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Swelling Kinetics of a Polyelectrolyte Gel in Water and Salt Solutions. Coexistence of Swollen and Collapsed Phases

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ABSTRACT: The swelling of polyelectrolyte gels in water and salt solutions is associated with the presence of up to three coexisting phases: a dry phase, a swollen phase, and a collapsed one due to the binding of metal ions to polyions. Swelling in pure water proceeds in two ways: a transition from the dry to swollen state, whose kinetics scales with the square of the initial gel size, and a further swelling that scales linearly with the initial gel size. We show that there exist various swelling paths depending on the gel interaction with metal ions and their concentration.

Introduction

The swelling behavior of hydrophilic networks in solvents of different thermodynamic quality has been studied intensively over the past 20 years. A volume phase transition of charged hydrogels was observed, and its dependences on mixture composition (good−bad solvent), degree of network ionization, and/or the presence of metal ions were reported in several theoretical and experimental studies (see, for example, refs 1−3). These phenomena were described theoretically mainly from the point of view of the change of osmotic pressure of mobile counterions.[2,4] In more recent publications it was shown that when a polyelectrolyte gel is placed in a salt-containing solution, the effect of counterions binding to the polyions of the network is of great importance.[5−7] The concentration redistribution of mobile ions in the presence of a polyelectrolyte gel[5] and the nature of ions also influence the state of the hydrogel.[5−7]

To describe properly the gel swelling behavior and its equilibrium state, it is necessary to consider the gel as a 3D object. In a theoretical approach recently developed by Doi and Tomari for temperature-sensitive hydrogels,[8] it was emphasized that several important phenomena cannot be described by a one-dimensional model. In particular, it was shown that it is necessary to take into account the coexistence of swollen and collapsed states inside a sample for describing the swelling and contraction of a gel. Our previous results[9,10] also showed that the penetration of ions inside the hydrogel sample with a moving front of a chemical reaction has to be considered to describe the swelling behavior of a charged gel immersed in a salt solution and interacting with ions.

In this article we continue the study of polyelectrolyte gel swelling behavior in water and in salt solutions where the interactions between mobile ions and polyions are strong enough to form an insoluble product. In ref 9 it was shown that when a dry gel particle is placed in such a salt solution, the swelling starts by absorbing mainly water. After some time an insoluble layer on the gel surface is formed, and after this the gel contracts. The growth of this insoluble layer is accompanied by the formation of a birefringent core. The birefringence arises due to the stresses associated with the coexistence of swollen and contracted regions.

Hydrogel swelling dynamics and the development of an insoluble layer depend on the ratio of polymer-to-salt concentration ($C_{\mathrm{pol}}/C_{\mathrm{s}}$).[9] When $C_{\mathrm{pol}} \approx C_{\mathrm{s}}$, the metal ions penetrate all over the gel particle, as shown in ref 9. If $C_{\mathrm{pol}} \ll C_{\mathrm{s}}$, the width of the birefringent layer slowly grows up to a certain extent and then stays constant.[9] In other words, the equilibrium state of a gel swollen in a very concentrated salt solution is a gel particle with a birefringent layer on its surface. The reason is that the insoluble layer is formed on the gel surface before the dry part inside the gel starts to swell, and metal ions are thus unable to react with the dry gel (see detailed discussion in ref 9).

In this article we show that three phases—contracted, swollen, and dry—may coexist during gel swelling in salt solution. We define them as follows: The contracted phase is the insoluble product of the chemical reaction between the gel and metal ions. It is the layer formed on the surface of the gel particle. The swollen phase is the gel swollen in the solvent. The dry phase is the initial state of the gel particle. During gel swelling it forms the core inside the particle.

To our knowledge, the evolution of such phases in time has not been studied in detail despite its importance for adequate understanding of gel-swelling dynamics and also its equilibrium state. For example, from our experience we know that the equilibrium state of a gel contracted in a salt solution where metal ions are binding polyions depends on the initial state of the gel. When a gel is swelling from a dry state, it swells through the coexistence of different phases. When a gel is initially swollen in water and then immersed in such a salt solution, the contraction kinetics and the equilibrium state differ from the case mentioned above.

