Polymer Bulletin 27, 577–583 (1992)

Polymer Bulletin

Phase transition in swollen gels

16. Effect of charge polarity in the side chain on the collapse of poly(acrylamide) networks

Z. Sedláková, K. Bouchal, J. Hrouz, and M. Ilavský*

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
CS-162 06 Prague 6, Czechoslovakia

Summary

The swelling and mechanical behaviour of networks of copolymers of acrylamide, methylenebisacrylamide and sodium 2-(2-carboxybenzoyloxy)ethylmethacrylate (mole fraction of salt $x_s = 0 - 0.2$) in water-acetone mixtures was investigated. In the range $x_s \geq 0.01$ phase transition (collapse) was observed, with both the extent of the collapse and the critical acetone concentration in the mixture at collapse, a_c, increasing with increasing concentration of the salt. A comparison between these results and those obtained for networks with a quaternary ammonium salt led to a conclusion that an exchange of the positive charge of the ammonium salt ($N^{\oplus}Cl^{\ominus}$) for the negative charge of the sodium salt ($COO^{\ominus}Na^{\oplus}$) in the side chain decreases the critical content of salt necessary for the collapse, x_s^c, from 0.03 to 0.01, and the collapse takes place at lower concentrations of acetone. The collapse may also take place in a mixed solvent water-ethanol; the dependence of network swelling on the concentration of ethanol is roughly the same as that on the concentration of acetone.

Introduction

With lightly crosslinked poly(acrylamide) (PAAm) gels prepared at high dilution and carrying a low number of charges on the chain (1-10 mol.%), phase transition of the first order (collapse) was observed when passing from a good (water) to a poor (acetone) solvent (1-6). The transition took place irrespective of the polarity of the charge introduced into the chain by the copolymerization of AAm with sodium methacrylate (2) (MNa) (negative charge) or quaternary ammonium salts (7,8) (the positive charge was situated at various distances from the main chain). It was found that while with MNa the collapse could be brought about by ~ 1 mol.% of charges on the chain, the efficiency of ammonium salts is three to ten times lower and the collapse occurs at higher critical concentrations of acetone, a_c, in the water-acetone mixture compared with MNa. Such drop in efficiency at the appearance and extent of collapse was interpreted (8) mainly by the fact that the positive charge is localized at a larger distance from the main chain compared with MNa, and also by consequences connected with the size of the ammonium group (which forms a weaker electrostatic field, due to which hydration of the group is smaller), and also by the influence of counterions on the hydration site (while the hydration number of the anion $Cl^{\ominus}$ is two, that of the $Na^{\oplus}$ cation is three).

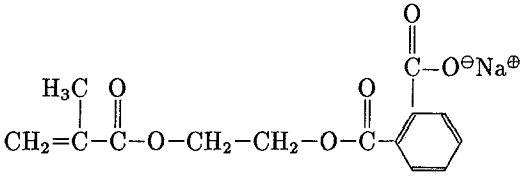
This study concerns the effect of concentration of the negative charge on the chain

---

*To whom offprint requests should be sent on the swelling and mechanical equilibria of PAAm networks obtained by the copolymerization of AAm with sodium 2-(2-carboxybenzoyloxy)ethylmethacrylate. Moreover, by comparing these results and those obtained earlier for a system of the networks of copolymers of AAm with N,N,N-trimethyl-N-4-methacryloyloxybutylammonium chloride it is possible to specify the effect of charge polarity in the side chain on the appearance and extent of the collapse, because the distance of charges from the main chain is similar.

Experimental

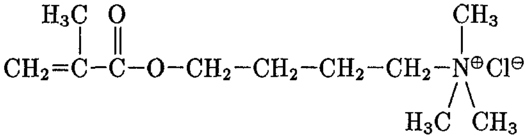
Sample preparation: The networks were prepared from 100 ml of an aqueous mixture,which contained 5 g acrylamide (AAm), 0.135 g N,N'- methylenebisacrylamide (MBAAm), 0.02 g ammonium persulfate and 150μl N,N'-tetramethylethylenediamine. Sodium 2-(2-carboxybenzoyloxy)ethylmethacrylate (9) (I)



I

was used as the ionogenic monomer. A series of networks was prepared with a varying mole fraction of the salt $x_s = 0 - 0.2$ (Table 1).

