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Phase Transition in Swollen Gels

4. Effect of Concentration of the Crosslinking Agent at Network Formation on the Collapse and Mechanical Behaviour of Polyacrylamide Gels

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Summary

The effect of concentration of the crosslinking agent on the swelling equilibrium and mechanical behaviour of poly(acrylamide) gels with a low content of sodium methacrylate (molar fraction $x_{MNa} = 0.012$) was investigated in acetone-water mixtures. The increasing concentration of the crosslinking agent suppresses the extent of phase transition Δ (determined by a change in the gel volume) and decreases the critical value of the interaction parameter χ_c (given by the composition of the acetone-water mixture) at which the collapse takes place; these dependences are in a semiquantitative agreement with the recent molecular theory which describes the swelling equilibria of polyelectrolyte networks.

Introduction

The phase transition (collapse) given by the coexistence of two polymer phases differing in the concentration and conformation of segments has been experimentally observed both on poly(acrylamide) (PAAm) gels in an acetone-water mixture (TANAKA 1979, STEJSKAL et al. 1980, JANAS et al. 1980, ILAVSKÝ 1982) and on poly(N,N-diethylacrylamide) gels in water alone (ILAVSKÝ et al. 1982). The jumpwise change in volume at the phase transition is accompanied by a jumpwise change in mechanical properties of the gel (ILAVSKÝ 1982, ILAVSKÝ et al. 1982). The conditions necessary to bring about a collapse appeared to be the existence of a small number of charges ($\approx$1 mol.%) on the chain and the possibility of preparation of homogeneous gels at high dilution at network formation. Also, it has been found theoretically that $\approx$1 mol.% of charges on the chain affect free energy of the swollen network ΔF to such an extent that under suitable conditions the gel undergoes phase transition (ILAVSKÝ 1981); A comparison between theory and experiment gave a semiquantitative fit (ILAVSKÝ 1982). Since a change in the elastic energy of the network with swelling is markedly operative in the swelling pressure of the network, one may expect that the occurrence and extent of phase transition may be affected by the concentration of the crosslinking agent and by the amount of diluent

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at network formation. The effect of these parameters on the collapse has not been studied yet; experimental data in this field will also allow us to verify earlier theory (HASA et al. 1975, ILAVSKÝ 1981) which describes swelling equilibria in polyelectrolyte gels.

This study is concerned with the effect of concentration of the crosslinking agent on the extent and position of phase transition and on the mechanical behaviour of poly(acrylamide) gels containing 1.2 mol.% of sodium methacrylate in acetone-water mixtures; the experimental results thus obtained are compared with an earlier theory describing the swellig equilibria of polyelectrolyte gels.

Experimental

Sample preparation: The samples were prepared from 100 ml of an aqueous solution which contained 7 g acrylamide (AAm), 1.27 ml of 0.96 M solution of sodium methacrylate (MNa) (corresponds to the molar fraction $x_{MNa} = 0.012$), 20 mg ammonium persulphate and 20 mg sodium pyrosulphite. Six samples, A,B,C, D,E and F, with a varying content of the crosslinking agent (N,N′-methylenebisacrylamide)(MBAAm) - 0.02, 0.10, 0.115, 0.13, 0.20 and 0.70 g respectively - were prepared for the experiments. All components with the exception of sodium pyrosulphite were dissolved in redistilled water and bubbled through with nitrogen; after the addition of pyrosulphite and stirring, the solution was poured into ampoules ≈1 cm in diameter which after that were sealed. The polymerization proceeded at room temperature for ≈3 h; after the polymerization the gels were removed from the ampoules and cut into specimens ≈1 cm long. Swelling: Acetone-water mixtures in the range 0-80 vol.% acetone were prepared from redistilled water and acetone (reagent grade); pH of the mixture was then adjusted to 7.5 with a concentrated NaOH solution (pH ≈7.5 guarantees that the degree of ionization in the networks equals the molar fraction x_{MNa} with an accuracy higher than 0.5 % of the originally weighed amount of MNa). While in the lower concentration range of acetone (<50 vol.%) the swelling was carried out on samples after the preparation, at higher acetone contents (>40 vol.%) partly dried samples were used for this purpose (cf.ILAVSKÝ 1982). After swelling for 28 days the swelling ratio X related to the state of network formation was determined from the equation