The development of contracted, swollen, and dry phases as a function of time, initial size of the gel particles, and salt concentration for the case when gel is swelling from a dry state is studied in here detail.

Experimental Section

Materials. The hydrogel sample used in this study is a poly(0.75 sodium acrylate−0.25 acrylic acid) cross-linked by *N,N*′-

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methylenebisacrylamide, with a 0.06% mole fraction of the cross-linking agent with respect to the monomer, kindly provided by Atochem. The initial state is a powder of dry spherical gel particles of radius from 0.05 to 0.1 mm.

Aqueous solutions of $CuSO_4{\cdot}5H_2O$ salt were used as a solvent. It is known (see, for example, refs 4, 6, 9, and 10) that the interaction of copper ions with polyacrylate leads to the formation of an insoluble compound. In addition, $CuSO_4{\cdot}5H_2O$ is a colored solution which allows the solvent penetration inside the gel particle to be clearly seen. Three relative salt concentrations C_s/C_{pol} (C_s is the salt concentration and C_{pol} is the monomer concentration, both calculated in mol/L for the total volume of the system gel + solution) were prepared: $C_s/C_{pol} = 0$ (distilled water), 10 ($C_s = 0.005$ M, pH = 5.1), and 1000 ($C_s = 1$ M, pH = 3.0).

Methods. The kinetics of hydrogel swelling/contraction in water–salt solutions and the salt penetration inside the particle were monitored by optical microscopy and recorded on videotapes. A dry gel particle was placed between two glass slides, and a certain amount of a solution was added. The total gel radius, the size of the dry inner phase, and the width of the contracted insoluble layer were measured as a function of time.

Results

In the paper of Tomari and Doi[8] two mechanisms for temperature-sensitive gel swelling are discussed: (i) gel swelling when there is coexistence of a swollen layer on the particle surface and a dry area in its center and (ii) gel swelling as a unit without phase coexistence. In all our experiments the gel was swelling with the coexistence of at least two phases: a swollen layer and a dry phase inside the particle. The presence of coexisting phases did not depend on the salt concentration. We obtained gel swelling without phase coexistence only when particles were initially partly swollen by the solvent vapors. To avoid confusion in the following, the initial state of the gel is always a completely dry particle.

Gel Swelling in Pure Water. The swelling of an initially dry particle starts by forming an outside swollen layer. There is then a coexistence of two phases: an inner dry core and a swollen outside corona. An example is shown in Figure 1 where the dry phase is dark and the swollen layer is almost transparent. The evolution of the gel radius in time for gel particles of three different initial sizes is presented in Figure 2. For an adequate comparison between samples we are using a reduced gel radius $r(t)/r_{max}$, where $r(t)$ is the total gel radius and r_{max} is the radius of the gel swollen in water at equilibrium. The decrease of the dry phase $r_{dry}(t)/r_{max}$ in time ($r_{dry}(t)$ is the radius of the dry phase) in the same particles is also shown in Figure 2.

Because the dry region disappears before the gel reaches its final equilibrium state (see Figures 1 and 2), the gel is swelling as a unit only at the end of the whole process, close to equilibrium. Similar results were obtained for a gel particle immersed in a salt solution where there is no strong interaction between metal ions and polyions (for example, in solutions of NaCl). The only difference was in the degrees of swelling at equilibrium which decreased with the increase of salt concentration.

Gel Swelling in a Dilute Copper Sulfate Solution. The dynamics of a gel particle swelling in a dilute $CuSO_4$ solution of $C_s/C_{pol} = 10$ is presented in Figure 3. At first the gel swells and absorbs mainly water. The process of swelling in its first stage is thus similar to the case of pure water. After a few minutes a contracted layer appears on the gel surface. The development of the reduced width of this layer $h(t)/r_{max}$ in time is presented in Figure 3, curve 3. The contracted phase is formed because of copper ions penetrating inside the particle and binding the gel (see photos in Figure 4). This process is described in detail in ref 9. The gel starts to contract before reaching its maximal potential degree of swelling ($r(t)/r_{max} < 1$).