The polymerization proceeded at room temperature ~ 5 h in ampoules with the diameter D=10 mm. After the polymerization the samples were extracted in redistilled water. Experimental data were compared with those reported earlier (8), obtained with PAAm networks prepared by employing the same procedure, but using a quaternary salt, N,N,N- trimethyl-N-4-methacryloyloxybutylammonium chloride (II).



$$CH_2=\overset{H_3C}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_2-\underset{H_3C\ \ CH_3}{\underset{/\backslash}{\overset{CH_3}{\overset{|}{N^{\oplus}}}}}Cl^{\ominus}$$

II

Swelling and mechanical measurements: The samples were swollen in water-acetone mixtures in the range between 0 and 90 vol% of acetone. Swelling proceeded ~ 28 days, after which the swelling ratio X related to the state of network formation was determined (Fig.1)

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

where D^* and D is the sample diameter after the preparation and after equilibrium swelling in mixtures respectively, V^* and V is the respective volume. The diameters were measured by means of an Abbe's comparator. Using the X values, it is easy to calculate the volume fraction of the polymer in the 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 cylindrical samples were carried out in a unidirectional compression using an apparatus described earlier (2). The sample, ~ $1 - 2$ cm high, was compressed to the ratio $\lambda(= l/l_0$, l and l_0 being the deformed and the initial height of the sample), and the force f was determined after relaxation for 30 sec; 10 values of λ_i and f_i in the range $0.7 < \lambda < 1$ were measured. The equilibrium modulus was determined from

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

in which S_0 is the initial cross-section of the sample (Fig.2).

Results and Discussion

Swelling and mechanical characteristics in water-acetone mixtures

It can be seen in Fig.1 that already at the lowest salt concentration $x_s = 0.01$ the network undergoes phase transition; only for the PAAm network alone the dependence of X on the acetone concentration, a, is a continuous one. With increasing salt concentration the stepwise change in the swelling ratios Δlog X at the collapse increases (extent of the transition), and the transition takes place at higher critical concentrations of acetone a_c in the acetone-water mixture (Table 1).

Table 1: Basic network characteristics at collapse

x_s	$10^5\nu_d$ mole.cm^{-3}	Δlog X	Δlog G	a_c vol.%
0	–	–	–	–
0.01	2.6	0.55	0.35	40
0.02	3.7	0.80	0.45	45
0.05	4.6	1.05	0.60	51
0.10	5.8	1.20	0.55	57
0.15	5.6	1.25	0.65	62
0.20	5.8	1.35	0.55	66

The dependence of the modulus G of the PAAm network alone on the swelling ratio is also continuous. All other networks with salt undergo phase transition reflected in a jumpwise change in the modulus (Fig.2) characterized by the value of Δlog G (Table 1). The jumpwise change in the modulus Δlog G correlates with a corresponding change in the volume Δlog X with a slope $\sim$ 0.5 (Δlog G= 0.5 Δlog X, Fig.3). The slope is larger that that observed earlier (8) for the system PAAm - quaternary ammonium salt (II) (where s = 0.35).

The concentrations of elastically active chains in the dry state $\nu_d = G_1/RTv^0$ (R is the gas constant, T is temperature, Table 1) were calculated from the modulus G_1 measured after network preparation. The low ν_d values indicate a low efficiency of the crosslinking reaction, which is a consequence of large cyclization caused by high dilution. Fig.4 shows that the crosslinking efficiency increases with increasing concentration of the salt x_s, but is independent of charge polarity in the side chain (increase in ν_d with x_s is the same for both the quaternary ammonium and sodium salt).

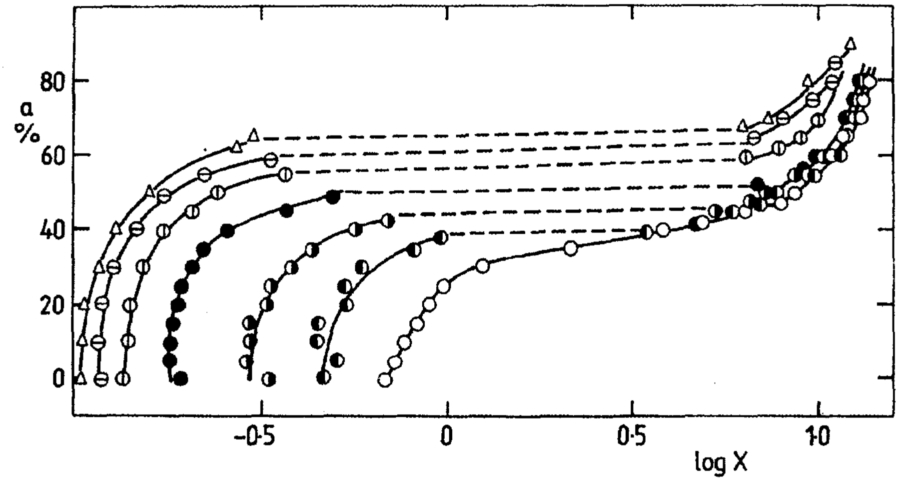


Figure 1: Dependence of the swelling ratio X on the concentration of acetone a (vol.%); salt I x_s: ○ - 0, ◐ - 0.01, ◑ - 0.02, ● - 0.05, ⦶ - 0.1, ⊖ - 0.15, △ - 0.20.

