

## Phase Transition in Swollen Gels

### 5. Effect of the Amount of Diluent at Network Formation on the Collapse and Mechanical Behavior of Polyacrylamide Networks

M. Ilavský and J. Hrouz

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

#### Summary

The effect of the concentration of diluent (water) at the formation of polyacrylamide networks with a small content of sodium methacrylate (mole fraction of MNa groups in the PAAM chain  $x_{MNa} = 0.012$ ) on the swelling and mechanical equilibria of gels in acetone-water mixtures was investigated. With increasing polymer content at network formation both the extent of phase transition  $\Delta$  (determined by a change in the macroscopic dimensions of gels) and the critical value of the interaction parameter  $\chi_c$  (given by the composition of the acetone-water mixture at the collapse) decrease; the observed dependences are in a semiquantitative agreement with the theory. The observed jumpwise change in the modulus of gels correlates well with a change in the gel volume at the collapse.

#### Introduction

Coexistence of two phases at the phase transition (collapse) of the swollen polymer network differing in the concentration and conformation of the segments was experimentally observed both in polyacrylamide (PAAM) (TANAKA 1979, STEJSKAL et al. 1980, JANAS et al. 1980, ILAVSKÝ 1982) and in poly(N,N-diethylacrylamide) (PDAAM) (ILAVSKÝ et al. 1982) networks. An infinitesimal change in external parameters (e.g., temperature or composition of the solvent) brings about an approximately tenfold to hundredfold change in the macroscopic volume of the gel; a jumpwise change in the volume is accompanied by a similar change in the equilibrium modulus of the gel. A condition of the occurrence of phase transition consists in the presence of a low number of charges on the chain and in the possibility to prepare homogeneous gels at high dilution at network formation. It has been found experimentally that both the increasing charge content on the chain (ILAVSKÝ 1982) and the decreasing network density (ILAVSKÝ and HROUZ 1982) increase the extent of phase transition and the critical value of the interaction parameter at which the collapse takes place.

Phase transition is determined by the balance of several forces in the swollen network, particularly by elastic force (corresponding to a change in the chain configuration with swelling), osmotic force (corresponding to the mixing of polymer segments with the solvent and to the mixing of ions with the solvent) and the force which corresponds to a change in the

energy of electrostatic interactions with swelling. It has been shown theoretically (ILAVSKÝ 1981) that by including all these forces into the swelling equilibrium of polyelectrolyte gels, a relationship is obtained for the free energy of the swollen network  $\Delta F$  which under suitable conditions may be used to predict phase transition (dependence of the swelling pressure  $P$  on the composition of gels has the shape of the van der Waals loop - i.e., it is nonmonotonic). Comparison between the theory and experimental data obtained both with gels having various charge contents on the chain and with gels of various network density  $\nu_d$  (at constant dilution at network formation) showed a semiquantitative agreement (ILAVSKÝ 1982, ILAVSKÝ and HROUZ 1982).

Another parameter which may affect the elastic energy of the gel is the amount of diluent at network formation at constant  $\nu_d$ ; the effect of this parameter on the formation and extent of the collapse has not yet been studied. This study is therefore concerned with the effect of the amount of water at the formation of polyacrylamide networks (these contain  $\approx 1.2$  mol.% of sodium methacrylate) on their swelling equilibria and mechanical behaviour in acetone-water mixtures; the results obtained are compared with a theory suggested earlier.

### Experimental

Sample preparation: To six samples, A,B,C,D,E and F containing 5,9,15,20,30 and 40 g acrylamide (AAM) respectively, sodium methacrylate (MNa) was added in such an amount that the mole fraction of MNa in PAAM chain was constant, i.e.  $x_{\text{MNa}} = 0.012$ . The crosslinking agent, N,N'-methylenebisacrylamide, was used in the respective amounts 0.15, 0.09, 0.03, 0.015, 0.01, and 0.008 g. After the addition of 20 mg of ammonium persulphate, all components were dissolved in redistilled water so as to bring the total volume of the mixture up to 100 ml. After the mixture had been flushed with nitrogen, 20 mg of sodium pyrosulphite was added, and on mixing the solution was poured into ampoules,  $\approx 1$  cm in diameter, which were then sealed. The polymerization proceeded at room temperature for some three hours; after that, the gels were removed and cut into specimens, about 1 cm long. The volume fractions  $\phi^*$  of the polymer at network formation calculated using the weight of the monomer and the density of the dry copolymer ( $\rho = 1.35 \text{ g cm}^{-3}$ ), were respectively 0.037, 0.068, 0.115, 0.156, 0.24 and 0.33 for samples A-F.