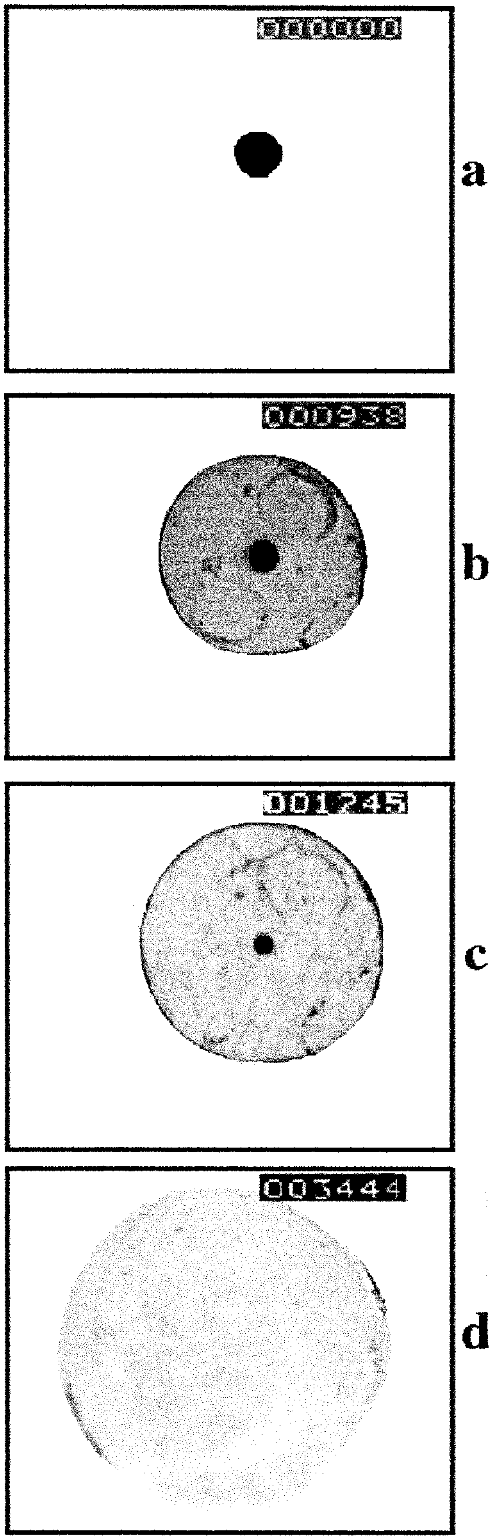

Figure 1. Optical micrographs showing the coexistence of swollen and dry phases in a gel particle swelling in water. The central dark part is the dry phase that is disappearing with time. Time of swelling is 0 (a), 0.5 (b), 0.7 (c), and 2.2 min (d).

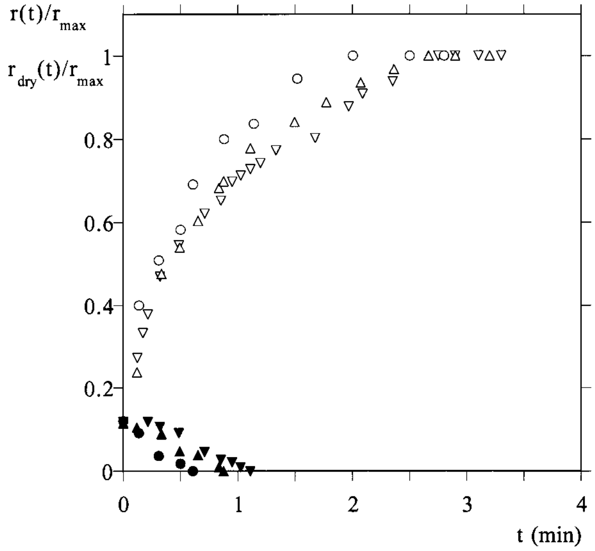

Figure 2. Kinetics of swollen (opened symbols, corresponding to $r(t)/r_{\max}$) and dry (dark symbols, corresponding to $r_{\mathrm{dry}}(t)/r_{\max}$) phase changes in a gel particle swelling in water. Initial gel radius is 0.07 (○, ●), 0.08 (△, ▲,) and 0.085 mm (▽, ▼).

