Phase Transition in Swollen Gels
9. Effect of the Concentration of Quaternary Salt on the Collapse and Mechanical Behaviour of Poly(Acryl Amide) Networks

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Summary

The swelling and mechanical behaviour of ionized networks of copolymers of acryl amide (AAm) with N,N,N,N-trimethyl-2-methacryloyloxyethyl ammonium chloride (MOAC) (mole fraction x_{MOAC} = 0-0.165) in water-acetone mixtures was investigated. In the range $x_{MOAC} \geqq 0.029$, phase transition was observed with increasing acetone content; both the extent of the transition, Δ, and the critical acetone concentration at which the collapse takes place increased with increasing x_{MOAC}. The effect of concentration of the positive charge at the end of side chains of MOAC on the formation and extent of the collapse is roughly five times smaller than that of the negative charge in networks of the copolymer of AAm with sodium methacrylate. The jumpwise change in the gel volume is accompanied by a similar change in the value of the equilibrium modulus.

Introduction

With loosely crosslinked poly(acryl amide) (PAAm) networks prepared at high dilution at network formation and containing a small number of charges on the chain (~1-5 mole %), first-order phase transition (collapse) was observed during the transition from a good to a poor solvent (1-5). The charges could be introduced into the chain either by a spontaneous hydrolysis of AAm groups (1,2,4) or by copolymerizing AAm with a suitable monomer (e.g., sodium methacrylate (3) or N-acryloxysuccinimide ester (4)). The collapse could also be brought about by a change in external conditions, such as an adjustment of the concentration of the low-molecular weight electrolyte in solution (6), electric field (7), temperature (8), pH of the solution (1), or by a change in network parameters, such as the degree of ionization (1,3), network density (9) or dilution at network formation (10). In all cases the negative charge was situated in close proximity of the main PAAm chain. It may be expected that the behaviour of PAAm networks with a small number of positive charges will also undergo phase transition; however, the introduction of positive charges localized in close proximity to the main chain (similarly to negative charges formed by carboxylic ions) is difficult from the experimental point of view (Hofmann´s degradation of amide groups of PAAm). Also, it was found that the theory of polyelectrolyte networks suggested

earlier (11) which considers the effect of electrostatic interactions of charges on the chain irrespective of their polarity gives a semiquantitative description of the formation and extent of collapse of PAAm networks in water-acetone mixtures; in some cases, the agreement between theory and experiment requires that the effective degree of ionization, α, should be lower than the stoichiometric one (5).

In this study we investigate the effect of the content of a quaternary salt - N,N,N-trimethyl-2-methacryloyloxyethyl ammonium chloride - on the swelling and mechanical equilibria of PAAm networks in water-acetone mixtures and compare experimental data with theory (11). Quaternary salts are strong electrolytes in which hydrolytic equilibrium is not operative, and the degree of ionization is independent of pH. Due to the bulkiness of the ammonium group the positively charged nitrogen atom forms a weaker electrostatic field, the centre of which is situated further from the PAAm chain than in the case of the carboxylic ion.

Experimental

Sample preparation. The samples were prepared from 100 ml of a mixture which contained 5 g of acryl amide (AAm), the corresponding amount of the quaternary salt, 0.135 g of N,N´-methylenebisacrylamide (MBAAm), 0.02 g of ammonium persulfate and 0.02 g of sodium pyrosulfite. Six series of networks were prepared with a varying content of salt - N,N,N,N-trimethyl-2-methacryloyloxyethyl ammonium chloride (MOAC)

$$CH_2=\underset{\underset{CH_3}{|}}{C}-CO-O-CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{\oplus}{N}}}-CH_3-Cl^{\ominus}$$
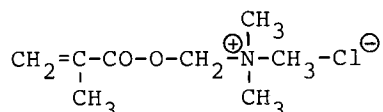
so that the mole fraction of MOAC, x_{MOAC}, would vary in the range between 0 and 0.165 (Table 1). All components with the exception of pyrosulfite were dissolved in redistilled water and the solution was bubbled with nitrogen; after that, pyrosulfite was added, the solution was stirred and dosed into ampoules with a diameter of ~1 cm. The polymerization proceeded at room temperature for 5 h. After the polymerization the gels were cut into specimens ~1 cm long which were further extracted in redistilled water.

