

Phase Transition in Swollen Gels XXIII. Effect of the Positive Charge Concentration on the Collapse and Mechanical Behavior of Poly(1-vinyl-2-pyrrolidone) Gels

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(Received February 9, 1998)

ABSTRACT: The swelling and mechanical behavior of ionized networks of copolymers of 1-vinyl-2-pyrrolidone, ionic comonomer, *N,N*-dimethyl-*N,N*-diallylammonium chloride (molar fraction of salt $x_s=0-0.27$) and crosslinker, 3,3'-ethylidenebis(1-vinyl-2-pyrrolidone) was investigated in water–acetone mixtures and aqueous NaCl solutions. The networks were prepared by a radiation copolymerization method. At $x_s \geq 0.038$, the first-order phase transition (collapse) was observed. While the critical acetone concentration in the mixture at collapse, $a_c = 76$ vol%, is independent of x_s , the extent of the collapse (jumpwise change in the gel volume), Δ , increases with increasing salt concentration. The jumpwise change in the gel volume is accompanied by a similar change in equilibrium modulus. The swelling and mechanical behavior of ionized networks in aqueous NaCl solutions were also measured. The expected decrease in the swelling and the increase in the modulus with increasing electrolyte concentration c_{NaCl} was found. The theory of swelling equilibria of polyelectrolyte networks, in which the effect of electrostatic interactions of the charges on the chain and a limited chain extensibility were included, semiquantitatively describes the swelling data provided an effective concentration of the charges (lower than x_s) was introduced. Mechanical behavior of networks is predominantly determined by their degree of swelling.

KEY WORDS Vinylpyrrolidone Networks / Polyelectrolytes / Swelling Equilibria / Mechanical Behavior / First-Order Phase Transition / Collapse Phenomenon /

Swollen polymer networks carrying low amounts of charges on the chain (1–10 mol%), when subjected to a change in the external parameters (temperature, composition of the mixed solvent, electric field and the like), undergo a first-order phase transition (collapse), at which the jumpwise change in volume of the gel can be from 10 to 1000 times.^{1–4} SANS experiments showed that in the expanded state, the chains have a coil shape, while in the collapsed state they are in globular form.⁵ It has been shown,² both experimentally and theoretically, that the conditions of network formation (concentration of crosslinker and diluent) and of the charge concentration have a great influence on the appearance and extent of the collapse. The jump in volume is accompanied by a jump in other physical properties, such as shear modulus, refractive index, dielectric permittivity, and the like.² Due to these changes, these systems are considered for use in various devices, sensors, mechanochemical actuators,^{6,7} etc. Most experimental results were obtained with charged poly(acrylamide) (PAAm), poly(*N*-isopropylacrylamide) (PIPAAm), and poly(*N,N*-diethylacrylamide) (PDEAAm) hydrogels.^{1–3,8} While in PAAm gels, the collapse can be brought about by the changes in the solvent composition, in PIPAAm and PDEAAm gels the transition can be induced in water, by a temperature change. With all these systems, the networks had to be prepared at high dilution (the volume fraction of polymer at network formation, $v^0 \sim 0.1$). In the expanded state of the gel, water has to be a good solvent for polymer network (with the Flory–Huggins interaction parameter $\chi < 0.5$).

The water-soluble poly(1-vinyl-2-pyrrolidone) (PVP) has found numerous medicinal applications.^{9–14} PVP also shows thermoresponsive properties¹¹ but its theta (lower critical solution) temperature in water is above the boiling point of water. Hydrogels of random copolymers of IPAAm/1-vinyl-2-pyrrolidone (VP) were used by Senel *et al.*¹⁴ as thermoresponsive systems. In all cases, a smooth decrease in the degree of swelling in water with increasing temperature was found, increasing the VP content shifts the transition to a higher temperature region. It was also found¹⁵ that at room temperature, a mixture of water/acetone 68/32 (by volume) is a θ -solvent for PVP. This finding suggests that the collapse in charged PVP networks could be observed in water/acetone mixtures, similarly to PAAm systems. As PVP can form reversible association complexes with dyes or some reactive polymers,^{12,13} the jumpwise change in the volume of crosslinked PVP systems could be explored in various, mostly biological applications.

In this study, charged networks of copolymers of VP and various amount of *N,N*-dimethyl-*N,N*-diallylammonium chloride, crosslinked with 3,3'-ethylidenebis(1-vinyl-2-pyrrolidone) were prepared by radiation copolymerization. The swelling and mechanical behavior of these systems was investigated in water/acetone mixtures as well as in aqueous NaCl solutions. Main attention was devoted to the appearance and extent of the first-order phase transition in these systems. The advantage of the ionic comonomer consists in the fact that the degree of ionization is pH-independent.

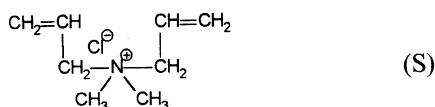
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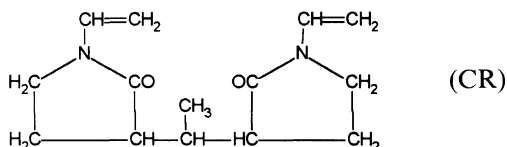
EXPERIMENTAL

