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Swelling-Induced Birefringence of a Polyelectrolyte Gel Strongly Interacting with Metal Ions

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ABSTRACT: The swelling behavior of a polyelectrolyte gel in aqueous salt solutions is studied in the case where metal ions are binding with polyions, forming insoluble compounds. The hydrogel swelling and contraction in such solutions and the metal ion penetration inside the network are monitored by polarizing optical microscopy. The growth of an insoluble layer on the surface of the gel particle is accompanied by the formation of a birefringent core. Changes of the thickness of the birefringent layer with time and the dependence of the birefringence on salt concentration are discussed.

Introduction

The relationship between the volume phase transition of charged hydrogels and factors such as mixture composition (good−bad solvent), degree of network ionization, and/or the presence of metal ions has been reported in several theoretical and experimental works.[1−3] The behavior was in terms of changes in the osmotic pressure of mobile counterions.[2,4] In more recent publications it was shown that when a polyelectrolyte gel is placed in a salt solution, the effect of the chemical binding of counterions and polyions in the network is of great importance.[5−8]

When a charged gel is placed in a salt solution in which the interaction between mobile ions and polyions is very strong, and where an insoluble product is formed, an avalanche line process starts above a certain concentration and the gel collapses to an almost dry state.[5] The concentration redistribution of mobile ions in the presence of a polyelectrolyte gel[5] and the nature of the ions also influence the state of the hydrogel.[5−8] Most investigations are limited to describing the final equilibrium state dependence between the degree of gel swelling or the surrounding salt concentration[5−7] and the initial salt concentration.

Reported here is an experimental study of the swelling kinetics of a strongly charged network placed in a water−salt solution, in which the interaction between mobile ions and polyions is very strong and an insoluble product is formed following the reaction. We will show that it is necessary to take into account the coexistence of a swollen state and collapsed states inside the sample in order to properly describe the swelling behavior of the gel. This is similar to what was developed theoretically by Doi and Tomari[9] for temperature sensitive hydrogels. It will be shown that the appearance of stress during swelling is a very important factor which cannot be neglected.

Experimental Part

The hydrogel sample used in this study was a poly(0.75 acrylate−0.25 acrylic acid) cross-linked by *N*,*N*′-methylenebisacrylamide, with a 0.06% mole fraction of the cross-linking agent with respect to the monomer, kindly provided by Atochem. The initial state was a powder of dry spherical gel particles of diameter 0.1 mm. Two salts of mono- and polyvalent metals ($CuSO_4{\cdot}5H_2O$ and $AgNO_3$) which are known to form an insoluble compound with sodium polyacrylate and acrylic acid[10] were chosen for our study.

The kinetics of hydrogel swelling and contraction in $CuSO_4$ and $AgNO_3$ solutions and salt penetration inside the particle were monitored by optical microscopy between crossed polarized light. A dry gel particle was placed between two glass slides, and the salt solution was added. A sealing system prevented evaporation.

Results and Discussion

It was important to choose a suitable range of salt concentrations for the experiments since the hydrogel state depends strongly on this factor. In ref 5 it was shown that two regimes are possible in the hydrogel + solution system. If $C_s \ll C_p$ (C_s being the salt concentration and C_p the polymer concentration, both calculated in mole per liter for the total volume of the system), ions do not penetrate inside the gel. This is valid even in the case when a hydrogel based on sodium polyacrylate is placed in a salt solution of polyvalent metal ions. The second regime is when $C_s > C_p$. Here metal ions start to penetrate inside the sample and an avalanche line process of chemical bonding of the gel takes place. Thus the relative salt concentration C_s/C_p is one of the main parameters in the system.

In the present paper we have chosen the regime where $C_s/C_p > 1$. Two concentrations of each of the salt solutions were selected, one with C_s being comparable with C_p ($C_s/C_p = 5$) and one with C_s greatly exceeding C_p ($C_s/C_p = 1000$).