Swelling. Water-acetone mixtures (0-80 vol.% of acetone) were prepared from redistilled water. The specimens were swollen in the mixtures at room temperature; for swelling in mixtures with a higher acetone content (>40 by vol.), partly dried specimens were used. After swelling for ~28 days we determined the swelling ratio X related to the state at network formation from

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

where D^* and D are the diameters of the specimens after preparation and swelling in the mixtures respectively, V^* and V

are the respective gel volumes. The measurements were per-
formed with an Abbé comparator (Zeiss Jena, accuracy
$\pm$ 0.002 mm); the X values in Fig.1 are the averages from at
least three samples.

Table 1. Basic network characteristics and phase transition
parameters

series	x_{MOAC}	G_1 g cm^{-2}	$10^5 \nu_d$ mol cm^{-3}	$\Delta(\log X)$	$\Delta(\log G)$	Δ	χ_c	ϕ
A	0	13.5	1.5	–	–	–	–	–
B	0.010	19.1	2.1	–	–	–	–	0.13
C	0.029	30.2	3.2	0.80	0.30	0.175	0.539	0.13
D	0.047	42.7	4.6	1.10	0.45	0.205	0.555	0.15
E	0.090	77.6	8.3	1.35	0.55	0.241	0.607	0.20
F	0.165	123.0	13.8	1.50	0.60	0.294	0.665	0.26

x_{MOAC} is the molar fraction of MOAC, G_1 is the extrapolated
shear modulus determined from the G vs X dependence for X=1,
ν_d is network density related to the dry volume, $\Delta(\log X)$ is
a change in the gel volume at collapse, $\Delta(\log G)$ is a change
in the gel modulus at collapse, $\Delta = \varphi_2'' - \varphi_2'$ is the extent of
the collapse, χ_c corresponds to the χ value of the acetone-
water mixture at which the collapse takes place, and ϕ is the
empirical correction factor ($\alpha = \phi x_{MOAC}$).

Mechanical characteristics. Deformational measurements of the
specimens were carried out using an apparatus described
earlier (12) in which a cylindrical specimen was compressed
to the compression λ (= $1/1_o$, where 1 and 1_o are respectively
the deformed and initial specimen length). After 30 s of
relaxation the force value f was read off and the whole
procedure was repeated; ten λ_i and f_i values were recorded
(in the range $0.7 < \lambda < 1$), and used to determine the shear
modulus G from