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

in which D and D^{*} are sample diameters after swelling or after preparation, and V and V^{*} respectively are gel volumes in the swollen state and after preparation. The measurements were carried out with an Abbé comparator (Zeiss Jena, accuracy ±0.002 mm); the X values in Table 1 and plotted in Fig.1 are

TABLE 1
Swelling and deformation characteristic

acet[a] vol%	A log X^b	A log G^c	B log X^b	B log G^c	C log X^b	C log G^c	D log X^b	D log G^c	E log X^b	E log G^c	F log X^b	F log G^c
0	-1.349	0.740	-0.849	1.507	-0.745	1.483	-0.678	1.585	-0.432	1.812	-0.367	2.237
5	-1.431	0.770	-0.848	1.554	-0.699	1.534	-0.658	1.600	-0.409	1.860	-0.252	2.220
10	-1.400	0.750	-0.827	1.558	-0.678	1.528	-0.602	1.638	-0.398	1.907	-0.187	2.245
15	-1.313	0.730	-0.826	1.590	-0.602	1.550	-0.569	1.693	-0.366	1.900	-0.119	2.280
20	-1.425	0.732	-0.775	1.600	-0.553	1.572	-0.481	1.691	-0.357	1.912	-0.027	2.243
25	-1.498	0.763	-0.751	1.554	-0.553	1.592	-0.523	1.706	-0.319	1.938	0	2.293
30	-1.345	0.806	-0.698	1.606	-0.523	1.649	-0.398	1.739	-0.294	1.963	0.037	2.298
35	-1.317	0.771	-0.639	1.633	-0.398	1.685	-0.252	1.788	-0.235	2.018	0.170	2.371
40	-1.201	0.857	-0.483	1.677	-0.284	1.804	-0.119	1.843	-0.175	2.035	0.283	2.320
							+0.385	2.135	+0.198	2.230		
42	-	-	-	-	-0.201	1.783	0.415	2.147	0.362	2.284	-	-
45	-1.110	0.840	0.526	2.242	0.610	2.265	0.615	2.267	0.681	2.355	0.500	2.490
47	0.727	2.141	0.590	2.340	0.693	2.282	0.697	2.250	0.695	2.372	0.683	2.514
50	0.746	2.316	0.661	2.325	0.721	2.300	0.744	2.319	0.775	2.419	0.750	2.640
53	-	-	-	-	0.771	2.305	0.778	2.335	0.824	2.507	0.819	2.642
55	0.798	2.386	0.703	2.412	0.809	2.398	0.803	2.392	0.829	2.468	0.854	2.618
60	0.847	2.429	0.770	2.509	0.866	2.412	0.876	2.445	0.881	2.550	0.875	2.666
65	0.869	2.665	0.814	2.532	0.895	2.387	0.870	2.530	0.890	2.644	0.926	2.665
70	0.890	2.836	0.848	2.640	0.949	2.446	0.919	2.529	0.954	2.631	0.936	2.770
75	1.014	3.012	0.878	2.665	0.903	2.486	0.972	2.540	0.986	2.672	0.978	2.750
80	1.045	3.108	0.911	2.800	1.001	2.550	1.001	2.665	1.002	2.683	1.013	2.857

[a] acetone content in acetone-water mixture, [b] swelling ratio determined by Eq.(1), [c] values of the modulus G in g cm^{-2}

the average from at least three measurements.
Mechanical characteristics: Along with swelling, the deformational characteristics were also measured with an apparatus described earlier (HROUZ et al. 1979) operating in simple compression. A cylindrical specimen (diameter $\approx$1 cm, height $\approx$1cm) was compressed between teflon surfaces to the compression λ, and after relaxation for 30 s the force f was read off; on the whole, 10 values λ (in the range $0.7 < \lambda < 1$) and f were determined. The modulus G was determined using the expression

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

in which S_o is the initial cross-section of the sample. The G values given in Table 1 and plotted in Fig.1 are the average from two measurements.

