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Continuous swelling or collapse of chemically crosslinked gel of polyvinylalcohol by borate complexation

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SUMMARY

The swelling behavior of chemically crosslinked poly(vinylalcohol) is studied in borax solution in presence or without added salt. In borax solution, the gel, initially neutral beads swells because anionic charges appear on the chain by complexation, the swelling depends on the mesh size. When NaCl is added, the charges on the polymeric chains are screened and the gel will contract.

INTRODUCTION

Macromolecular gels, loosely crosslinked, raise up an increasing interest in the field of thickening agents or hydrogels. So a special attention is now focus on experimental swelling or collapse properties of these kind of materials. For instance, the behavior of partly hydrolyzed polyacrylamide according to the solvent composition (aceton-water) (1), the temperature (2) or the application of an external electric field (3) has been extensively investigated by Tanaka.

The contraction and the dilatation observed are related to the total osmotic pressure of the gel. As in most of the cases, the macromolecular chains are polyelectrolytes, the total pressure is obtained by addition of three effects which are expected to be independent :

- the rubber elasticity of the chains between two tie points of the network.
- the polymer-polymer affinity
- the influence to the counterions and more generally the ionic strength effect.

Unfortunately, in most practical situations, the balance between the swelling or collapse mechanisms can not be established because it is difficult to induce a progressive change of crosslinking or ionic unit-content for a given gel.

We present here the behaviour of a series of chemical gels prepared by crosslinking polyvinylalcohol (PVA) with a dialdehyde (4) and by modifying these gels by addition of borax : borate leads to monodiol and didiol complexes which are negatively charged. The monodiol just induces polyelectrolyte effects on the originally PVA chains previously neutral, the didiols acts as a crosslinking unit. All the swelling results were theoretically predicted by L. Leibler and al.(5), we found that the experimental data are in good agreement with the theoretical prediction.

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EXPERIMENTAL

PVA is supplied by JANSSEN CHIMICA. The molecular weight is determined by steric exclusion chromatography with refractive index and light low angle scattering detectors (chromatix Cx 100) $\bar{M}w$ = 170 000. The residual acetate groups, 2.1% in mole, and tacticity 48.5% of meso diad are measured by ^{1}H NMR. The polymer is purified by ultrafiltration and is lyophilized. Glutaraldehyde, borax (which is a boric acid-borate buffer and gives in solution two borate molecules per borax), sodium chloride and silicon oil are commercial products and used without further purification. All the solutions are made in desionized water (Milli Q system of Millipore).

The chemical reticulation is carried out in a water/silicon oil suspension to obtain spherical beads. The pregel mixture is an aqueous PVA solution with an adequate amount of glutaraldehyde to obtain a gel with the expected mesh size. The polymer concentration (Cp = 7% W/W) is far from the overlap concentration C^{*} (C^{*} = 1.2%), determined by low shear viscometry.

The gelation of the PVA-glutaraldehyde system in aqueous solution is studied by viscometric measurements, performed on a Low Shear viscometer (CONTRAVES) as a function of time. The viscosity increases with the reaction time or the conversion ratio. Near the gelification point, the viscosity diverges and we choose this criterion to determine the gelation time tg. Experimentaly, we observe that the gelation rate depends on temperature, polymer concentration Cp and glutaraldehyde concentration Cg ($tg \simeq (Cp * Cg)^{-1}$).

We check the presence in the gel of any unreacted aldehyd group of the difunctional crosslinker by addition of an amine in the reaction mixture to form a Schiff base. The pink colored medium obtained is analyzed by UV spectroscopy and we find only a few per cent (0.5%) of unreacted adehyde groups. These results give evidence that the crosslinking reaction can be considered as complete.

A catalytic amount of hydrochloric acid is necessary to the onset of the ketalization reaction. The crosslinking reaction in oil suspension is kept at 40°C. during 1 hour. A mechanical stirring is applied during all the reaction to prevent the bead coalescence. Beads are recovered (size 1-3mm) washed twice with a mixture of ethanol-water and then, by water. Two series of different length between tie points gels have been prepared (DP_c = 100, DP_c = 200) where DP is the number of monomer units.