Swelling: Twenty water-acetone mixtures in the range 0-80 vol.% of acetone were prepared from redistilled water and acetone (analytical grade purity). The specimens of freshly prepared networks were used for swelling in mixtures with low acetone concentrations (<50 vol.%); partly dried specimens were used for swelling in mixtures with high acetone concentrations (>40 vol.%, cf. ILAVSKÝ 1982). After swelling for 28 days, the swelling ratio  $X$  related to the state at network formation was determined from

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

where  $D^*$  and  $D$  respectively is the diameter of the sample

after network formation and after swelling, and  $V^*$  and  $V$  respectively is the gel volume after the preparation or after swelling in the mixture. The diameters of the gels were measured with an Abbé comparator (Zeiss Jena, accuracy  $\pm 0.002$  mm); the  $X$  values plotted in Fig.1 are the average from at least three measurements. The  $X$  values can be used in the calculation of the volume fraction of the polymer in the swollen state  $\phi_2 = V_d/V = \phi^*X$  ( $V_d$  and  $V$  respectively is the dry and swollen gel volume).

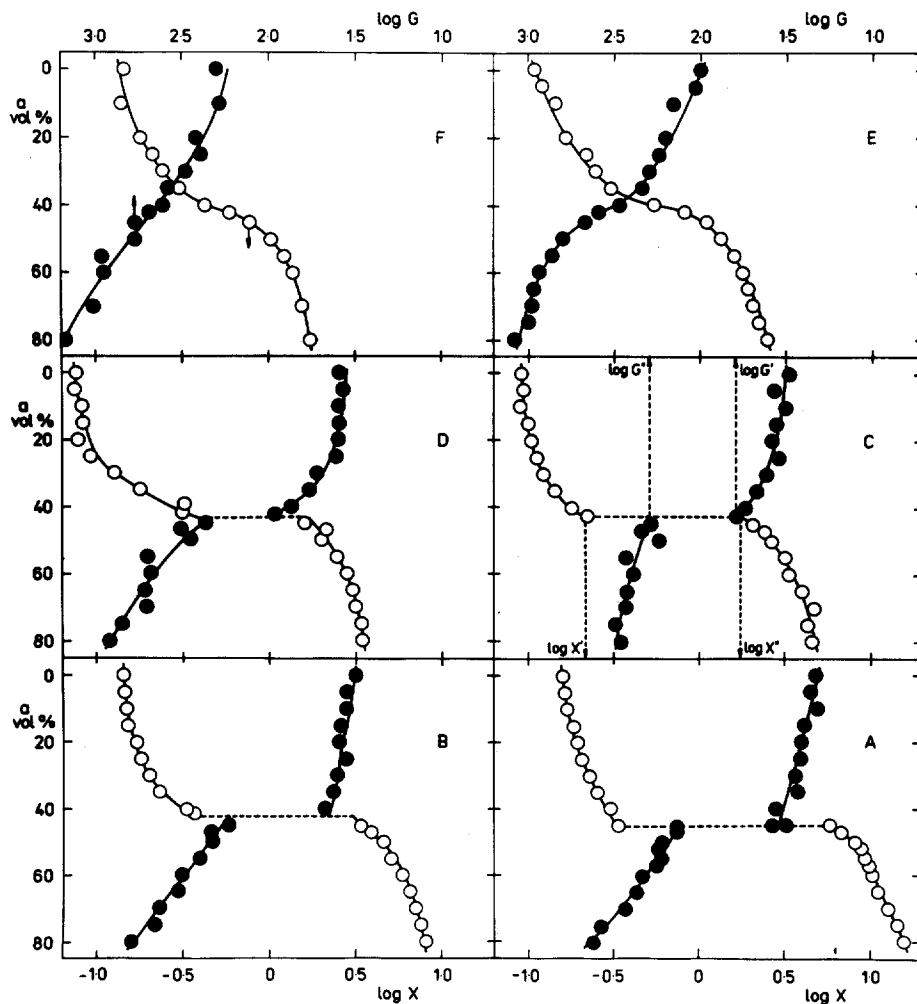


Fig.1 Dependence of the swelling ratio  $X$  and of the modulus  $G$  ( $\text{g cm}^{-2}$ ) on the acetone content  $a$  (vol.%) in acetone-water mixtures