When a dry gel particle is placed in a salt solution, the gel starts to swell and adsorbs mainly water at the start. The changes of the sample dimensions in time $r(t)/r_0$ (here $r(t)$ is the radius of the swelling particle and r_0 is the radius of the dry particle) are given in Figure 1 for a hydrogel placed in $CuSO_4$ and $AgNO_3$ solutions. The relative salt concentration C_s/C_p in this case was 1000.

After the gel was immersed in the salt solution, a layer of insoluble compound appeared on its surface. The layer was seen to be birefringent when between crossed polarizers (Figure 2b). The formation of an anisotropic layer on the surface of a charged gel placed in a poor solvent was theoretically predicted in ref 11. No experimental confirmation of this result has yet been reported. Indeed, we did not see any birefringent layer either on the surface of a swollen-in-water gel placed in a poor solvent (acetone) or on a hydrogel immersed

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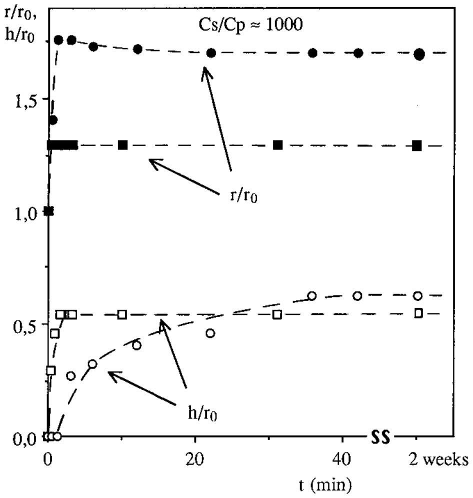

Figure 1. Reduced radius r/r_0 and reduced thickness of the birefringent layer h/r_0 for a gel placed in high concentration ($C_s/C_p = 1000$) $CuSO_4$ (●, ○) and $AgNO_3$ (■, □) solutions, as a function of time.

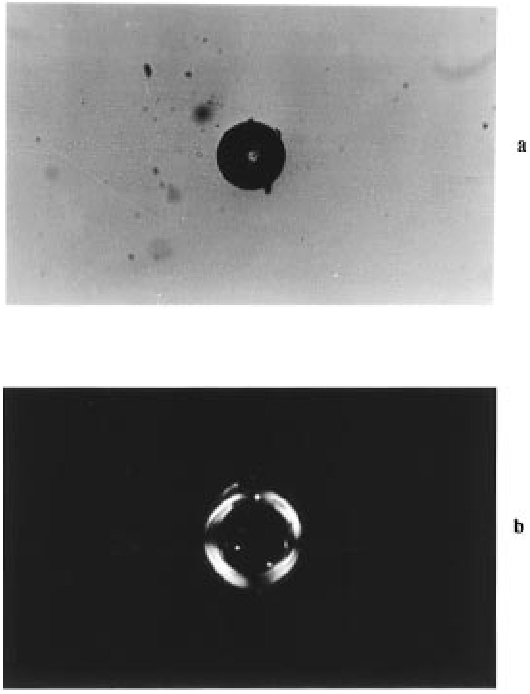

Figure 2. Optical micrographs taken between crossed polarizers of a gel swelling in $CuSO_4$ solutions of $C_s/C_p = 1000$: (a) dry gel particle, (b) 6.75 min after immersion, similar to the equilibrium state.

in a salt solution in the case where metal ions do not cross-link the gel (for example, solutions of NaCl, $K_3[Fe(CN)_6]$, etc.).

The change in the width of the birefringent layer with time $h(t)/r_0$ is given in Figure 1 for $CuSO_4$ and $AgNO_3$ solutions for $C_s/C_p = 1000$. From Figure 1 it is clear that the hydrogel is first of all swelling in the salt solution and that then the sample size is decreasing slightly. The width of the birefringent layer is increasing in time; it then remains constant along with the gel size. The final state of the hydrogel swollen in a very concentrated solution of $CuSO_4$ and $AgNO_3$ is a gel particle with a birefringent layer on its surface which is stable over a time of more than half a year. There is a difference in kinetics of hydrogel behavior in $CuSO_4$ (final state reached in 40 min) and $AgNO_3$ solutions (final state reached in 1.5 min). This may be due to different chemical activity of Cu^{2+} and Ag^+ ions reacting with COO^-.