Materials

VP (Fluka) was distilled under vacuum at 60°C/13 Pa. *N,N*-dimethyl-*N,N*-diallylammonium chloride (Fluka, 65 vol% aqueous solution of monomer/water)



was used as ionic comonomer. As the crosslinker was used 3,3'-ethylidenebis(1-vinyl-2-pyrrolidone)



which was synthesized as shown previously.¹⁶

Preparation of Networks

Ionic networks, copolymers of VP, various amounts of ionic comonomer S (molar fraction of salt, $x_s = 0-0.27$) and crosslinker CR (molar fraction $x_{cr} = 0.002-0.01$), were prepared by radiation polymerization in the presence of redistilled water. Various amounts of the three monomers were dissolved in water (volume fraction of monomers, $v_m = 0.05-0.13$), and the solutions were flushed with nitrogen. Glass ampoules 10 mm in diameter (D^*) were used as polymerization reactors. The tubes were placed in a γ -irradiator (Co⁶⁰, Artim Prague) with a fixed dose rate of 0.8 kGy h⁻¹ and left for a required polymerization time to obtain a dose of γ at room temperature. After preliminary experiments shown in Figures 1 and 2, the final network formation conditions (v_m , γ , and x_{cr}) were chosen for seven ionic networks used in the collapse investigations (see Table I). The basic requirement was to obtain a constant modulus after preparation (constant concentration of elastically active network chains at constant dilution at network formation). As follows from Table I for dilution at network formation $v_m = 0.1$, the molar fractions of crosslinker $x_{cr} = 0.002$ and 0.003 and radiation doses ranging from 2 to 15 kGy were used. After crosslinking copolymerization, the samples were cut to pieces of 10 mm in length and extracted with redistilled water.

From all networks a sample $\sim 1 \text{ cm}^3$ in volume was extracted in 10 ml deionized water for evaluation of unbound ionic comonomer S and the sol fraction by determination of chloride ions in external water. The content of Cl⁻ was determined by potentiometric titration with a 0.01 M AgNO₃ solution. In all cases it was found that titrated amount of Cl⁻ is less than 1 wt% of initially added amount of chloride. As one can expect that ionic comonomer is bound also in the sol this fact means that all three monomers were bound in network structure.

Swelling and Mechanical Measurements

After extraction, the samples ($\sim 1 \text{ cm}^3$ in volume) were immersed in 200-ml water/acetone (w/a) mixtures or in

100 ml aqueous NaCl salt solution ($c_{\text{NaCl}} = 10^{-5}-1 \text{ mol l}^{-1}$). Swelling proceeded for ~ 28 days, after which the inverse swelling ratio X relative to the state at network formation was determined from²

$$X = (D^*/D)^3 = V^*/V \quad (1)$$

where D^* and D , respectively, are the sample diameters after preparation and swelling in the mixtures and V^* and V , respectively, are the corresponding sample volumes. The diameters were measured with an Abbé comparator (accuracy $\sim 0.002 \text{ mm}$). From the X values, the volume fraction of polymer in the swollen state, $v_2 = v^0 X$ (where $v^0 = v_m/\rho = 0.085$ is the volume fraction of polymer at network formation, $\rho = 1.17 \text{ g cm}^{-3}$ is the density of dry networks and $v_m = 0.1$), or the swelling degree relative to the dry state, Q ($Q = 1/v_2$) can easily be calculated.

The mechanical measurements were carried out in a uniaxial compression in an earlier described apparatus.¹⁷ The specimen, $\sim 10 \text{ mm}$ high, was compressed to a ratio Λ ($\Lambda = l/l_0$, where l and l_0 , respectively, are the compressed and initial heights) and force f was measured after 30 s of relaxation. Usually ten values of Λ and f were determined in the range $0.8 < \Lambda < 1$. The shear modulus G was determined from

$$G = f/[S_0(\Lambda^{-2} - \Lambda)] \quad (2)$$

where S_0 is the initial cross-section of the specimen. The experiments were done with samples immediately after preparation (modulus G_1 , Table I) and with samples swollen to equilibrium in water/acetone mixtures or in aqueous salt solutions.

Using modulus G_1 , the concentration of elastically active network chains related to the dry state, v_d , was calculated from¹⁸

$$v_d = G_1/(RTv^0) \quad (3)$$

where R is the gas constant and $T = 298 \text{ K}$ is temperature (Table I).

RESULTS AND DISCUSSION

Effect of Preparation Conditions on the Network Structure

It is generally known⁹⁻¹² that, probably due to unfavorable copolymerization parameters, it is difficult to form networks by radical copolymerization of VP with crosslinkers of methacrylate, acrylate, or acrylamide types. Due to the fact, we synthesized the *N*-vinylactam type of crosslinker (CR).¹⁶ As our networks had to be prepared at high dilution in water ($v^0 \sim 0.1$), it was difficult to find a proper water-soluble initiator system and we have decided to use a radiation crosslinking polymerization for synthesis of PVP networks.

From Figure 1 it can be seen that at constant radiation dose, $\gamma = 2 \text{ kGy}$, and crosslinker molar ratio, $x_{cr} = 0.003$, the initial modulus G_1 increases with increasing volume fraction of monomers v_m in the polymerization mixture. Such increase is expected since it is known that the efficiency of crosslinking increases with decreasing dilution at network formation due to the decreasing cyclization.¹⁸ On the other hand, strong decrease in modulus G_1 with increasing salt concentration x_s suggests that ionic comonomer, though having two double bonds, does

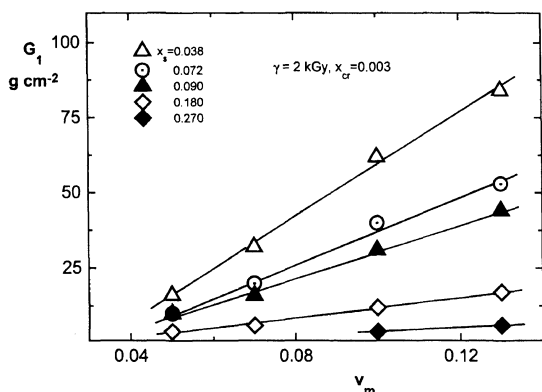


Figure 1. Dependence of modulus G_1 measured after preparation on the volume fraction of monomers v_m in the polymerization mixture.