Samples denoted in the Figure,  $\circ$   $X$ ,  $\bullet$   $G$

Mechanical behaviour: Along with swelling the deformational characteristics were measured in simple compression using an apparatus described earlier (HROUZ et al. 1979). A cylindrical sample was compressed by teflon surfaces to compression  $\lambda$  and after 30 s of relaxation the force  $f$  was read off; ten values  $\lambda$  and  $f$  were determined (in the range  $0.7 < \lambda < 1$ ). The shear modulus  $G$  (Table 1, Fig.1) was determined from

$$G = f/S_0 (\lambda^{-2} - \lambda), \quad (2)$$

where  $S_0$  is the initial cross-section of the sample.

### Results and Discussion

It can be seen in Fig.1 that the increasing monomer content at network formation suppresses the extent of the collapse  $\Delta \log X = \log X'' - \log X'$ ; in samples E,F the dependence of the swelling ratio  $X$  on the acetone concentration is already continuous. A similar effect of monomer concentration at network formation may also be observed in the dependence of the shear modulus  $G$  on the acetone-water mixture composition. While with samples A-D the dependence of  $G$  on concentration is discontinuous, the same dependence in the case of samples, E,F is a continuous one. Also, Fig.1 shows that the critical acetone concentration at which phase transition takes place depends on the monomer concentration only little (it varies from  $\approx 45$  vol.% to  $\approx 42$  vol.% of acetone in samples A-D).

The magnitude of the change in the modulus at the collapse  $\Delta \log G = \log G'' - \Delta \log G'$  (cf.Fig.1) as a function of the extent of the collapse  $\Delta \log X$  is shown in Fig.2, which also presents data obtained earlier both with samples having a different number of charges on the chain (ILAVSKÝ 1982) and with those having a different concentration of the crosslinking agent at network formation (ILAVSKÝ and HROUZ 1982). In the first approximation this dependence is a straight line with a slope of  $\approx 0.65$ . This means that a jumpwise change in the equilibrium modulus at phase transition is due to a similar change in the macroscopic gel volume.

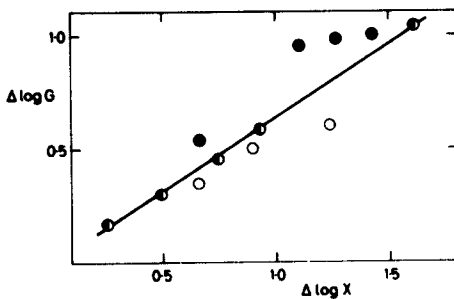


Fig.2 Dependence of the jumpwise change in the modulus  $\Delta \log G$  on the jumpwise change in the swelling ratio  $\Delta \log X$  at phase transition  
 ● data from the paper ILAVSKÝ (1982) obtained with samples with varying  $x_{MNa}$  content,  
 ◐ data from the paper ILAVSKÝ and HROUZ (1982) with varying content of the crosslinking agent, ○ this paper