Results and Discussion

Swelling and mechanical characteristics

Data in Table 1 and plotted in Fig.1 show that in series A with the lowest concentration of the crosslinking agent there exists a pronounced phase transition reflected in a large discontinuity in the dependence of the swelling ratio X on acetone concentration. The increasing content of the crosslinking agent suppresses the phase transition, and in series F with the highest MBAAm content the dependence X on composition of the mixture is continuous. A similar effect can be seen also in the dependence of modulus G on acetone concentration. While in series A the discontinuity in the dependence of G on the composition of the mixture is largest, it decreases with increasing MBAAm content, and in series F the dependence becomes continuous. Also, it can be seen in Fig.1 that the extent of the transition $\Delta\log X$ ($\Delta\log X = \log X'' - \log X'$) markedly decreases with the content of the crosslinking agent; on the other hand, the critical acetone concentration at which the phase transition takes place depends on the MBAAm content only little (varying between $\approx$45 and $\approx$40 vol.% of acetone). It is quite obvious, therefore, that the increasing concentration of the crosslinking agent (at a constant charge concentration on the chain, x_{MNa}) is reflected in an opposite effect compared either with the time of ageing of PAAm gels (TANAKA et al. 1980, STEJSKAL et al. 1980, JANAS et al. 1980) or with a rise in the number of charges in such system (ILAVSKÝ 1982).

The dependence of the shear modulus G on the swelling ratio X is given in Fig.2. The modulus (at constant X) increases with increasing concentration of the crosslinking agent as expected; at lower X, parallel straight lines with slope of $\approx$0.65 may be drawn through the log G vs. log X dependences in the individual series A-F. The same slope was found earlier for networks