The dependence of the critical concentration of acetone a_c and of the extent of the collapse Δlog X on the molar concentration of the salt x_s is shown in Fig.4, along with results obtained for networks with a quaternary ammonium salt. While the extent of the collapse Δlog X remains virtually unaffected by the structure of the salt, the critical acetone concentrations at collapse a_c are displaced in the case of the sodium salt by ~ 10 % to lower a_c values in the mixed solvent, being roughly at the level found for P(AAm-

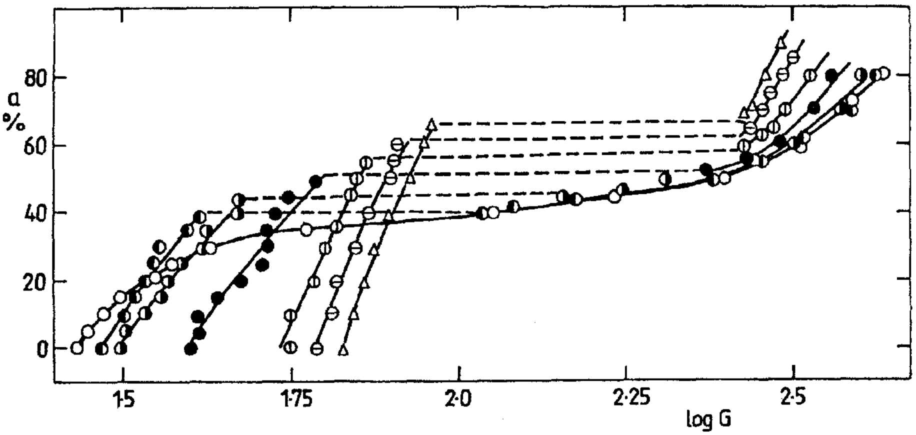


Figure 2: The dependence of modulus G(g cm^{-2}) on the concentration of acetone a (vol.%). Samples denoted as in Fig.1.

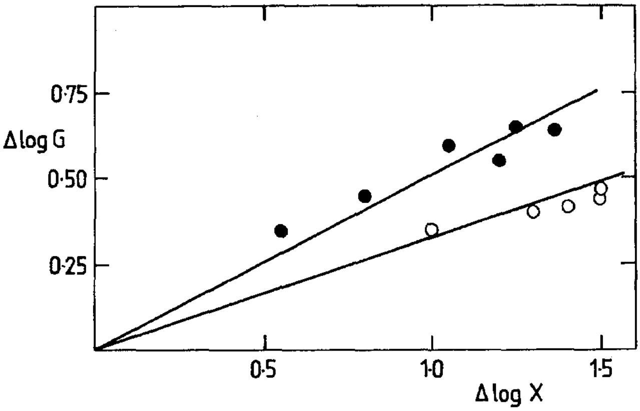


Figure 3: Dependence of the jumpwise change in modulus Δlog G on the jumpwise change of the swelling ratio Δlog X; salt: ● - I, ○ - II.

sodium methacrylate) networks (2). The critical value of the amount of salt at which the transition appears for the first time, x_s^c, is lower for P(AAm-salt (I)) networks ($x_s^c = 0.01$) than for P(AAm-salt (II)) networks, where the concentration of salt was $x_s^c = 0.03$. It can be said, therefore, that the negative charge $COO^{\ominus}$ of the side chain has a stronger effect on the occurrence of collapse than the positive charge of the nitrogen atom $N^{\oplus}$.

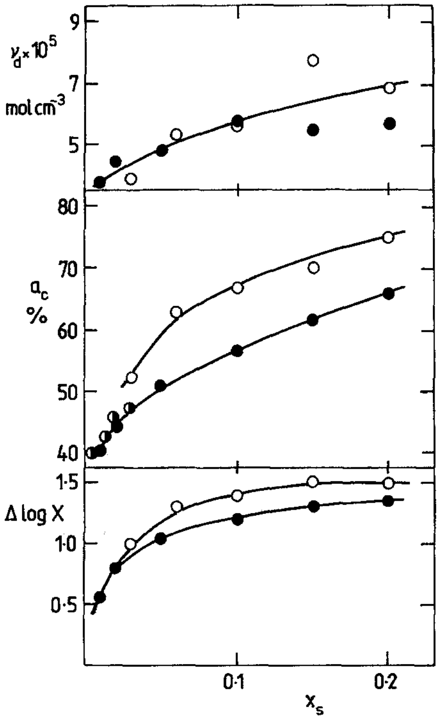


Figure 4: Dependence of the extent of collapse Δlog X, of the critical concentration of acetone at collapse a_c and of the concentration of elastically active chains ν_d on the molar concentration of salt x_s;
● - salt I, ○ - salt II, ◑ - networks P(AAm-MNa) (2).

