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Collapse of Polyacrylamide Gels

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SUMMARY

Ageing of polyacrylamide gels is connected with the formation of charged groups on network chains. The presence of the electrostatic charges is required for the observation of the gel collapse.

INTRODUCTION

Recently there has been renewed interest (TANAKA 1978, 1979, KHOKHLOV 1980) in the collapse transition of gels (DUŠEK and PATTERSON 1968, DUŠEK and PRINS 1969). In particular, Tanaka used polyacrylamide (PAAm) gels in simple and instructive experiments showing this transition in acetone-water mixtures. In interpreting these, he explicitly modified Flory´s early theory (FLORY 1953), but the later theory (FLORY 1956) is perfectly adequate and this was extensively treated by DUŠEK and PRINS (1969) in their classical review. In trying to elucidate some puzzling aspects of Tanaka´s experiments, we repeated and substantially confirmed them, but we have found the contributory effect of some importance for their proper understanding.

EXPERIMENTAL

Polyacrylamide gels were prepared by the procedure according to TANAKA (1978, 1979). 5 g of acrylamide, 133 mg N,N´-methylene-bis-acrylamide, 40 mg of ammonium persulphate and 160 µl of tetramethylethylenediamine were dissoved in distilled water at laboratory temperature up to 100 ml of solution. A gel was formed in approx. 30 minutes and left to mature for the defined time.

RESULTS AND DISCUSSION

The time of cure (or ageing) of gels prepared in water plays a central role in phase equilibria studied subsequently (TANAKA 1978, 1979). Theory (DUŠEK and PRINS 1969) predicts that the collapse of the gel is faciliated by increase in cross-link density (Fig. 1).

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Tanaka believed that storing of PAAm gels, originally prepared in water, with gelation times of the order of minutes, would lead to significant changes of network structure (with increase in cross-link density) continuing for tens of days. If this were the only effect occuring over long periods, the gel should show in good solvents swelling degrees decreasing with increasing time of storage. Inspection of Tanaka's data shows the opposite effect. Our own experiments do so also (Fig.2).

Fig. 3a shows the steady increase of swelling in water with increasing curing time. One would expect this cure to be accelerated by increase in temperature and this is indeed marked (Fig. 3b).

In trying to unravel the true mechanism of slow changes in these gels, we came to test proposals by KULICKE et al. (1978, 1980), who observed ageing of aqueous PAAm solutions and by FORSMAN et al., on importance of hydrogen bonding in aqueous solutions of linear PAAm.

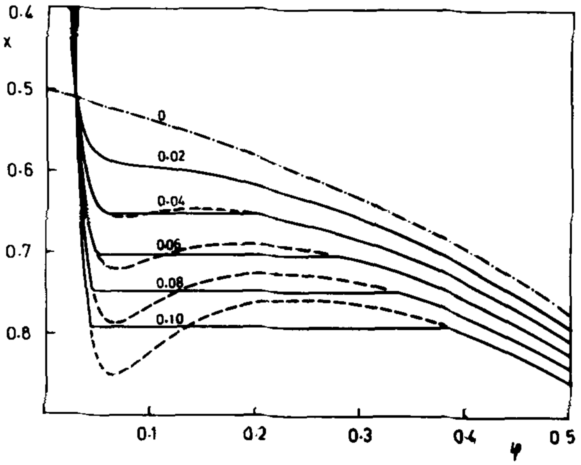

Fig. 1 Swelling curves for gels of different cross-link density calculated according to DUŠEK and PRINS (1969)

χ is FH interaction parameter, φ volume fraction of polymer in a gel. This fraction for the gel in reference state taken $\varphi_0 = 0.01$. Cross-link density characterized by $\nu^*\bar{v}_1$(reciprocal value of this parameter is closely related to the average number of polymer segments between two cross-links) given at the individual curves. Swelling curves in the collapse region denoted by broken lines.