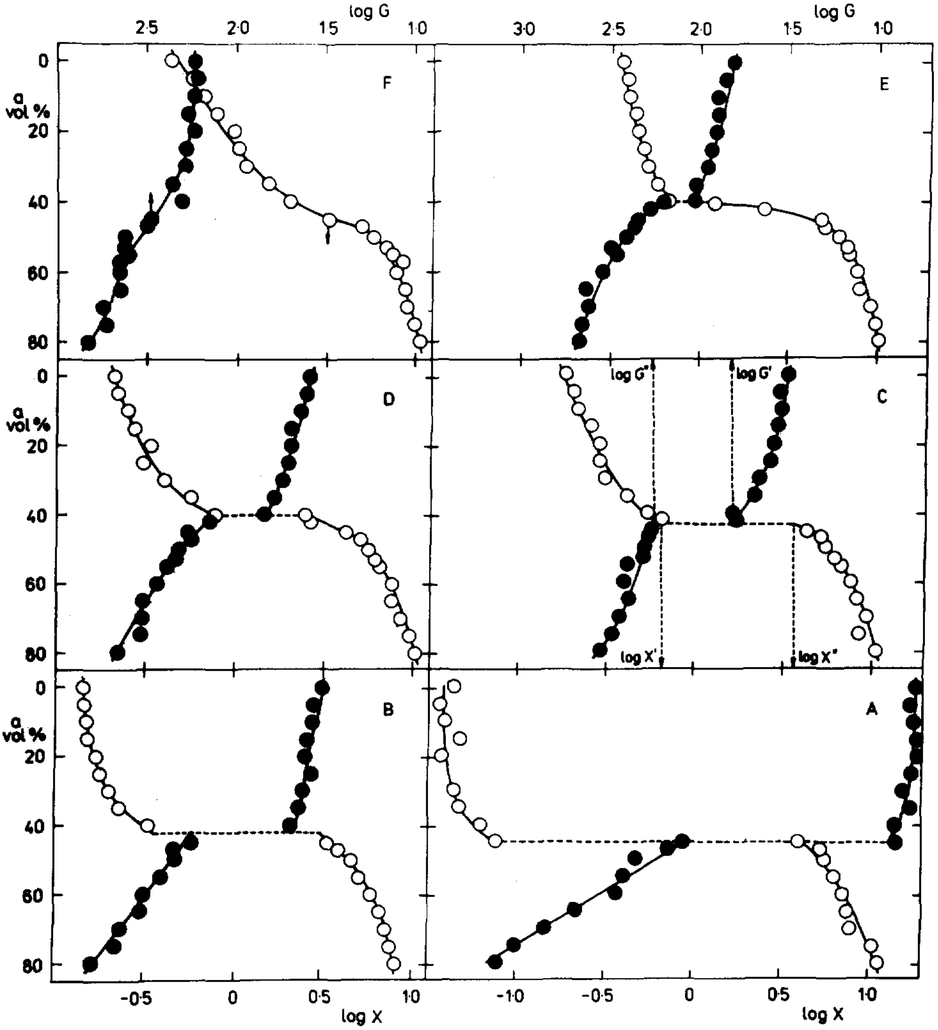

Fig.1 Dependence of the swelling ratio X and modulus G (g cm^{-2}) on the acetone content a (vol.%) in acetone-water mixtures Samples denoted in the Figure, ○ X, ● G

with a varying x_{MNa} (ILAVSKÝ 1982). Departures from the linear dependence of log G on log X in the range X > 8 may be interpreted through the effect of the main transition region on G as it has been done before (ILAVSKÝ 1982). The dependence of log G on log X for samples A-F was used to determine the extrapolated values of the modulus G_1 for X= 1 (G_1 = 44, 70, 78, 88, 135 and 187 g cm^{-2}) , and from G_1 the concentration of elastically active chains related to the dry state $\nu_e=G_1/RT\varphi^o$ (ν_e=3.6, 5.7,

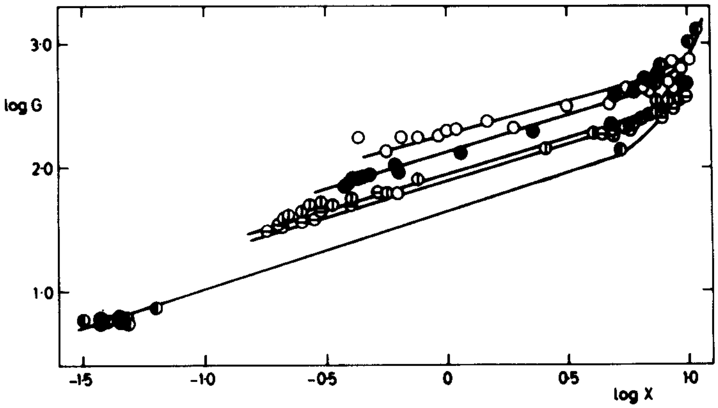

Fig.2 Dependence of the modulus G $(g\ cm^{-2})$ on the swelling ratio X
Samples: ◐A, ⊖ C, ⦶ D, ● E, ○ F

6.3, 7.1, 10.9, 15.2 $\ast$ 10^{-5} mol cm^{-3}) where $\varphi^{o}=0.052$ is the volume fraction of the polymer at network formation calculated using the density of the dry polymer $\rho=1.35 g\ cm^{-3}$.The low ν_e values suggest high cyclization accompanying the structure formation, which is a consequence of high dilution in the system.

Comparison between theory and experiment

A necessary condition of phase transition in the gel consists in the existence of the van der Waals loop in the dependence of the swelling pressure P or of the interaction parameter $\bar{\chi}$ on the volume fraction of the polymer in the swollen state φ_2. The composition of phases (φ_2' and φ_2'') is given by (ILAVSKÝ 1981)

$$\int_{\varphi_2'}^{\varphi_2''} (\bar{\chi} - \chi_c)d\varphi_2 = 0 \qquad (3)$$

where φ_c is the critical value of the interaction parameter (in our case, given by the composition of the acetone-water mixture) at which the collapse takes place. The dependence of $\bar{\chi}$ on the composition of the gel (determined by φ_2) in the case of free swelling considered here is determined by the condition P=0. Using the known molecular parameters: experimentally determined network density ν_e and the degree of ionization $i=x_{MNa}=0.012$ and by means of Eq.(6) from (ILAVSKÝ 1981), the dependence of $\bar{\chi}$ on φ_2 was determined for experimentally found $\varphi_2 = \varphi^{o}X$ values (Fig.3).