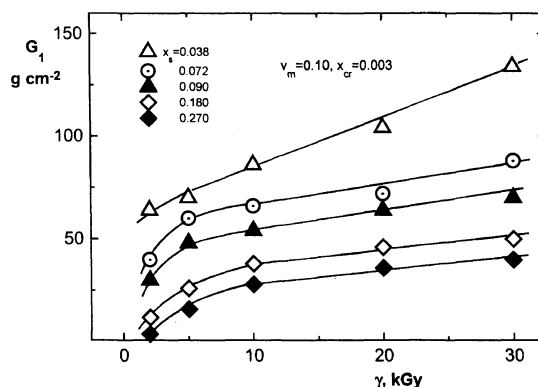
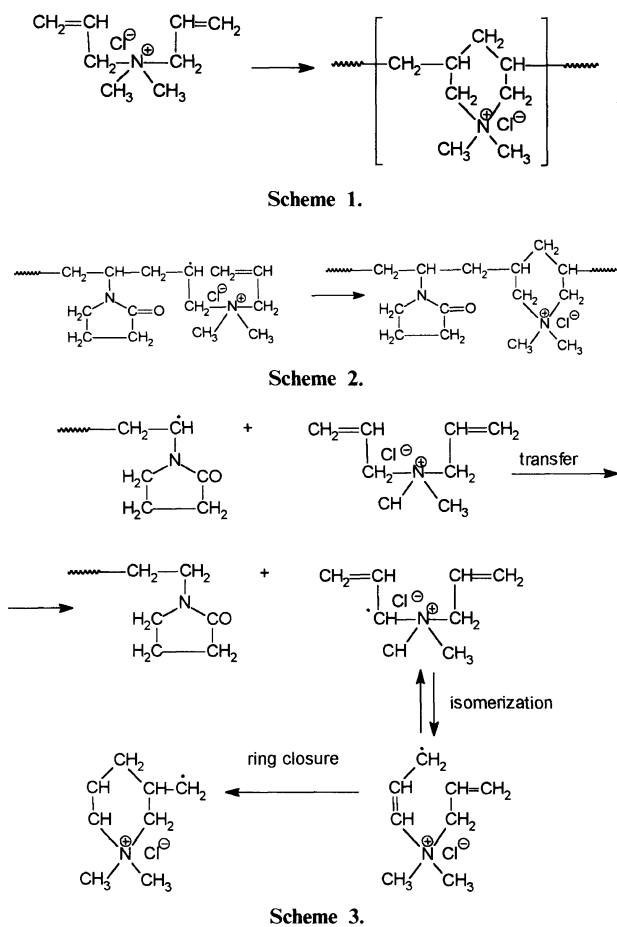


Figure 2. Dependence of modulus G_1 on the radiation dose γ .



not act as a crosslinker. Actually, it was found by Butler *et al.*^{19,20} that polymerization of diallylammonium salts (CR type) in water leads to the formation of linear cyclic structures^{19–22} as shown in Scheme 1. The charged chains are then formed by copolymerization shown in Scheme 2. The large decrease in G_1 with increasing x_s (Figure 1) suggests that also a transfer reaction followed by isomerization and ring closure reaction of the radical according to Scheme 3 is operative in the polymerization. From Figure 1 it follows that the extent of transfer reaction increases with salt concentration.

As expected with increasing dose γ at a constant concentration of monomers ($v_m=0.1$) and amount of crosslinker ($x_{cr}=0.003$), the initial modulus G_1 increases (Figure 2). As in the previous case (see Figure 1), the G_1 values decrease with increasing ionic salt concentration

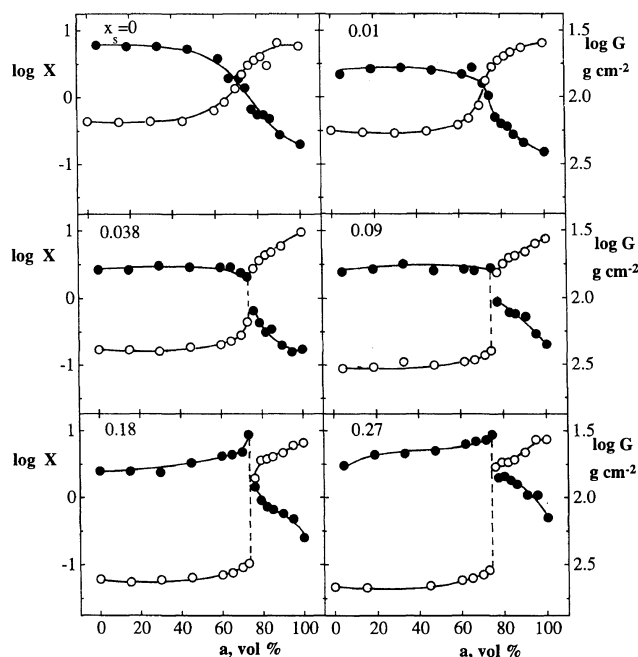


Figure 3. Dependence of the swelling ratio X and modulus G on the acetone concentration a for gels with the ionic comonomer concentrations x_s : (○) X ; (●) G .

x_s , showing the increasing role of transfer reaction. The results shown in Figures 1 and 2 have allowed us to specify the network formation conditions which lead to the modulus $G_1 \sim 35\text{--}70\text{ g cm}^{-2}$ for six ionic networks used for collapse investigation (the value of modulus $G_1 \sim 50\text{ g cm}^{-2}$ was found earlier^{2,17} to be most convenient for the collapse investigation).