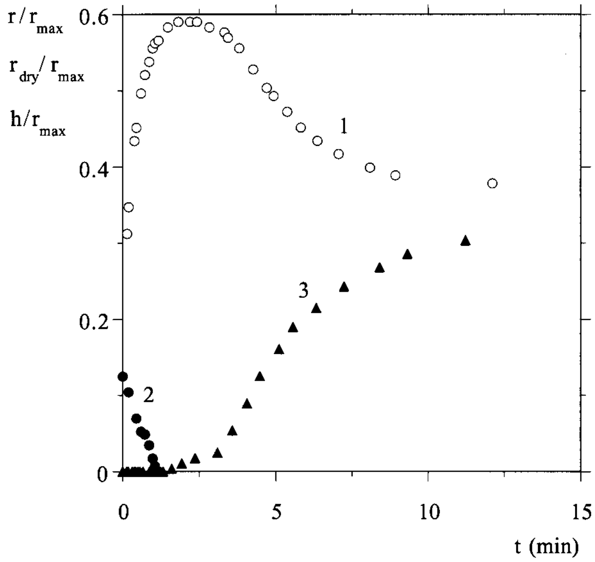

Figure 3. Change of the reduced gel radius $r/r_{\max}$ (1), the reduced dry phase radius $r_{\mathrm{dry}}/r_{\max}$ (2), and the reduced contracted layer thickness $h/r_{\max}$ (3) as a function of time for a gel swelling in a $CuSO_4$ solution of $C_s/C_{\mathrm{pol}} = 10$.

This case is more complicated than swelling in pure water or in salt solutions where metal ions are not binding polyions because here an insoluble layer is formed on the gel surface. However, as the initial salt solution is very dilute, it takes time for the contracted layer to appear. It becomes of noticeable size after 2−3 min; by this time the dry phase had already disappeared. This is why the time needed for the dry phase to disappear is the same as that for the gel swelling in pure water or in a dilute salt solution.

Gel Swelling in a Concentrated Copper Sulfate Solution. A significant influence of the salt concentration on the development of the dry, swollen, and contracted phases was detected when a gel was immersed in a concentrated $CuSO_4$ solution of $C_s/C_{\mathrm{pol}} = 1000$. The results of the evolution of gel radius, dry phase, and contracted layer in time are shown in Figure 5. Contrary to the case with a dilute copper sulfate solution, where the gel first swells and then contracts, here the gel just adsorbs a small amount of solvent and afterward does not change its size. (The degree of swelling at equilibrium here is 200 times lower than that in water.)