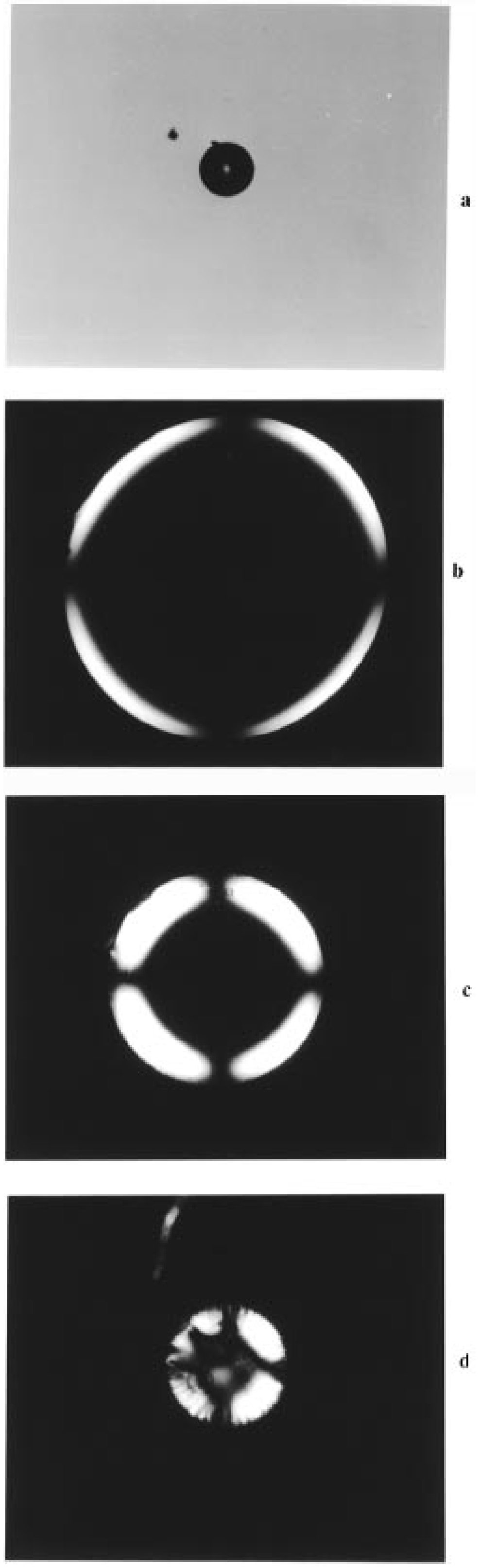

Figure 3. Optical micrographs taken between crossed polarizers of a gel swelling in $AgNO_3$ solutions of $C_s/C_p = 5$: (a) dry gel particle; (b) after 14 min; (c) after 24 min; and (d) after 50 min, similar to the equilibrium state.

When the gel is placed in a low concentration of $CuSO_4$ or $AgNO_3$ solution, with $C_s/C_p = 5$, the beginning of the swelling process is the same as that observed in concentrated salt solutions with $C_s/C_p = 1000$ (Figure

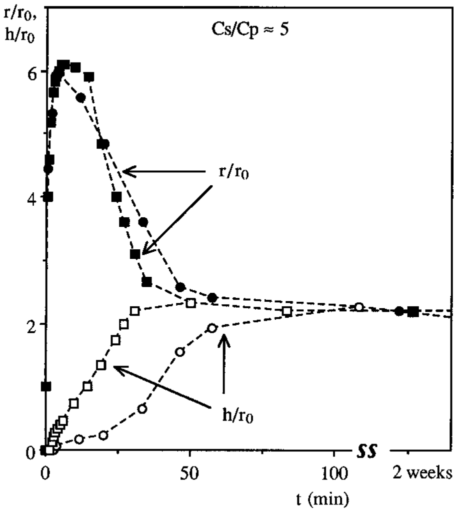

Figure 4. Changes of the reduced radius r/r_0 and reduced thickness of the birefringent layer h/r_0 in time for the gel placed in low concentration (C_s/C_p = 5) $CuSO_4$ (●, ○) and $AgNO_3$ (■, □) solutions.