Swelling and Mechanical Characteristics in Water/Acetone Mixtures

A continuous or jumpwise change in the volume of the gel (in the swelling ratio X) with the volume fraction of acetone, a , in the w/a mixtures can be seen in Figure 3. The jumpwise change in X takes place in networks with $x_s \geq 0.038$. Table I and Figure 3 show that the critical acetone concentration, at which collapse appeared, $a_c = 75\text{ vol}\%$, is independent of the charge concentration. On the other hand, the jump in the volume of the gel, characterized by the value $\Delta \log X (= \log X'' - \log X')$, where X' is the swelling ratio of the expanded state and X'' is the swelling ratio after the collapse, increases with increasing x_s (Table I, Figure 3). As expected, a jump in

Table I. Network preparation conditions and collapse parameters

Sample ^a	x_s	M_0	γ kGy	x_{cr}	G_1 g cm ⁻²	Q_w	ϕ	$\Delta \log X$	$\Delta \log G$	Q^*	χ^*	$v_d 10^5$ mol cm ⁻³
S1	—	111.0	2	0.002	59.3	27.0	—	—	—	26.0	0.497	2.7
S2	0.010	111.5	2	0.003	73.1	37.5	0.39	—	—	—	—	3.4
S3	0.020	112.0	2	0.003	68.1	45.9	0.28	—	—	22.8	0.501	3.2
S4	0.038	113.0	2	0.003	58.5	69.9	0.19	0.79	0.25	23.5	0.502	2.7
S5	0.090	115.4	5	0.003	58.4	131.9	0.15	1.17	0.26	—	—	2.7
S6	0.180	119.6	10	0.003	41.2	211.9	0.07	1.27	0.34	29.7	0.498	1.9
S7	0.270	136.8	15	0.003	34.9	270.2	0.09	1.54	0.39	33.5	0.496	1.6

^a The volume fraction of all the three monomers in the mixture $v_m=0.1$, x_s and x_{cr} , respectively, are molar fractions of ionic salt S and crosslinker CR, M_0 is average molecular weight of monomer unit, γ is a radiation dose, G_1 is the modulus after preparation, Q_w and Q^* , respectively, are the swelling degrees in water and in 1 M NaCl aqueous solution, ϕ is the correction factor, $\Delta \log X$ and $\Delta \log G$, respectively, are collapse parameters, χ^* is the interaction parameter and v_d is the concentration of elastically active network chains related to the dry state.

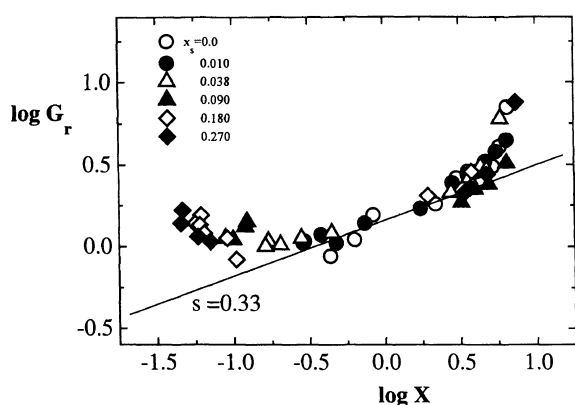


Figure 4. Dependence of the reduced modulus $G_r = G/G_1$ on the swelling ratio X , for variously ionized gels swollen in various water/acetone mixtures. The slopes $s=0.33$ corresponds to the rubber elasticity theory prediction.

the volume of the gel, $\Delta \log X$, is reflected also in a jumpwise change in the shear modulus, $\Delta \log G$ ($= \log G'' - \log G'$); $\Delta \log G$ increases with the salt concentration x_s , similarly to $\Delta \log X$ (Table I). For two networks with $x_s=0$ and 0.01, continuous dependences of X on a are accompanied by continuous dependences of modulus G on a (Figure 3).

The dependences of the reduced shear modulus, $G_r = G/G_1$ on swelling ratio X are shown in Figure 4 for all networks. For comparison, the predicted rubber elasticity slope²³ for the dependence of $\log G$ vs. $\log X$, $s=0.33$, is also shown. In the range of high swelling ($\log X < -1$), the increase in modulus G_r with increasing swelling can be seen for two most ionized networks with $x_s=0.18$ and 0.27; this increase is probably due to the finite extensibility of the chains. Departures from the straight line in the region of low swelling ($\log X > 0.75$) are probably due to the influence of the main transition region (vitrification) at high acetone concentrations.¹⁷ Detailed inspection of the $\log G_r$ vs. $\log X$ dependences for individual networks with $x_s=0, 0.01, 0.038$, and 0.09, consisting in the use of the least squares method to all measured data, leads to the values of slopes $s=0.5, 0.4, 0.3$, and 0.2. In this respect, the charged PVP networks differ from ionized PAAm or PDEAAm networks,^{2,17} where values s were independent of the charge concentration. The value of $s=0.33$ was found²⁴ for positively charged PAAm networks with the quaternary ammonium group attached to the main chain through the amide

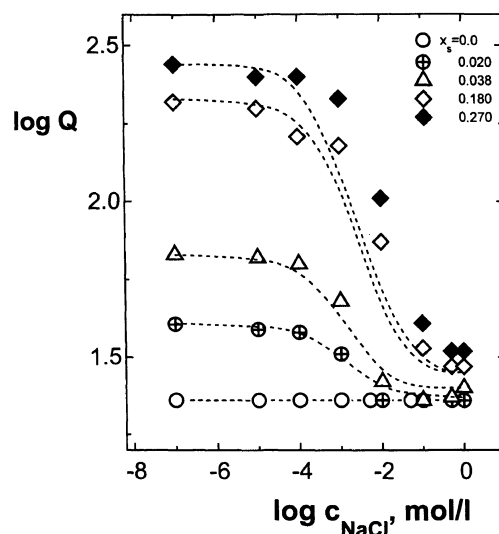


Figure 5. Dependence of the swelling degree Q on the NaCl concentration for networks with indicated x_s values. --- theoretical dependences from eq 4.

group. On the other hand, if ammonium group was attached to the main chain through the ester group, a high value of $s=0.7$ was found²⁵ for charged PAAm networks in water/acetone mixtures. The swelling dependence of the modulus with the slope $s=5/6$ was recently suggested by the theory of Rubinstein *et al.*²⁶ based on the scaling concept of the polyelectrolyte chain.