Table 1: Swelling and deformation characteristics

vol. %	A		B		C		D		E		F	
	$\log x^b$	$\log G^C$	$\log x^b$	$\log G^C$	$\log x^b$	$\log G^C$	$\log x^b$	$\log G^C$	$\log x^b$	$\log G^C$	$\log x^b$	$\log G^C$
0	-0.790	1.312	-0.849	1.507	-1.042	1.480	-1.121	1.605	-0.962	1.991	-0.831	2.297
5	-0.778	1.342	-0.848	1.554	-1.029	1.571	-1.127	1.575	-0.913	2.032	-	-
10	-0.765	1.294	-0.827	1.558	-1.116	1.494	-1.089	1.602	-0.837	2.161	-0.848	2.282
15	-0.726	1.373	-0.826	1.590	-0.998	1.555	-1.085	1.600	-	-	-	-
20	-0.703	1.393	-0.775	1.600	-0.979	1.577	-1.112	1.605	-0.781	2.203	-0.737	2.420
25	-0.681	1.393	-0.751	1.554	-0.949	1.537	-1.041	1.621	-0.662	2.241	-0.663	2.392
30	-0.635	1.423	-0.698	1.606	-0.914	1.614	-0.901	1.736	-0.609	2.300	-0.609	2.482
35	-0.588	1.413	-0.639	1.633	-0.843	1.671	-0.754	1.773	-0.520	2.341	-0.516	2.580
40	-0.510	1.542	-0.483	1.677	-0.752	1.676	-0.498	1.880	-0.267	2.470	-0.369	2.610
42	-	-	-0.440	1.660	-0.680	1.701	-0.510	1.970	-0.092	2.590	-0.223	2.690
45	-0.462	1.477	0.526	2.242	0.310	2.286	-0.199	2.373	0.037	2.673	-0.109	2.772
47	0.775	2.110	-	-	-	-	-	-	-	-	-	-
47	0.836	2.112	0.590	2.340	0.381	2.345	0.326	2.520	-	-	-	-
50	0.916	2.207	0.661	2.325	0.417	2.235	0.300	2.457	0.116	2.800	0.011	2.770
52	0.953	2.234	-	-	-	-	-	-	-	-	-	-
55	0.974	2.213	0.703	2.412	0.498	2.434	0.383	2.711	0.203	2.863	0.088	2.962
57	1.007	2.243	-	-	-	-	-	-	-	-	-	-
60	1.018	2.323	0.770	2.509	0.520	2.390	0.443	2.688	0.246	2.940	0.136	2.950
65	1.049	2.359	0.814	2.532	0.600	2.421	0.477	2.725	0.278	2.972	-	-
70	1.113	2.424	0.848	2.640	0.627	2.426	0.495	2.715	0.308	2.980	0.188	3.010
75	1.159	2.573	0.878	2.665	0.613	2.490	0.529	2.868	0.345	3.000	-	-
80	1.194	2.615	0.911	2.800	0.651	2.449	0.535	2.930	0.394	3.081	0.240	3.170

<sup>a</sup> Acetone content in acetone-water mixtures, <sup>b</sup> swelling ratio determined by Eq. (1),  
<sup>c</sup> values of the modulus G in g cm<sup>-2</sup>

With increasing monomer content at network formation the modulus  $G$  also increases (at constant  $X$ ), and the  $\log G$  vs.  $\log X$  dependences of the individual A-F samples in the range of lower  $X$  may be represented by approximately parallel straight lines with the slope  $s \approx 0.5-0.6$  (Fig.3). A similar

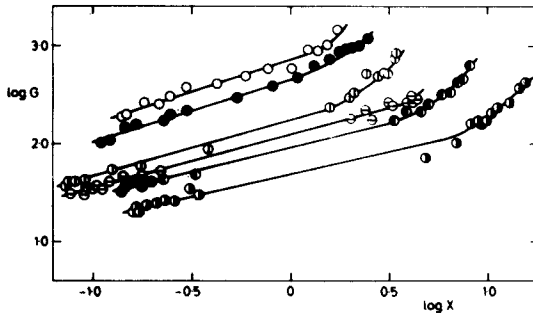


Fig.3 Dependence of the modulus  $G$  ( $\text{g cm}^{-2}$ ) on the swelling ratio  $X$   
Samples: ● A, ○ B, ◻ C, ◻ D, ● E, ○ F

slope has been observed earlier for networks with a varying number of charges on the chain (ILAVSKÝ 1982) and for those with various concentration of elastically active chains (ILAVSKÝ and HROUZ 1982). From the  $\log G$  vs.  $\log X$  dependences of samples A-F, the  $G_1$  values were extrapolated for  $X=1$  ( $G_1 = 51, 98, 126, 170, 439$  and  $757 \text{ g cm}^{-2}$ ). From  $G_1$ , the concentrations  $\nu_d$  of elastically active chains related to the dry state were calculated ( $\nu_d = G_1/\phi^*RT$ ,  $\nu_d = 5.5, 5.8, 4.4, 4.4, 7.3$  and  $9.1 \times 10^{-5} \text{ mole cm}^{-3}$ ). The required constant  $\nu_d$  value of samples A-F was achieved by a large decrease in the concentration of the crosslinking agent, which suggests a quick rise in the efficiency of the crosslinking reaction with increasing monomer content at network formation. Obviously, the efficiency of the crosslinking reaction increases mainly owing to the lower cyclization at network formation.

