{CH_3}{\underset{COO^{\ominus}Na^{\oplus}}{C}}{-}NH{-}CO{-}CH{=}CH_2$$

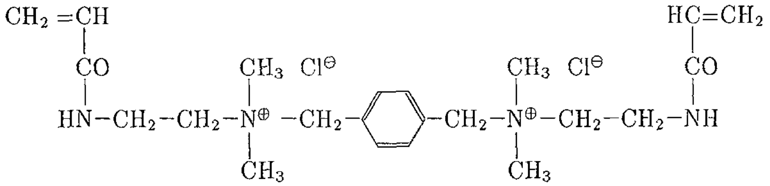
I

was used as ionic crosslinker in network preparation (molecular weight $M_I = 234$). Two series of networks were prepared: a) In series 1 the samples were made from 100 ml of an aqueous solution which contained 5 g acrylamide (AAm), 0.04 g ammonium persulfate, 150 μl N,N,N′,N′-tetramethylethylenediamine, and various amounts of ionic crosslinker I. Six networks with varying mole fraction of the crosslinker, x_I, ranging from 0.005 to 0.1 were prepared (Table 1). b) In series 2 the samples were prepared from the same solutions as in series 1 but in addition, to each solution the non-ionic crosslinker N,N′-methylenebisacrylamide (MBAAm, $M_{BAAm} = 154$) was added in such amount that $x_I + x_{MBAAm} = 0.05$. Six networks with $x_I = 0.005$ to 0.5 and $x_{MBAAm} = 0.045$ to 0 were prepared (Table 1).

Table 1: Basic network characteristics and the collapse parameters

x_I	x_{MBAAm}	G_I g cm^{-2}	$10^5\nu_d$ mol cm^{-3}	$10^4 c$ mol cm^{-3}	$\Delta \log X$	$\Delta \log G$	e_c vol. %
				Series 1			
0.005	0	17.4	1.38	0.94	1.1	0.40	45
0.010	0	32.8	2.60	1.86	1.2	0.45	50
0.020	0	51.4	4.07	3.66	1.0	0.41	52
0.050	0	119.9	9.50	8.64	1.0	0.31	56
0.075	0	181.2	14.36	12.40	0.9	0.25	58
0.100	0	242.6	19.22	15.90	0.8	0.20	60
				Series 2			
0.005	0.045	74.6	3.53	8.96	–	–	–
0.010	0.040	99.1	5.48	8.92	0.60	0.25	48
0.020	0.030	93.1	7.38	8.85	0.75	0.25	50
0.030	0.020	110.0	8.72	8.78	0.75	0.25	53
0.040	0.010	110.5	8.76	8.70	0.90	0.35	55
0.050	0	119.9	9.50	8.64	1.00	0.30	56

The redistilled water was used and the polymerization proceeded at room temperature for 5 h in glass ampoules with inner diameter of 10 mm. After polymerization, the samples were cut to the pieces of height ≈ 10 mm and extracted with redistilled water for 7 days. The swelling and mechanical data were compared with those (7) obtained on the similar PAAm networks which contained positively charged crosslinker II – N,N'-(1,4-phenylenedimethylene)bis(2-acrylamidoethyl-dimethylammonium chloride) ($M_{\mathrm{II}} = 459.5$)



II

In Table 1 also the molar concentrations of the crosslinkers in unit volume of the dry networks, c (in mol cm^{-3}), are given.

Swelling: About twenty water-ethanol mixtures containing 0–80 vol.% of ethanol were prepared from redistilled water and ethanol and extracted specimens of networks were used for swelling in water-ethanol mixtures. After 28 days of swelling, 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, respectively, are the diameter of the specimen after network formation and after swelling and V^* and V, respectively, are the sample volume after preparation and after swelling in the mixture. The diameters were measured with an Abbe's comparator (Zeiss Jena, accuracy ±0.002 mm); the X values plotted in Figs 1 and 2 are averages from at least three measurements. The X values can be used for the calculation of the volume fraction of the polymer in the swollen state $v_2 = V_{\mathrm{d}}/V = v^{\circ}X$ (V_{d} is the dry gel volume and v° is the volume fraction of the polymer at network formation; $v^{\circ} = 0.05$).

Mechanical behaviour: Along with swelling the stress-strain dependences were measured in simple compression using an apparatus described earlier (6). A cylindrical sample was compressed by Teflon surfaces to compression λ and after 30 s of relaxation the force f was read off; ten values λ and f were determined in the range $0.7 < \lambda < 1$. The shear modulus G was determined from

$$G = f/[S_{\mathrm{o}}(\lambda^{-2} - \lambda)] \tag{2}$$

where S_{o} is the initial cross-section of the swollen sample (Figs 1 and 2).