Swelling in the water-ethanol mixtures

Both in the PAAm network alone and in the network with a charge the dependences of the swelling ratio X on the acetone content (a) in water-acetone mixtures, or on ethanol (eth) in water-ethanol mixtures are virtually the same (Fig.5). This means that the collapse of PAAm networks with charges can be brought about also by the transition from water to ethanol, as has been observed earlier (10).

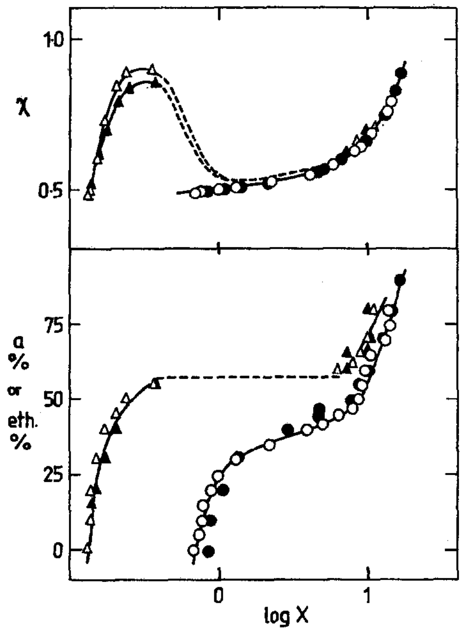


Figure 5: Dependence of the concentration of acetone, a, or of ethanol, eth, and of the Flory-Huggins interaction parameter χ on the swelling ratio X; ○ - $x_s = 0$, mixture w - a; ● - $x_s = 0$, mixture w - eth; △ - $x_s = 0.1$, mixture w - a; ▲ - $x_s = 0.1$, mixture w - eth.

The introduction of the effect of electrostatic interactions into the theory of swelling equilibria led to the prediction of the swelling pressure P in the form (11,12)

$$P = P_m + P_{el} + P_{os} + P_{els} \tag{3}$$

where the contribution P_m corresponds to the mixing of chain segments with the diluent (involving the Flory-Huggins interaction parameter χ), P_{el} corresponds to a change in the elastic energy of the chain with swelling, P_{os} corresponds to the mixing of ions with the diluent, and P_{els} is determined by a change of the energy of electrostatic interactions with swelling. Ref. (11) gives the terms P_i in molecular parameters (network density ν_d, molar volume of the mixed solvent, degree of ionization $\alpha = x_s$, density d = 1.35 gcm^{-3}) and volume fractions of the polymer in the swollen network, v_2. Using Eq.(3), it is easy to calculate the dependence of the interaction parameter χ on X (or on v_2) by employing a procedure described in detail earlier (2,11) for P(AAm-MNa) networks (due to free swelling, in Eq.(3) P=0).

It can be seen in Fig.5 that the dependence of χ on the ratio X is virtually independent of the component used in the mixed solvent (acetone or ethanol). For the charge-free network, χ increases with X in the range $\chi = 0.48$ (water) to $\chi = 0.9$ ($\sim$ 90%

acetone or ethanol). On the other hand, the dependence of χ on X for the charge-carrying network ($x_s = 0.1$) shows a van der Waals loop, characteristic of the existence of phase transition, which allows the extent of the collapse and the critical value of the interaction parameters to be determined by employing a procedure reported earlier (2,12).

References

1 Tanaka T, (1979) Polymer 20: 1404
2 Ilavský M, (1982) Macromolecules 15: 782
3 Tanaka T, Nishio I, Sun S-T, Uemo-Nishio S, (1982) Science 218: 467
4 Stejskal J, Gordon M, Torkinton J A, (1980) Polymer Bull. 3: 621
5 Hrouz J, Ilavský M (1984) Polymer Bull 12: 515
6 Ilavský M, Hrouz J, Stejskal J, Bouchal K (1984) Macromolecules 17: 2868
7 Ilavský M, Hrouz J, Bouchal K (1985) Polymer Bull 14:301
8 Ilavský M, Bouchal K, (1988) in "Biological and Synthetic Polymer Networks" ed by Kramer O, Elsevier Publ, N.Y. p.435
9 Sedláková Z, Bouchal K, Ilavský M (1991) Angew Makromol Chem to be published
10 Starodubcev S G, Khokhlov A R, Pavlov N R and Vasilevskaya V V (1985) Vysokomol Soed B 27: 500
11 Hasa J, Ilavský M (1975) J Polym Sci Polym Phys Ed 13: 263
12 Ilavský M (1981) Polymer 22: 1687

Accepted October 30, 1991 C