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

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

Results and Discussion
Swelling and mechanical characteristics
While for the networks A and B the dependence of the
swelling ratio, X, on the acetone content is continuous, the
C-F networks with $x_{MOAC} \geq 0.029$ undergo phase transition
reflected in a jumpwise change in the gel volume (Fig.1). It
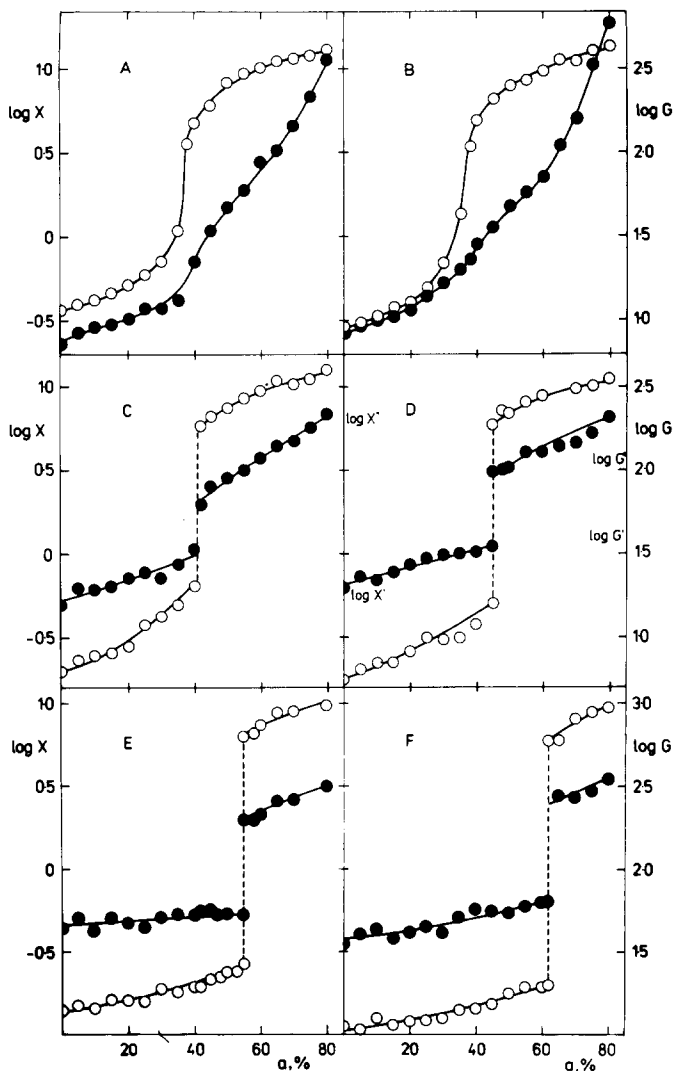is evident that the extent of the collapse $\Delta(\log X)$

Fig.1. Dependence of the swelling ratio X and of the modulus G
(g cm^{-2}) on the acetone content a (vol.%) for networks A-F
with different content of the quaternary salt MOAC
Molar fraction of MOAC, x_{MOAC}: A - 0, B - 0.010, C - 0.029,
D - 0.047, E - 0.090, F - 0.165; ◯ - X values, ● - G values.

(= log X" - log X') increases with increasing MOAC; the criti-
cal acetone concentration in the mixture at which the collapse
takes place also increases with x_{MOAC} (Fig.1). Qualitatively
the same conclusions were obtained earlier for ionized networks
of copolymers of AAm with sodium methacrylate (MNa) (3) and for

variously aged PAAm networks (1,5). Thus, as expected, the formation of phase transition is independent of the charge polarity, but in order to bring about the collapse of these networks one has to use an approximately five times higher concentration of MOAC compared with MNa.

In networks which undergo the collapse a jumpwise change in the gel volume is accompanied by a similar change in the equilibrium modulus $\Delta(\log G)$ (= $\log G'' - \log G'$) (Fig.1). As expected, the change in volume correlates well with a change in the modulus $\Delta(\log G) = 0.4 \ \Delta(\log X)$ (Table 1); somewhat higher slope values were found earlier for PAAm networks bearing a negative charge (3,8-10). The dependence of the modulus $\log G$ on the swelling ratio $\log X$ in the range of small X is linear and has the slope s ~ 0.4 (Fig.2).
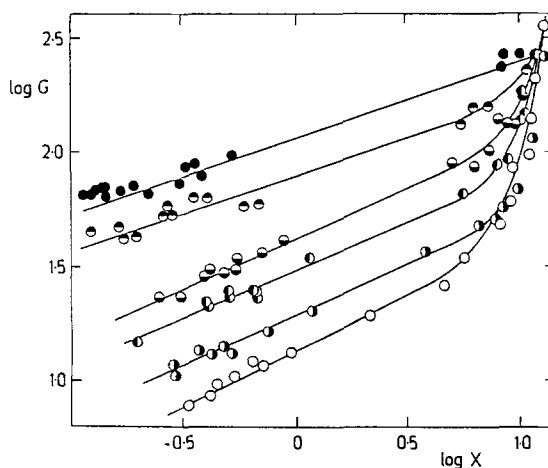

Fig.2. Dependence of the modulus G (g cm^{-2}) on the swelling ratio X. Networks: $\bigcirc$ - A, $\circleddash$ - B, $\circleddash$ - C, $\circleddash$ - D, $\circleddash$ - E, $\bullet$ - F.