The stress-strain measurements on samples immediately after the polymerization were also carried out. From these dependences the value of the modulus G_1 was determined using Eq.(2) (Table 1). The concentration of elastically active network chains (EANC's) related to the dry volume of network, ν_{d}, was determined from (8)

$$\nu_{\mathrm{d}} = G_1/\mathbf{R}Tv^{\circ} \tag{3}$$

where $\mathbf{R}$ is the gas constant and T is temperature (Table 1).

Results and discussion

It can be seen from Figs 1 and 2 that networks of series 1 and 2 undergo phase transition reflected in a jumpwise change in the swelling ratio X from the expanded (at low ethanol concentrations, e) to the collapsed state (high e values). An exemption is made with network of series 2 with the lowest concentration of ionic crosslinker $x_I = 0.005$, where the dependence of X on e is continuous. The difference in the swelling behaviour of network series 1 with $x_I = 0.005$ and that of series 2 with $x_I = 0.005$ is caused by the presence of nonionic MBAAm crosslinker in sample of series 2. It was predicted (5) and

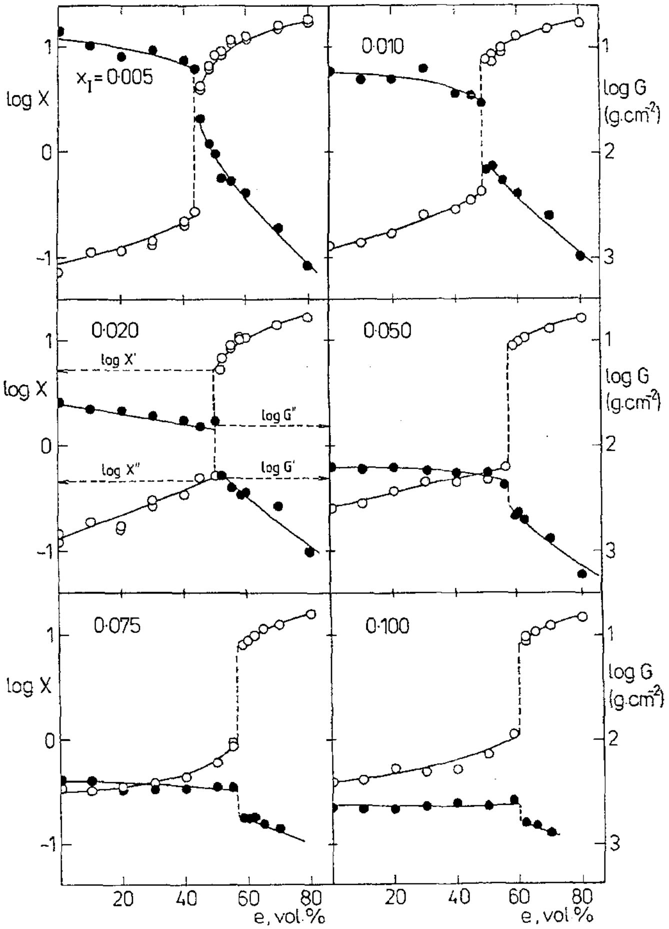


Figure 1: The dependence of the swelling ratio X (○) and modulus G (●) on the concentration of ethanol e in networks of series 1; the numbers correspond to the mole fraction of ionic crosslinker, x_I