Swelling and Mechanical Behavior in Salt Solutions

Figure 5 shows the dependences of the swelling degree Q on aqueous sodium chloride concentrations, c_{NaCl} (data shown at the 10^{-7} M concentration were obtained in pure water). It is obvious that the value of equilibrium swelling depends on both the amount of ionic comonomer x_s and the ionic strength of solution. As expected, as the ionic strength increases, the charged gels deswell and at a concentration $c_{NaCl} \sim 1$ M, all gels show approximately the same value of the swelling degree Q^* (Table I). This is well-known behavior of polyelectrolyte hydrogels and can be explained as the effect of increasing concentration of counter-ions (Cl^-) in the gel volume with increasing c_{NaCl} . A drastic decrease in swelling is observed between 10^{-4} and 10^{-1} M salt concentrations when NaCl concentrations of the external aqueous solutions exceed the concentrations of dissociated charges on the chain.

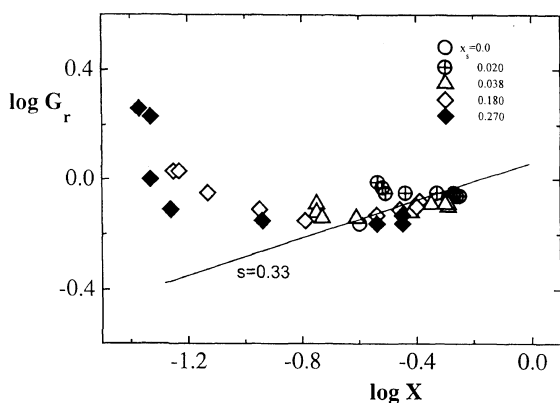


Figure 6. Dependence of the reduced modulus $G_r = G/G_1$ on the swelling ratio X for variously ionized gels swollen in aqueous NaCl solutions. The slope $s = 0.33$ corresponds to the rubber elasticity theory prediction.

It was found that with increasing NaCl concentration the shear modulus G increases; this increase is more pronounced in the concentration range from 10^{-4} to 10^{-1} M, where a drastic change in swelling was observed. In Figure 6, the reduced moduli G_r , ($G_r = G/G_1$) in dependence on the ratio X are shown together with the slope $s = 0.33$. Departures from the straight line in the high swelling region ($\log X < -1$) can be, as in the previous case (Figure 4), attributed to the finite extensibility of the chains. From the results presented in Figure 6, it follows that mechanical behavior in aqueous salt solutions is predominantly determined by the swelling degree of the gel similarly to that in water/acetone mixtures.

Comparison of the Theory of Swelling Equilibria of Polyelectrolyte Networks and Experiment

In literature, several theoretical models have been suggested for interpreting thermodynamic properties of charged gels, in which the effect of repulsion of the charges on the chain and finite chain extensibility were included.^{27–32} For comparison of experimental swelling data with the theoretical prediction, we will use the theory discussed in ref 28 and 29. This theory has predicted the swelling pressure, P , in the form

$$P = \mu_1/V_1 = P_m + P_{el} + P_{os} + P_{els} \quad (4)$$

where μ_1 is the chemical potential of the solvent, V_1 is the molar volume of the solvent, P_m is the mixing term given by the mixing of solvent with chain segments (Flory–Huggins equation with interaction parameter χ), P_{el} is the elastic term given by the change in elastic energy in which finite chain extensibility was included, P_{os} is the osmotic term given by the mixing of network ions with the solvent and P_{els} is the electrostatic term determined by the interactions (repulsion) of charges on the chain. This theory was used for the description of collapse and it was shown that in first approximation, it describes the swelling data of ionized PAAm networks^{2,17} if the effective degree of ionization was introduced.

In the previous papers,^{28,29} the individual terms P_i of

eq 4 were expressed in network molecular parameters—concentration of network chains ν_d , density of polymer $\rho = 1.17 \text{ g cm}^{-3}$, degree of ionization $\alpha = x_s$, average molecular weight of the monomer unit M_o , molar volume of the water/acetone mixtures V_1 , dilution at network formation $\nu^0 = 0.085$, dielectric constant ϵ of water/acetone mixtures—and in experimental values of ν_2 or Q . Using eq 4, the dependence of the interaction parameter χ on ν_2 can be calculated from experimental ν_2 values determined in water/acetone mixtures (as the experimental data are measured for free swelling, $P = 0$ in eq 4) by employing the same procedure described in detail earlier.²⁹ In this approach the water/acetone mixtures are considered as a *pseudo*-pure solvent with an average χ parameter (as acetone is bad solvent for PVP chain χ increases with increasing content of acetone in the mixtures).