3b). The width of the layer increases in time, and this prevents further hydrogel swelling. The gel then starts to collapse (Figure 3c), and this process is accompanied by a continuous increase of the birefringent layer (Figure 4). The final state is a contracted gel which is birefringent everywhere, which suggests that the metal ions had penetrated right through the sample (r/r_0 = h/r_0, Figure 3d and Figure 4). The distribution of metal ions inside the gel, swollen in low-concentration salt solution, differs from the final state of the hydrogel in a concentrated (C_s/C_p = 1000) salt solution (see Figures 2b and 3d). The birefringence in low-concentration salt solutions is much higher than that in the high concentration case. These results show that hydrogel contraction in salt solutions in which metal ions bind the gel depends mainly on the relative salt concentration C_s/C_p in the gel + solution system.

The interaction of the swollen gel with the metal ions induces the formation of an insoluble compound which has different properties compared with those of the swollen gel (density, elasticity, etc.). As no form birefringence can be present, the birefringence which is observed comes from the polymer + salt chains oriented by the stress created by the constraint of the presence of a swollen inner core. The polymer chains are oriented along the surface of the gel particle in the birefringent layer, as seen by inserting a gypsum plate.

The difference in the birefringence of the gel in solutions of low or high salt concentrations can be understood as follows. A dry gel particle placed in a low concentration salt solution will swell a lot with a high swelling rate (Table 1). The formation of the insoluble compound leads to the contraction of the outer part of the gel, which cannot collapse immediately because of the core which is still swollen. This induces a large stress which is elongating the chain along the surface of the gel (see result with the gypsum plate), inducing a large birefringence. On the contrary, the gel in a solution of high salt concentration will swell a small amount with a low swelling rate (Table 1). At the same time, the formation of the insoluble compound takes place, with very little concurrent gel contraction. Thus, almost no stress is produced between the core and the insoluble outer part. Without stress, the network chain can take many orientations while being transformed into the insoluble compound. The birefringence is thus much lower than that in the former case.

Table 1. Summary of the Main Results Concerning Gel Swelling in Solutions with High and Low Salt Concentrations

	low salt concentration	high salt concentration
maximum degree of swelling	high (200 g/g)	low (8 g/g)
rate of swelling	high (3/min)	low (0.7/min)
contraction ($r_{max} - r_{equil}$)	high	nearly zero
birefringence	high	low

What remains to be explained is why, in the case of highly concentrated salt solutions, we obtain the equilibrium state with a birefringent ring rather than a homogeneous distribution of the salt inside the whole hydrogel particle. We would like to note that this occurs for the cases when an insoluble compound is formed. It does not depend on the valence or the size of the ion. A possible explanation may be based on the idea discussed in the paper of Tomari and Doi[9]. When a dry gel particle starts to swell, it swells only from its surface so that during some "incubation" time the unswollen part still remains in the center. If a hydrogel swells in a solution in the presence of Cu^{2+} or Ag^+ ions of high concentration, an insoluble compound is formed almost immediately on the gel surface. The insoluble layer is formed before the dry part of the gel in its center starts to swell. The metal ions are thus unable to react with the dry gel, and they can "cross-link" only that part of the gel which was swollen at the first moments. The reaction is then stopped. This is why the gel does not contract (see Table 1) and why the birefringent zone has a ring-type distribution.

Conclusions

The swelling of a gel in aqueous salt solutions occurs in two steps—first water is absorbed, and then it interacts with the metal ions. The metal ions form an insoluble compound with the gel, and the birefringence due to chain orientation arises because of the stress associated with the coexistence of swollen and unswollen regions. The results show the importance of considering the gel as a 3D object.

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