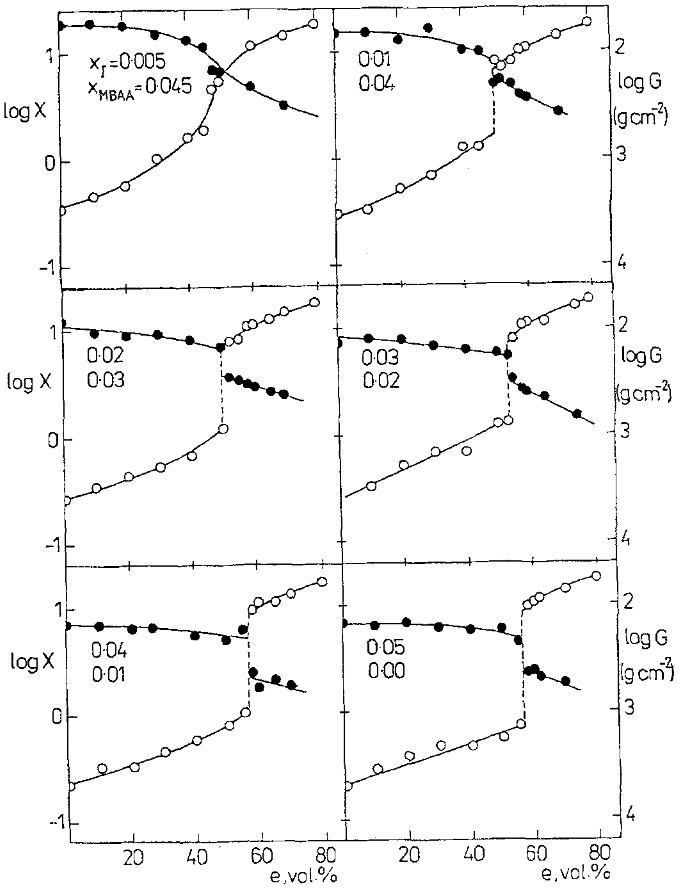


Figure 2: The dependence of the swelling ratio X (○) and modulus G (●) on the concentration of ethanol e in networks of series 2; the numbers correspond to the mole fraction of ionic, x_I, and non-ionic, x_{MBAAm}, crosslinkers

experimentally proved (9) that increasing crosslinking density suppresses the occurrence and extent of phase transition. While the extent of the collapse, $\Delta \log X = \log X' - \log X''$, (Fig. 1) decreases for samples of series 1 with increasing concentration of ionic crosslinker, x_I, for networks of series 2 $\Delta \log X$ with x_I increases (Table 1). On the other hand, the critical ethanol concentration in the water-ethanol mixture at which collapse takes place, e_c, increases with increasing x_I in both network series (Table 1).

As expected, with increasing ionic crosslinker concentration x_I in networks of series 1 the value of the modulus measured after polymerization, G_1, increases together with the concentration of EANC's, ν_d (Table 1, Fig. 3). 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

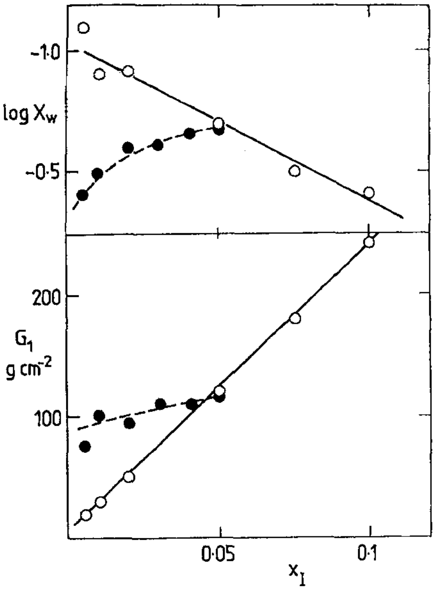


Figure 3: The dependence of the swelling ratio in water, X_w, and modulus measured after the polymerization, G_1, on the molar concentration of the charged crosslinker x_I; ○ series 1, ● series 2

constant total amount of both the crosslinkers in the system. The swelling degree of the networks of series 2 in pure water, q, characterized by the swelling ratio X_w ($q \sim 1/X_w$) increases with x_I (Fig. 3), i.e. with increasing ionization of the system. On the other hand, the swelling in water decreases with x_I for networks of series 1, which means that the increase in swelling due to the increasing charge concentration is overruled by the decrease in swelling due to the increasing network density.

The dependence of the concentration of elastically active network chains, ν_d, in networks with ionic crosslinker I and in those prepared with ionic crosslinker II earlier (7) on the molar concentration of the croslinker in unit volume, c, is shown in Fig. 4. The low values of the slopes, s, of the linear dependences of ν_d on 2c (ideal theoretical value of EANC's concentration) in both series indicate the low efficiency of the crosslinking reaction due to the large cyclization in the systems. As the same high dilutions were used in both systems it is interesting to note that the efficiency of the crosslinking with the

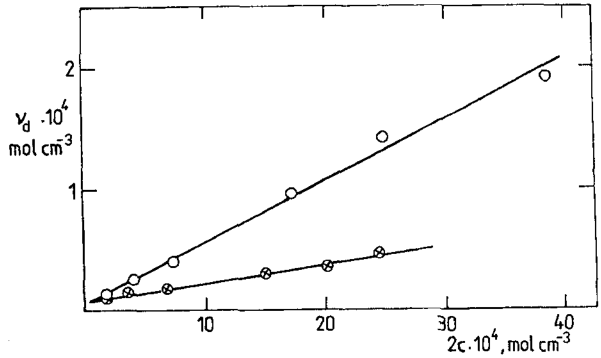


Figure 4: The dependence of the concentration of the elastically active network chains, ν_d, on the ideal theoretical network density, 2c; ○ series 1, ⊗ networks with crosslinker II from (7)

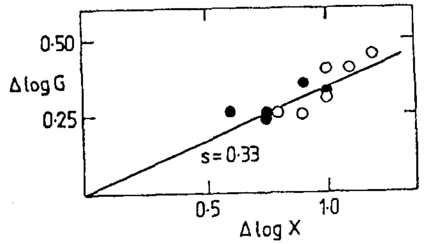


Figure 5: The dependence of the jumpwise change in the modulus $\Delta \log G$ on the change in the swelling ratio $\Delta \log X$ at the collapse; ○ series 1, ● series 2

crosslinker I is roughly three times higher than that with crosslinker II.