#### Comparison between theory and experiment

If the dependence of swelling pressure  $P$  (cf. Eqs (1)-(5) in the paper ILAVSKÝ 1981\*) on the volume fraction of the polymer in the swollen state  $\phi_2$  (characterizing the composition of the gel) shows the van der Waals loop, two phases with the compositions  $\phi_2'$  and  $\phi_2''$  may coexist in the network. In the case of free swelling ( $P=0$ ) the composition of the coexisting phases is determined by the condition (ILAVSKÝ 1981)

$$\int_{\phi_2'}^{\phi_2''} (\bar{\chi} - \chi_c) d\phi_2 = 0 \quad (3)$$

where the dependence of the interaction parameter  $\bar{\chi}$  on  $\phi_2$  (also having the van der Waals loop) is determined by the

\*In this paper the contribution  $\phi_4$  in Eq. (5) should be negative

condition of free swelling, i.e.  $P=0$  (Eq.(6) in the paper by ILAVSKÝ 1981), and  $\chi_c$  is the critical value of the interaction parameter (in this case given by the composition of the acetone-water mixture) at which the collapse takes place.

From the known molecular parameters (molecular weights of the monomer unit  $M_0 = 71 \text{ g mole}^{-1}$ , density  $\rho = 1.35 \text{ g cm}^{-3}$ ,  $T = 298 \text{ K}$ , experimental  $\phi^*$  values, mole volume  $V_1$  of the acetone-water mixture, experimental network density  $\nu_d$  and the degree of ionization  $i = x_{MNa}^- = 0.012$ ) and using Eq.(6) of the paper by ILAVSKÝ (1981), the  $\bar{\chi}$  vs.  $\phi_2$  dependence was calculated for the experimentally determined  $\phi_2^*$  of samples A-F (Fig.4).

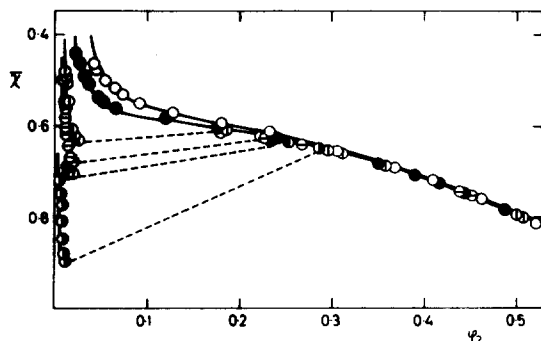


Fig.4 Dependence of the interaction parameter  $\bar{\chi}$  on the volume fraction of the polymer in the swollen state  $\phi_2$ . Samples denoted as in Fig.3

While for samples E and F with the highest  $\phi^*$  values the  $\bar{\chi}$  vs.  $\phi_2$  dependence is continuous, a discontinuity is observed with A-D samples (characteristic of the phase transition), the magnitude of which increases with decreasing monomer content in the polymerization mixture. Application of Eq.(3) to the  $\bar{\chi}$  vs.  $\phi_2$  dependence (Maxwell's construction, cf. Fig.7 in the paper ILAVSKÝ 1982) of samples A-D allowed both the extent of the collapse  $\Delta = \phi_2'' - \phi_2'$  and  $\chi_c$  to be determined (in the discontinuity range the  $\bar{\chi}$  vs.  $\phi_2$  dependence was calculated using Eq.(6) in the paper ILAVSKÝ 1981); the values  $\Delta$  and  $\chi_c$  were then compared with the experimental ones (Fig.5).

Fig.5 Dependence of the extent of the collapse  $\Delta$  and critical value of the interaction parameter  $\chi_c$  on the volume fraction of the polymer at network formation  $\phi^*$ . — theoretical prediction given by Eq.(3),  $\circ$  experimental  $\Delta = \phi_2'' - \phi_2'$ ,  $\bullet$  corresponds to  $\chi_c$  of the acetone-water mixture of the polyacrylamide network without charges (ILAVSKÝ 1982) at which the collapse takes place

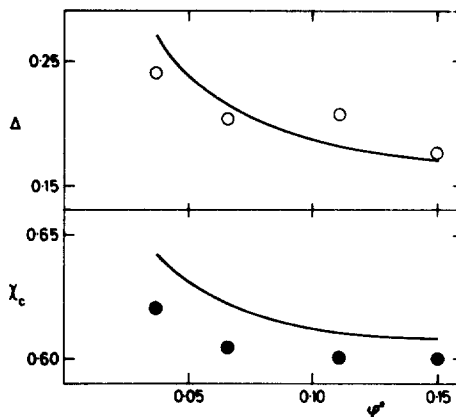


Fig.5 shows that with increasing  $\phi^*$  both  $\Delta$  and  $\chi_c$  decrease, in agreement with the theoretical prediction; while the fit between the experiment and theory in the extent of the collapse  $\Delta$  is good, for the interaction parameter  $\chi_c$  it is less satisfactory.

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