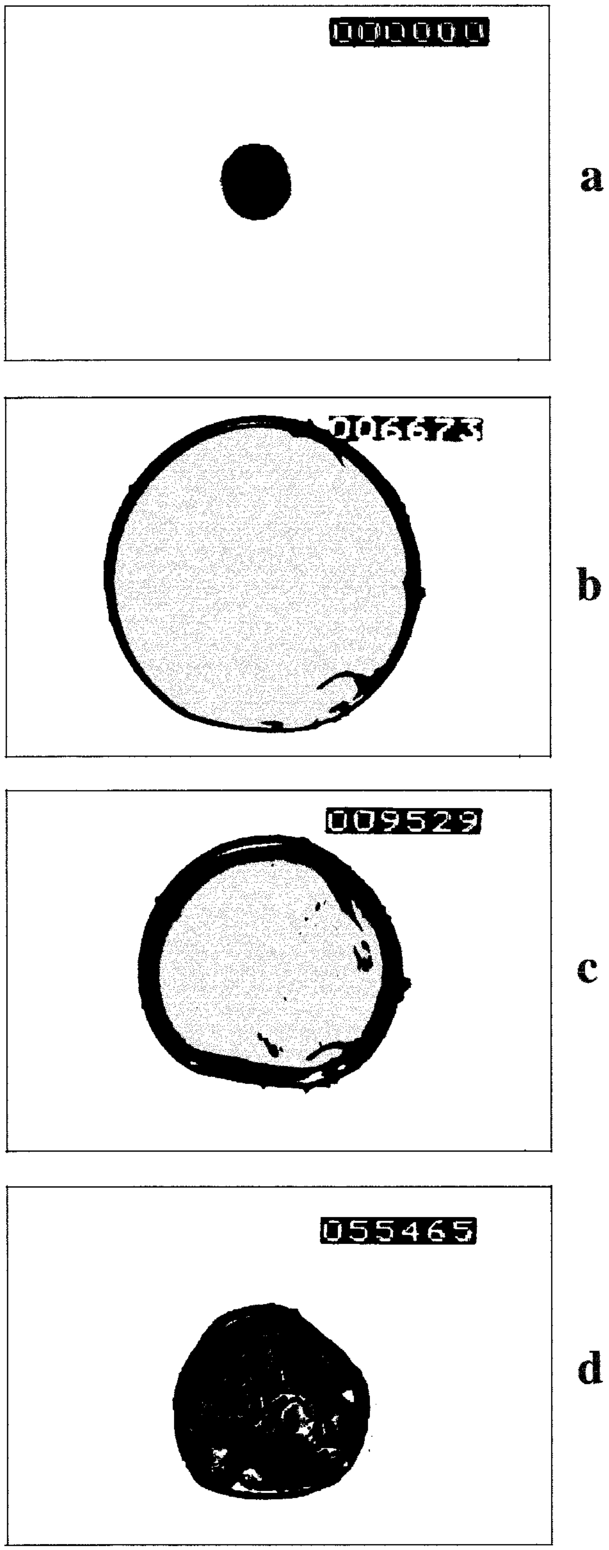

Figure 4. Optical micrographs a a hydrogel swelling in a diluted $CuSO_4$ solution of $C_s/C_{\mathrm{pol}} = 10$. In photo b the dark layer around the particle corresponds to the beginning of the formation of the contracted phase. This phase grows up to the point where it invades the whole particle (photo d). Time of swelling: 0 (a), 3.7 min (b), 5.6 min (c), and equilibrium state (d).

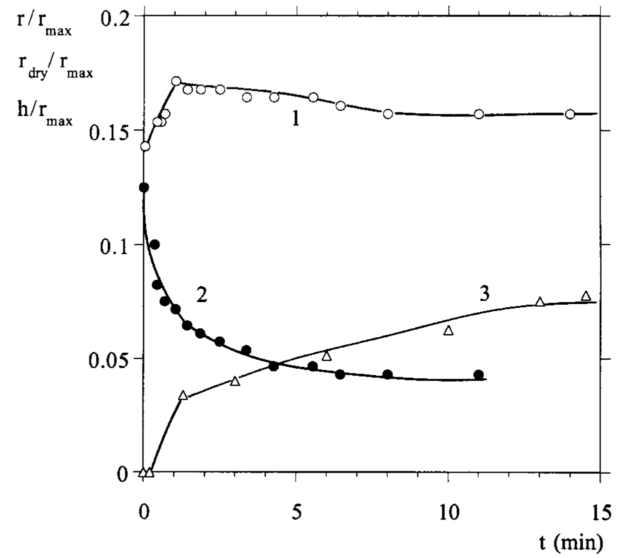

Figure 5. Same as Figure 3 for a gel swelling in a concentrated $CuSO_4$ solution of $C_s/C_{pol} = 1000$.

The copper ions do not penetrate all over the gel particle ($h(t_{max}) \neq r(t_{max})$ where the time to attain equilibrium t_{max} is defined as a time when gel radius does not change any more[9], and the dry phase does not disappear completely at equilibrium because the contracted layer is formed immediately after immersion on the gel surface. This prevents further solvent penetration inside the particle. The gel stops swelling, and the dry phase remains unswollen in the center of the particle.

As a result, the equilibrium structure of a gel particle, swollen in a very concentrated copper sulfate solution, can be seen as a particle with three coexisting phases: a dry central part, a slightly swollen layer, and an insoluble layer on the hydrogel surface which is a product of a chemical reaction between metal ions and polyions. It is not clear whether this is a real equilibrium state or not. We should consider it as a quasi-equilibrium state, because no further changes were observed during times that are several orders of magnitude greater than the time of the swelling process.