The phase transition of networks is reflected also in a jumpwise change in the modulus (Figs 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 decrease with x_I in network series 1 and increase with x_I in networks of series 2 (Table 1). According to Fig. 5, the jumps in the modulus, $\Delta \log G$, correlate with the corresponding jumps in the ratio $\Delta \log X$. This means that the mechanical behaviour at the collapse is determined by swelling. The slope in the linear dependence of $\Delta \log G$ on $\Delta \log X$, $s = 0.33$, fits in with the value predicted by the kinetic theory of rubber elasticity, being in agreement with the slope found for networks with crosslinker II (7) and for acrylamide - sodium methacrylate (P(AAm/MNa)) networks (3,6).

The dependence of the extent of collapse, $\Delta \log X$, and of the critical ethanol concentration, e_c, on the charge concentration, x_I, for network series 1 and 2 and for networks with crosslinker II (7) can be seen in Fig. 6. At constant value x_I, the $\Delta \log X$ values of networks prepared with crosslinker I are always lower than those of networks prepared with crosslinker II. The lower $\Delta \log X$ values of networks of series 1 and 2 are mainly due to higher crosslinking density ν_d and lower charge concentration in these gels in comparison with the networks prepared with crosslinker II. It was predicted (5) and

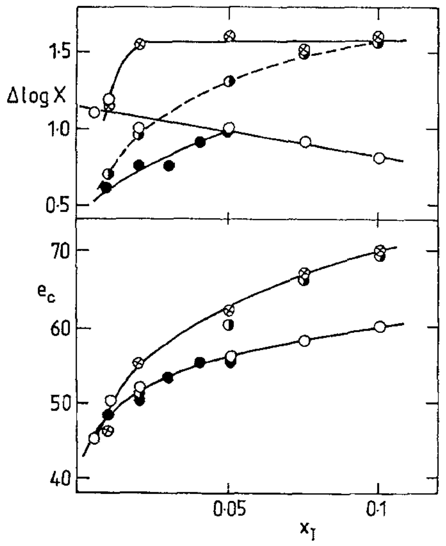


Figure 6: The dependence of the extent of the collapse, $\Delta \log X$, and of the critical ethanol concentration at the collapse, e_c, on the molar concentration of the charged crosslinker, x_I; ○ series 1, ● series 2, ⊗, ◑ networks with crosslinker II from (7)

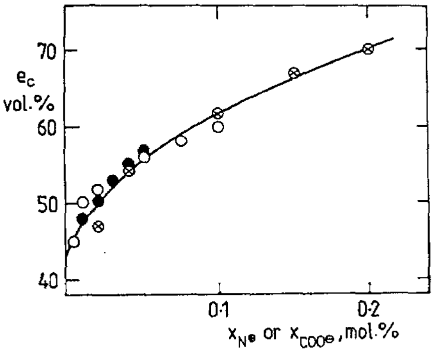


Figure 7: The dependence of the critical ethanol concentration, e_c, on the molar concentration of negative $x_{COO^\ominus}$ (= x_I for network of series 1 and 2) or positive $x_{N^\oplus}$ (= $2x_{II}$ for networks with crosslinker II); ○ series 1, ● series 2, ⊗ networks with crosslinker II from (7)

experimentally proved (3) that increasing ν_d and decreasing x_I suppress the extent of phase transition.

The critical ethanol concentration, e_c, at which the collapse takes place increases with x_I in all networks (Fig. 6). The e_c values of series 1 and 2 are lower than those of networks with crosslinker II and this finding is in accord with the previous results on P(AAm/MNa) networks with different concentrations of either MBAAm crosslinker or MNa ionic monomer (6,7). It should be mentioned that the dependence of e_c on x_I in networks of series 1 and 2 is identical, which means that the charge concentration predominantly determines the e_c value. This fact is confirmed in Fig. 7 where one can see the universal dependence of e_c on the molar concentration of a negative charge $x_{COO^\ominus} = x_I$ for series 1 and 2 or positive charge $x_{N^\oplus}$ ($x_{N^\oplus} = 2x_I$, where x_I is the concentration of crosslinker II).

Thus we can conclude that the effect of the negative charged crosslinker I on the appearance and the extent of collapse in polyacrylamide hydrogels is less pronounced than that of the positively charged crosslinker II. This is mainly due to the fact that the crosslinking efficiency of crosslinker I is considerably higher than that of crosslinker II.

Acknowledgement

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