From Table I it follows that swelling degree in water Q_w increases with salt concentration x_s . The use of eq 4 for the uncharged PVP network swollen in water ($x_s = 0$, $P_{os} = P_{els} = 0$) led to the expected value of the interaction parameter $\chi = 0.495$ for the water/PVP system. Similarly to the previous case,^{2,24} for water-swollen ionic networks with the degree of ionization $\alpha = x_s > 0$, eq 4 gives high unrealistic values of χ parameters (for $x_s = 0.01, 0.02, 0.038, 0.09, 0.18, \text{ and } 0.27$ the values $\chi = 0.545, 0.647, 0.961, 2.745, 6.525, \text{ and } 12.650$ were found). Since, as it was introduced in used theory, χ is a measure of polymer–water interaction when all charges are screened (the effect of charges is included in P_{os} and P_{els} terms), $\chi = 0.495$ may be, in the first approximation, required also for all ionic hydrogels. This requirement can be met by assuming that the effective degree of ionization is lower than the salt concentration, *i.e.*, $\alpha = \phi x_s$, where ϕ is the correction factor (see footnote*¹). The ϕ values thus calculated lie in the range $0.07–0.39$ (Table I) and are much lower than those found for P(AAm/sodium methacrylate) hydrogels¹⁷ ($\phi \sim 0.96–0.99$) and variously aged PAAm networks³³ ($\phi \approx 0.51–1$). On the other hand, the values of ϕ are comparable with those found for ionic P(AAm/quaternary ammonium salts) hydrogels³⁴ with $\phi \sim 0.1–0.4$. From this comparison it seems that it is mainly the low efficiency of ammonium salts, which leads to low ϕ values (probably a large size of ammonium group which forms a weaker electrostatic field, due to which the hydration of the group is smaller).

Using the above mentioned molecular parameters (all values of parameters $\nu_d, M_o, V_1, \rho, \nu^0$, and ϵ are independently known) and the effective degree of ionization $\alpha = \phi x_s$, the dependence of the interaction parameter χ vs. ν_2 was calculated from experimental swelling data in water/acetone mixtures; the condition for free swelling, $P = 0$ in eq 4, was used (Figure 7a). While for networks with $x_s = 0$ and 0.01 , the χ on ν_2 dependences are continuous, discontinuity appears with higher ionic comonomer S contents, as expected. As was described previously,²⁹ the van der Waals loop in the dependence of χ on ν_2 is a necessary condition for the collapse and the critical interaction parameter χ_c and compositions of

*¹ The correction factor is related to the activity coefficient of counter-ions and involves other effects not considered in eq 4, *e.g.*, the effect of possible heterogeneity of highly diluted networks. As this factor was calculated from swelling degree in water Q_w it may reflect also water structure around of PVP chains.

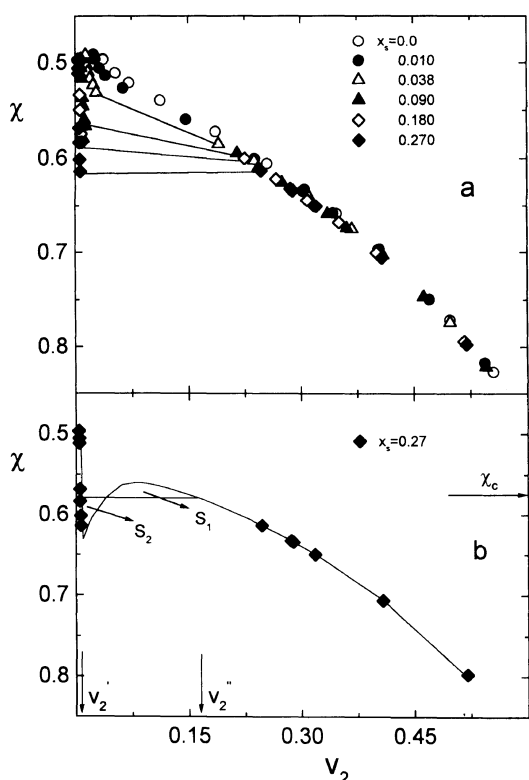


Figure 7. Dependence of the interaction parameter χ on the volume fraction of the dry network v_2 . The critical parameters for network with $x_s=0.27$, χ_c and $\Delta=v_2''-v_2'$ are defined by the condition that the areas S_1 and S_2 are equal (eq 5). — the course determined by eq 4.

coexisting phases (the values v_2' and v_2'') at the transition are given by the condition²⁹

$$\int_{v_2'}^{v_2''} (\chi - \chi_c) dv_2 = 0 \quad (5)$$

In Figure 7b, the van der Waals loop calculated from eq 4 with known molecular parameters is shown for network with $x_s=0.27$ together with the application of eq 5 (Maxwell's construction is applied to the χ vs. v_2 dependence, *i.e.*, χ_c is determined by the requirement that the areas S_1 and S_2 are equal). In such way, the values χ_c and the extent of the collapse, $\Delta=v_2''-v_2'$, can be determined for networks with $x_s=0.038$, 0.09, 0.18, and 0.27 (Table I). As the v_2 vs. a dependences for ionic networks are known from swelling experiments, the dependences of χ vs. v_2 can be easily transformed to the dependences of χ vs. a and the critical acetone compositions a_c can be determined from χ_c values. The comparison of the theoretically determined a_c and Δ values with the experiment is shown in Figure 8. From this figure it is seen that the theory underestimates the a_c and Δ values.