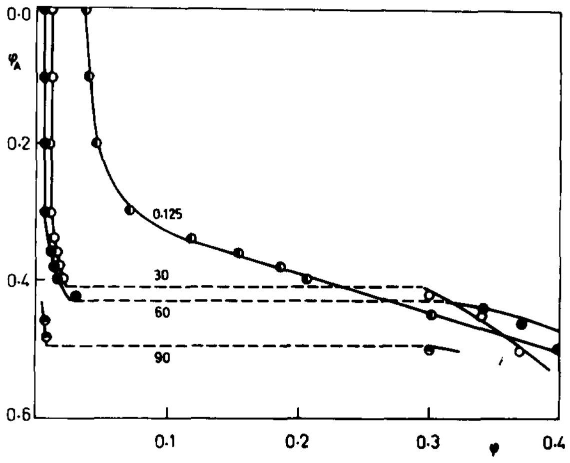

Fig. 2 Swelling of polyacrylamide gels (volume fraction of polymer in a gel, φ) in acetone-water mixtures

5% polyacrylamide gels prepared in water, cured at 20°C for 0.125 (◐), 30 (○), 60 (●), and 90 (⊖) days, were immersed in acetone-water mixtures (composition given by volume fraction of acetone, φ_A). Observed collapse denoted by broken lines.

Considerable shrinkage is clearly observed when low-molecular weight electrolyte is added (Fig. 4). Swelling of uncharged gels is expected to be affected by addition of low-molecular weight electrolyte (DUŠEK and JANÁČEK 1975), however, here the steep deswelling of aged gels clearly demonstrates the presence of electrostatic charges attached to the network and their screening by the added electrolyte. The gradual increase in concentration of these charges would be responsible for the observed increase in equilibrium swelling with time already mentioned (Fig. 3a). This "curing" process is of course irreversible. Charged groups, suspected to be acidic, have been also detected by potentiometric titration in linear PAAm solutions (FRANÇOIS et al. 1979). The polyelectrolyte effect in aged PAAm gels has been recently established independently by TANAKA (1980). We conclude that the formation of charged groups is also responsible for the time-dependent change in properties of linear PAAm solutions.

Observation of collapse of PAAm gels in acetone-water mixtures seems to require the electrostatic effects, since the addition of small amount of sodium chloride is found to reduce swelling curves to the

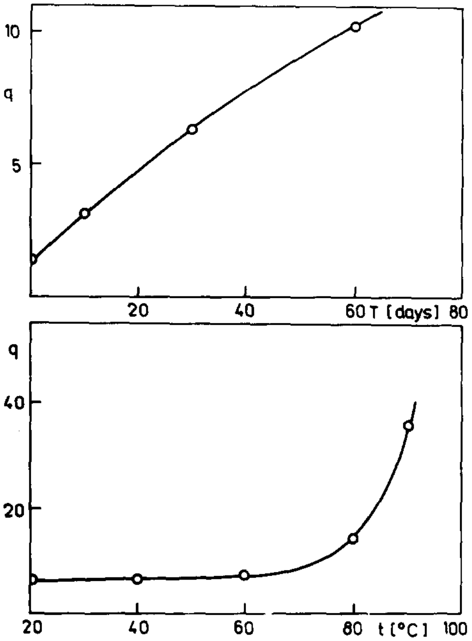

Fig. 3a,b
Swelling of polyacrylamide gels in water (swelling ratio, q, with respect to the state of preparation in dependence on
(a) curing time, T, at 20°C;
(b) temperature, t, (here 5% gels cured for 30 days at 20°C were kept at given temperature for 7 days).

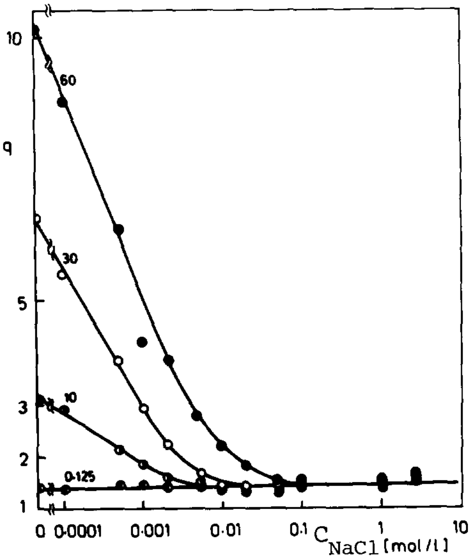

Fig. 4
Swelling of polyacrylamide gels as a function of molarity of aqueous sodium chloride solutions, C_{NaCl}
5% gels cured at 20°C for 0.125 (◑), 10 (◐), 30 (○), and 60 (●) days.

gradually declining course, as in a plot of Fig. 2, without collapse.

The good agreement between the experimental observation of collapse and theoretical prediction should be considered carefully as the cause of collapse seems to be due to electrostatic interactions which above theories do not account for.

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