Swelling experiments

We put one bead in a cell with the adequate solutions (water or salt solution) during 24h. We measure the gel size before one addition of borax and after swelling equilibrium with a given amount of borax by using sight equipped with a graduated reticle. The swelling versus time is observed (Fig. 1), and we note the final equilibirum swelling (the swelling is proportional to the gel size at the third power). All the results are given in relative swelling which is the ratio of the swelling in borate solution to the swelling in the same solution without borate, as a function of the ionic strength. The ionic strength is the sum of borate concentration,Cb and salt concentration, Cs.

$$I = Cb + Cs \quad (C \text{ in Mol} \times l^{-1})$$

RESULTS

Fig. 2 and 3 show the evolution of relative swelling versus the ionic strength.

Curve A : without added monovalent passive salt (NaCl), the chemical gel swells continuously by addition of borax and then levels off.

Curve B : if we start from a gel in equilibrium with a small concentration of salt (B_1, B_2), the swelling decreases then passes through a minimum and increases again when more borax is added. The plateau value is lower than the previous one, obtained without salt. When salt concentration increases (compare B_1, B_1', B_1'') the minimum swelling value and the value at the plateau decreases. At the same time, the borate amount which gives a swelling ratio equal to one, is increasing.

Curve C : we consider a gel swollen in borate solution. When salt (NaCl) is added, the swelling decreases, becomes lower than the value obtained for the same gel in aqueous solution and finally collapses.

- the mesh size effect is studied by comparison of the two figures 2 and 3 .
- without salt (compare curves A_1 and A_2), the plateau value increases with the length between chemical crosslinks.
- At constant salt concentration, the minimum swelling value (compare curves $B_1'$and B_2') decreases when mesh size increases. The total amount of borax needed to recover the initial swelling increases with the mesh size of the gel.

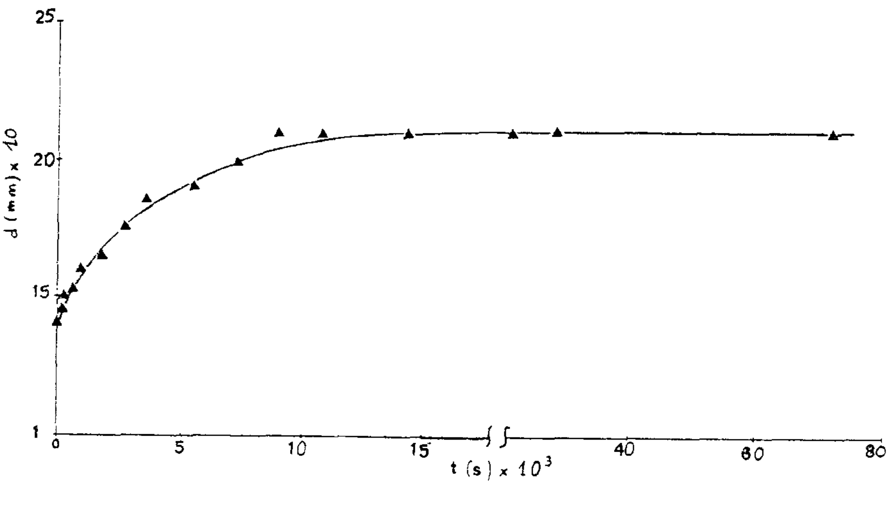


Fig. 1 : Kinetic of swelling. Gel size. d versus time

DPc = 100 borate concentration 0.001 Mol x l^{-1}

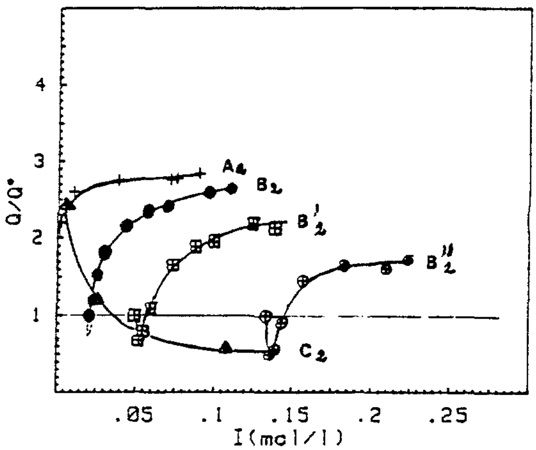


Fig. 3 : Swelling Q versus ionic strength I.
Gel mesh size DPc = 100

A_2	PVA + borax without NaCl
B_2, B_2', B_2''	PVA + borax + constant amount of NaCl, respectively 0.02, 0.05, 0.135 Mol x l^{-1}
C_2	PVA + NaCl + constant amount of borate, respectively 0.005 Mol x l^{-1}