The requirement that $\chi=0.496$ for all ionic networks swollen in water seems to be the most serious approximation which was used in application of eq 4, since it neglects a possible copolymerization contribution of ionic comonomer (connected with replacement of VP monomer by S comonomer) to the value of interaction parameter χ . If the charge concentration is low, like in P(AAm/MNa) hydrogels,¹⁷ ($x_s \leq 0.025$), the constancy of χ seems to be justified, but in our case, the highest charge concentration is much larger, ($x_s=0.27$). If we

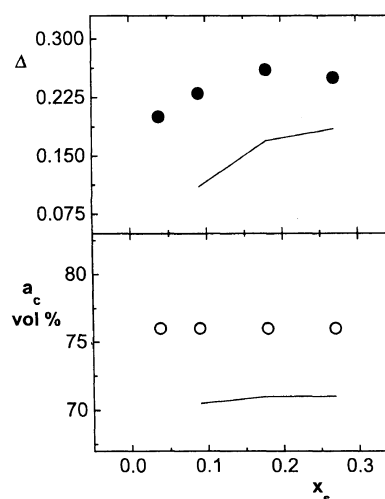


Figure 8. Dependence of the jump in volume at the collapse Δ and of the critical acetone concentration in the mixture at collapse, a_c , on ionic comonomer concentration x_s . —, theoretical prediction (eq 4); (○), (●) experimental data.

suppose that in 1 M NaCl solutions, all polyelectrolyte networks behave as uncharged systems, we can apply eq 4 with $P_{os}=P_{els}=0$ to the swelling data obtained in 1 M solutions (shown as Q^* values in Table I), and calculate χ^* parameters. As can be seen from Table 1, the χ^* values are, within experimental scatter, independent of x_s . Thus, the copolymerization effect of the ionic comonomer cannot account for large decrease in the correction factor ϕ .

The use of eq 4 for theoretical description of the swelling equilibria in aqueous NaCl salt solutions requires the knowledge of the amount of mobile co-ions x_{Na^+} and their activity coefficient, f , inside the gel phase. The amount of co-ions x_{Na^+} can be calculated from the Donnan equilibrium from the relation³⁵ (see APPENDIX)

$$x_{Na^+} = \frac{x_{N^+} + 2x_{NaCl}\beta}{2(1-\beta)} \left\{ \left[1 + \frac{4\beta(1-\beta)x_{NaCl}^2}{(x_{N^+} + 2x_{NaCl}\beta)^2} \right]^{1/2} - 1 \right\} \quad (6)$$

where x_{N^+} is the amount of the bound positive charges in the gel phase, x_{NaCl} is the amount of salt in the solution phase and $\beta=(V_g/V_s)^2$, V_g , and V_s , respectively, being the volumes of the gel and the salt solution phase. If the amounts of the bound ions in the gel phase and NaCl salt in the solution phase are given in moles than the molar concentration of co-ions in the gel phase is $c_{Na^+}=(x_{Na^+}/V_g)$, where gel volume V_g is given in litres. The calculated c_{Na^+} concentrations for four ionized networks with $x_s=0.02$, 0.038, 0.18, and 0.27 are given Table II for various values of the external aqueous salt concentration c_{NaCl} used in the swelling experiments (see Figure 5). Due to the presence of the positive charges from ionic comonomer S bound on the chains, the c_{Na^+} concentrations are essentially lower than c_{NaCl} values at low NaCl concentrations and these differences increase with increasing x_s .

The values c_{Na^+} together with other network molecular parameters (v_d, M_o, ρ, v^0), $\chi=0.496$ and effective ionization $\alpha=\phi x_s$ were used for theoretical description (eq 6) of the swelling data shown in Figure 5. The dotted lines in Figure 5 are theoretical dependences; semi-quantita-

Table II. The concentrations of co-ions c_{Na^+} in the gel phase determined by the Donnan equilibrium according to eq 6

$\log c_{\text{NaCl}}/\text{mol l}^{-1}$	$\log c_{\text{Na}^+}/\text{mol l}^{-1}$			
	$x_s=0.02$	0.038	0.18	0.27
-5	-7.72	-7.74	-8.00	-8.02
-4	-5.73	-5.75	-6.00	-6.02
-3	-3.80	-3.82	-4.08	-4.10
-2	-2.18	-2.20	-2.46	-2.48
-1	-1.02	-1.03	-1.13	-1.15
0	-0.01	-0.01	-0.02	-0.03

tive agreement between theory and experiment can be seen.

CONCLUSIONS

From the swelling and mechanical measurements carried out on the ionic networks of copolymers of VP with various amounts of ionic quaternary ammonium salt S and crosslinker CR, prepared by the radiation method, swollen in water/acetone mixtures and in aqueous NaCl salt solutions, the following conclusions can be made:

(a) Using the radiation method, the ionic networks with required mechanical properties at high dilution in water (90% of water in the polymerization mixture) can be prepared. With increasing amount of ionic comonomer S, the efficiency of crosslinking reaction decreases as S acts as a terminator.

(b) The degree of swelling of P(VP/S) gels in water and aqueous NaCl solutions is strongly influenced by the amount of charges on the chain and by the NaCl concentration. A comparison of experimental results with theory of polyelectrolyte gels shows that the agreement is reasonably good if the effective amount of charges (correction factor ϕ) is introduced.

(c) Gels with ionic salt concentrations $x_s \geq 0.038$ undergo a first-order phase transition in water/acetone mixtures. While the extent of the collapse, Δ , increases with increasing x_s , the critical acetone concentration a_c is x_s -independent. The proposed theory semi-quantitatively describes the collapse phenomenon.

(d) The jump in the modulus G correlates with the jump in the swelling ratio X . Also the dependences of $\log G$ on $\log X$ are roughly the same regardless of x_s and c_{NaCl} concentrations. This means that the mechanical behavior is predominantly determined by the degree of swelling for all gels.