Similarly to earlier cases (3), departures from linearity in the range X>8 may be interpreted by the influence of time effects due to the proximity of the main transition region. The $\log G - \log X$ dependences of A-F networks were used in the determination of extrapolated values of the G_1 moduli for X=1 (Table 1). The concentration of elastically active chains related to the dry state (EANC), $\nu_d = G_1/RT \varphi$ were calculated from the G_1 values ($\varphi° = 0.037$ is the volume fraction of the polymer at network formation). Low ν_d values, and hence the low efficiency of the crosslinking reaction ($\sim 10\%$) indicate great cyclization, which is a consequence of the high dilution of the system.

Comparison between theory and experiment

Inclusion of the effect of electrostatic interactions of charges on the chain in the kinetic theory of rubberlike elasticity (11) gave the expression for the swelling pressure P

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

where the contribution P_m is given by the mixing of chain segments with the solvent (Flory-Huggins relationship with the interaction parameter χ), P_{os} is given by the mixing of gel ions with the solvent, P_{el} is given by a change in the elastic free energy with swelling, and P_{els} is determined by a change in the free energy of electrostatic interactions with swelling. The individual contributions are expressed in detail in molecular parameters in Eqs (2)-(5), Ref.(11). Using known parameters (dry polymer density $\rho = 1.35$ g cm^{-3}, molar volumes of acetone-water mixtures V_1, EANC concentration ν_d, degree of ionization x_{MOAC} and experimental values of the volume fractions of the polymer in the swollen state $\varphi_2 = \varphi°X$), the dependences of the interaction parameters χ of A-F networks on φ_2 were calculated (due to free swelling P=0 in Eq.(3)). The same procedure was used earlier with PAAm networks having a negative charge (2,5,8-10).

For the PAAm network alone swollen in water it was found that $\chi = 0.48$; the same value was determined earlier for aqueous solutions and PAAm networks (3,13). Similarly to variously aged PAAm networks investigated earlier (5), in our case too the use of the degree of ionization x_{MOAC} led to unrealistically high values $\chi = 0.74$-14.5 for ionized networks B-F swollen in water alone. Since χ is a measure of the polymer-solvent interaction when the charges are screened (effect of charges in Eq.(3) is included in the contributions P_{os}, P_{els}), in the first approximation one may require that $\chi = 0.48$ also for the B-F networks swollen in water. The requirement $\chi = 0.48$ for the B-F networks swollen in water may be met by assuming that the effective degree of ionization α is smaller than x_{MOAC}, i.e. $\alpha = \phi x_{MOAC}$ where ϕ is an empirical correction factor (Table 1). The ϕ values thus calculated and ranging between ~0.1 and 0.25 (Table 1) are much lower than those found earlier for PAAm networks with a negative charge introduced either by the copolymerization with sodium methacrylate (3) or by the spontaneous hydrolysis of AAm groups (5) (Fig.3).

There are probably several reasons for the low value of the correction factor ϕ (14):

(1) The bulkiness of the ammonium group has as a result that the electrostatic field of the positively charged nitrogen atom is weaker compared with the electrostatic field of the carboxylic anion. Hence, the degree of hydration of the ammonium group is lower.