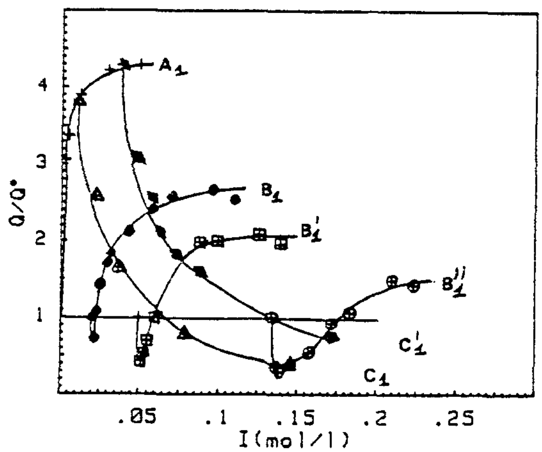
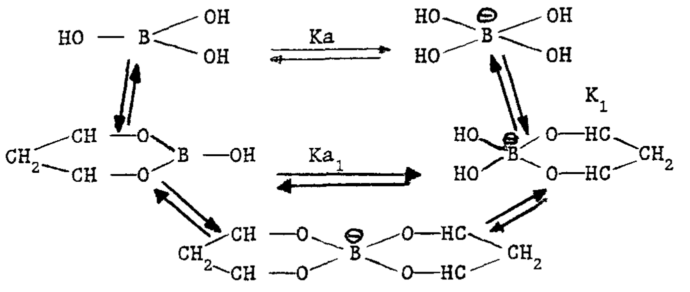


Fig. 2 : Swelling Q versus ionic strength I.
Gel Mesh size DPc = 200

A_1	PVA + borax without NaCl
B_1, B_1', B_1'',	PVA + borax + constant amount of NaCl, respectively 0.02, 0.05, 0.135 Mol x l^{-1}
C_1, C_1'	PVA + NaCl + constant amount of borate, respectively 0.012, 0.038 Mol x l^{-1}

DISCUSSION

The gel behaviour results from the interaction between borax and the complexing diol sites on the chain.. ^{11}B NMR investigations show the formation of monocomplexes I and dicomplexes II. Complexation reactions are given below :



I

II

The stable species are charged. The distribution of charges on the previously neutral PVA chains depends only on the thermodynamic equilibrium and leads to interchain and intrachain crosslinks.

Didiol complex formation and the swelling of a gel in borax solution are governed by two phenomenons :

- The electrostatic repulsion between charges on the polymer chain

- The contraction due to dicomplex formation

Qualitatively, we can explain the gel behaviour in this way :

- in aqueous solution, the electrostatic repulsions are predominant, the gel swells until no more complexe can be formed without decomplexation

- at constant salt concentration, the charges induced by complexation are screened in the earlier stage, the predominant factor is the contraction due to dicomplexation. But when more borate is added electrostatic repulsive interactions can take place and the gel will swell. The borate amount needed to reach the minima increases with the salt concentration, the charge screening becomes more important, therefore the complexation equilibrium moves to the didiol complex formation.

- For the solution with constant borate concentration, the addition of salt will screen the charges and contract the gel which collapses at sufficiently high salt concentration. The mesh size effects can be explained by a short chain model. The end to end distance R of a chain between two tie points is proportional to the second virial coefficient B and to the square root of the average chain molecular weight between crosslinks.

$$\left(\frac{R}{Ro}\right)^3 \alpha \; B \; Mc^{1/2} \qquad [1]$$

where Ro is the end to end distance of neutral chain in aqueous or salt solution.

Without salt, the swelling plateau value scales like $Mc^{1/2}$. The minimum swelling value decreases as a function of $Mc^{1/2}$, at fixed salt concentration. The results are in good agreement . See Table 1.

CURVE	Mc	Q
A_1	200	4.3
A_2	100	2.7
B_1'	200	0.45
B_2'	100	0.65

Table 1. Effect of the mesh size on the gel swelling.

A Flory model describing these results will be presented in a forthcoming paper.

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