APPENDIX

We will consider the charge equilibrium of positively charged PVP gel with the molar amount of the bound charges x_{N^+} and with the gel volume V_g immersed in aqueous NaCl solution bath with initial molar amount of salt x_{NaCl} and with volume V_s . We will consider that the activity coefficient of co-ions Na^+ is equal one, and the amount of charges in the gel phase is: bound x_{N^+} , mobile x_{Na^+} and x_{Cl^-} and those in the external salt solution phase is: mobile y_{Na^+} and y_{Cl^-} . From the neutrality condition of the both phases we have:

$x_{\text{Cl}^-} = x_{\text{N}^+} + x_{\text{Na}^+}$ and $y_{\text{Na}^+} = y_{\text{Cl}^-} = x_{\text{NaCl}} - x_{\text{Na}^+}$. From the Donnan equilibrium we can write the relation

$$x_{\text{Na}^+}(x_{\text{N}^+} + x_{\text{Na}^+})/V_g^2 = (x_{\text{NaCl}} - x_{\text{Na}^+})^2/V_s^2 \quad (7)$$

Equation 6, used for calculation of the molar concentration of co-ions c_{Na^+} in the gel phase, can be easily derived from eq 7 if parameter $\beta = (V_g/V_s)^2$ is introduced.

Acknowledgments. The financial support of the Grant Agency of the Czech Republic (Grant No. 203/95/1318) is gratefully acknowledged. We thank Dr. M. Řeřichová from Artim s.r.o. (Prague, Czech Republic) for irradiation of samples.

REFERENCES

1. M. Shibayama and T. Tanaka, *Adv. Polym. Sci.*, **109**, 1 (1993).
2. M. Ilavský, *Adv. Polym. Sci.*, **109**, 173 (1993).
3. S. H. Gehrke, *Adv. Polym. Sci.*, **110**, 81 (1993).
4. A. Khokhlov, S. Starodubtsev, and V. V. Vasilevskaya, *Adv. Polym. Sci.*, **109**, 123 (1993).
5. J. Pleštil, Yu. M. Ostanevich, S. Borbely, J. Stejskal, and M. Ilavský, *Polym. Bull.*, **17**, 465 (1987).
6. D. De Rossi, K. Kajiwara, Y. Osada, and A. Yamauchi, Ed., "Polymer Gels: Fundamental and Biomedical Applications," Plenum, New York, N.Y., 1991.
7. M. Suzuki and O. Hirasu, *Adv. Polym. Sci.*, **110**, 241 (1993).
8. S. Saito, M. Kanno, and H. Inomata, *Adv. Polym. Sci.*, **109**, 207, (1993).
9. J. W. Breitenbach, *J. Polym. Sci.*, **23**, 949 (1957).
10. J. Goldfarb and S. Rodriguez, *Makromol. Chem.*, **116**, 96 (1968).
11. P. Sakellariou, *Polymer*, **33**, 1339 (1992).
12. N. H. Chen, T. E. Smith, and D. M. Vitus, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 461 (1985).
13. G. N. Sheth, *J. Appl. Polym. Sci.*, **32**, 4333 (1986).
14. S. Senel, B. Isik-Yuruksoy, H. Cicek, and A. Tuncel, *Polymer*, **38**, 1775 (1997).
15. H. G. Elias, *Makromol. Chem.*, **50**, 1 (1961).
16. F. Haaf, A. Sanner, and F. Straub, *Polym. J.*, **17**, 143 (1985).
17. M. Ilavský, *Macromolecules*, **15**, 782 (1982).
18. M. Ilavský and K. Dušek, *Macromolecules*, **19**, 2139 (1986).
19. G. B. Butler, A. Crawshaw, and W. L. Miller, *J. Am. Chem. Soc.*, **80**, 3615 (1958).
20. G. B. Butler, *J. Polym. Sci.*, **48**, 279 (1960).
21. C. G. Motsoyan, M. G. Pogoyan, O. A. Dzagaljan, and V. A. Mushegjan, *Vysokomol. Soedin.*, **5**, 854 (1963).
22. D. A. Topchiev, A. I. Martynenko, Yu. E. Kabanova, L. M. Timofeeva, V. D. Oppengeim, A. S. Shashkov, and A. M. Drabkina, *Vysokomol. Soedin.*, **36**, 1242 (1994).
23. K. Dušek and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).
24. M. Ilavský, Z. Sedláková, K. Bouchal, and Pleštil, *Macromolecules*, **28**, 6835 (1995).
25. M. Ilavský and K. Bouchal, in "Biological and Synthetic Polymer Networks," O. Kramer, Ed., Elsevier, New York, N.Y., 1988, p 435.
26. M. Rubinstein, H. R. Colby, V. A. Dobrynin, and J.-F. Joanny, *Macromolecules*, **29**, 398 (1996).
27. A. Katchalsky, Z. Alexandrowicz, and O. Kedem, in "Polyelectrolyte Solutions in Chemical Physics and Ionic Solutions," B. E. Conway and R. C. Barrads, Ed., Wiley, New York, N.Y., 1966.
28. J. Hasa, M. Ilavský, and K. Dušek, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 253 (1975).
29. M. Ilavský, *Polymer*, **22**, 1687 (1981).
30. C. Konák and R. Bansil, *Polymer*, **30**, 677 (1989).
31. U. P. Schröder and W. Oppermann, *Makromol. Chem., Macromol. Symp.*, **73**, 63 (1993).
32. S. A. Dubrovskii, M. Ilavský, and G. N. Arkhipovich, *Polym. Bull.*, **29**, 587 (1992).
33. M. Ilavský, J. Hrouz, J. Stejskal, and Bouchal, *Macromolecules*, **17**, 2868 (1984).
34. M. Ilavský, *Macromol. Symp.*, **109**, 169 (1996).
35. G. S. Manning, *J. Chem. Phys.*, **51**, 924 and 934 (1969).