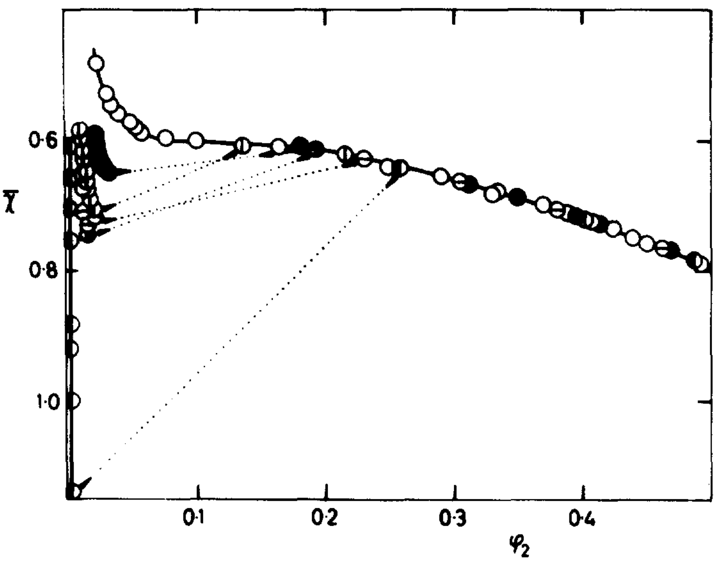

Fig.3 Dependence of the interaction parameter $\bar{\chi}$ on the volume fraction of the polymer in the swollen state φ_2
Samples: ◐ A, ◑ B, ⊖ C, ⦶ D, ● E, ○ F

While for the highest network density the $\bar{\chi}$ vs. φ_2 dependence is a continuous one, discontinuity appears with decreasing ν_e; the extent of this discontinuity increases with decreasing ν_e. Application of Eq.(3) to the $\bar{\chi}$ vs. φ_2 dependence (Maxwell construction, cf. ILAVSKÝ 1981, ILAVSKÝ 1982) allowed both the extent of the collapse $\Delta = \varphi_2'' = \varphi_2'$ and χ_c to be determined. Fig.4 shows that the observed experimental de-

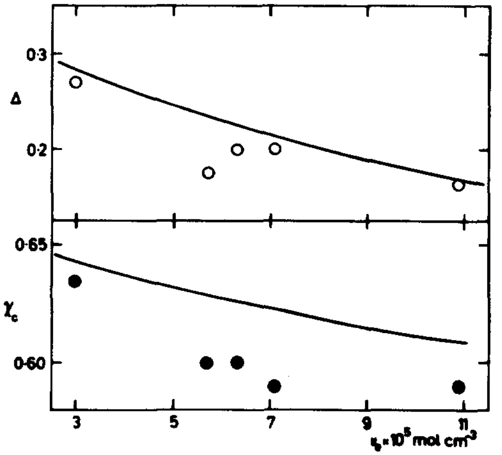

Fig.4 Dependence of the extent of the collapse Δ and critical values of the interaction parameter χ_c on the network density ν_e
— theoretical prediction (cf.Eq.(3)), ○ experiment $\Delta = \varphi_2'' - \varphi_2'$; ● corresponds to χ of the acetone-water mixture at which the collapse takes place

creases of both Δ and χ_c with increasing ν_e are in agreement with the earlier theory (ILAVSKÝ 1981); while the agreement in Δ is rather good, it is less satisfactory with the parameter χ_c.

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