(2) The degree of hydration of the centres of electrostatic charges is affected by counterions (15). In the case of quaternary salts the anion has the average number of hydration two, while that of the sodium cation is three.
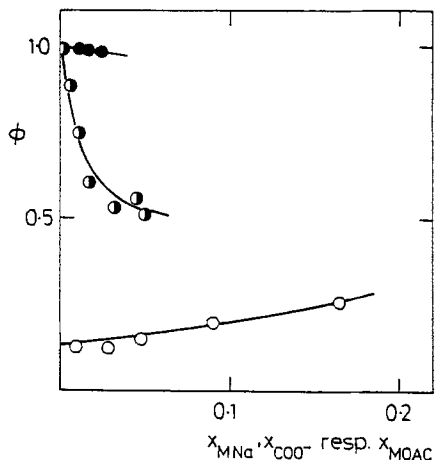
Fig.3. Dependence of the correction factor ϕ on mole fractions: of sodium methacrylate x_{MNa}, of COO^- ions x_{COO^-} and of MOAC salt x_{MOAC}
● - copolymers of AAm and MNa (2), ◐ - variously aged samples of PAAm (4), ○ - copolymers of AAm and MOAC.

Due to this, a higher degree of hydration of electronegative centres compared with positive centres may be anticipated.
(3) Positively charged centres are localized at a larger distance from the main chain, which is probably reflected in a smaller influence on its conformation.
(4) One may expect differences in the association of counterions for negatively and positively charged centres, and thus also participation of ionic pairs.
While points 1-3 are reflected in a decrease in ϕ, the effect of the association of counterions is difficult to discuss.
In the case of the C-F networks, which undergo a collapse, the dependence of χ on φ_2 is characterized by the van der Waals loop (11). The extent of the phase transition $\Delta = \varphi_2'' - \varphi_2'$ and the critical value of the interaction parameter χ_c can be determined from the relationship (for detailed description see Ref.(11))

$$\int_{\varphi_2'}^{\varphi_2''} (\chi - \chi_c)\,d\varphi_2 = 0 \tag{4}$$

A comparison between the theory and experiment is given in Fig.4 which also contains earlier data obtained with PAAm bearing a negative charge (3,5) (the dependence of χ on φ_2 was determined using the effective degree of ionization $\alpha = \phi x_{MOAC}$). While the agreement between theory and experiment for χ_c is good, for Δ it is less satisfactory. It may be said, however, that by using Eqs (3) and (4), also the swelling equilibria of PAAm networks bearing the positive charge
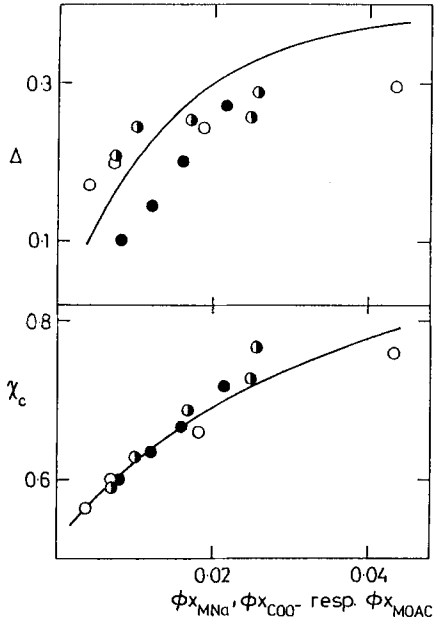
Fig.4. Dependence of the extent of the collapse Δ and critical values of the interaction parameter χ_C on the effective degree of ionization for networks of the copolymer AAm with sodium methacrylate ϕx_{MNa}, variously aged PAAm networks ϕx_{COO^-} and networks of the copolymer of AAm with MOAC ϕx_{MOAC} ● - copolymers of AAm with MNa (2), ◑ - variously aged PAAm networks (4), ○ - copolymers of AAm with MOAC, —— theory (Eq.(4)).

in water-acetone mixtures may be described in the first approximation, assuming that ϕx_{MOAC} is taken as the effective degree of ionization.

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