Discussion

Gel Swollen in Water. *Influence of the Initial Gel Size.* From Figure 1 it is clear that the smaller the gel particle, the less time is needed to reach equilibrium swelling and for the dry phase to disappear. A general scaling approach concerning the influence of the size of a swelling gel particle is based on the assumption that if the size of a gel is increased by a factor α, then the time needed to reach equilibrium swelling increases by the factor α^2 (see, for example, refs 8 and 11).

In our case, there are two characteristic times describing the kinetics of gel reaching the equilibrium state. The first is the time needed for the dry phase to disappear, t_{dry}. The second is the time required for the whole gel radius to become constant, t_{max}. We shall now analyze whether the square scaling law ($t \sim r_0^2$, where r_0 is the radius of a dry particle) can be applied to a highly swelling polyelectrolyte gel.

The dependence of t_{dry} on r_0 in logarithmic coordinates is shown in Figure 6. The slope here is 2.2; thus, the dependence of t_{dry} on r_0 can be approximated by a scaling law: $t_{dry} \sim r_0^2$.

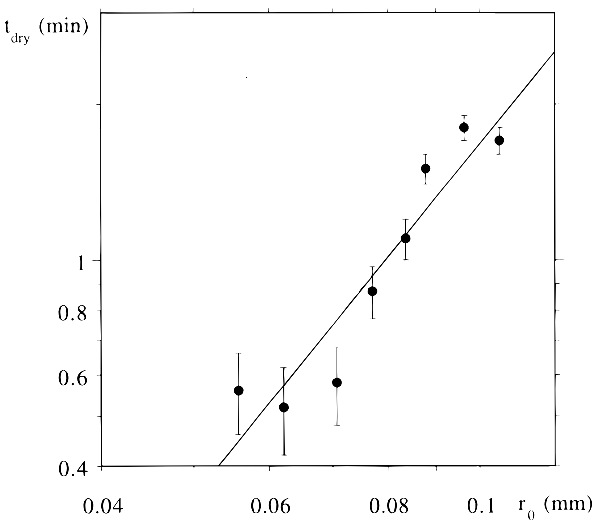

Figure 6. Gel swelling in water: dependence of the time needed for a dry phase to disappear t_{dry} on the initial gel radius r_0.

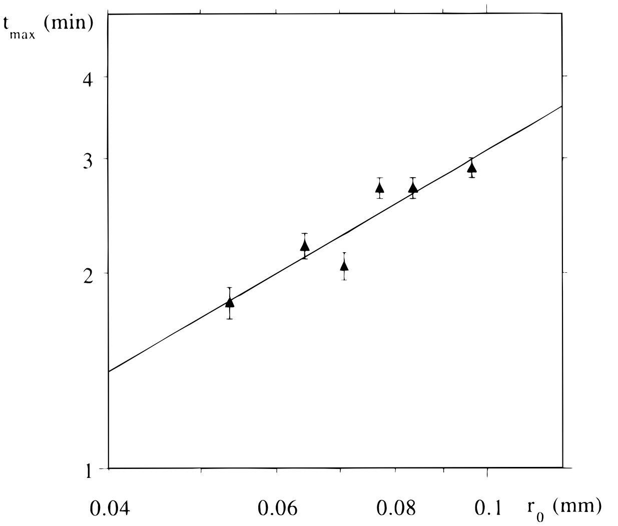

Figure 7. Gel swelling in water: time needed to reach equilibrium state t_{max} vs r_0.

The dependence of the time required for the gel to reach equilibrium t_{max} on the initial size of the particle is presented in Figure 7. Here the slope is 0.9 and the scaling law is thus $t_{max} \sim r_0$.

The exponent in the scaling law for t_{max} is one-half that of the one for t_{dry} because the gel continues to swell even after the dry phase has disappeared. We cannot yet answer why the dependence of t_{max} on r_0 is linear. However, it is clear that the two different mechanisms are both acting during the swelling of strongly charged polyelectrolyte gels (see also ref 12 for a polyelectrolyte gel swelling under load).

The first mechanism transfers the dry part into a swollen part. For neutral gels it is usually described by the contribution of elastic and polymer−solvent interaction forces. Tomari and Doi[8] considered the cost of elastic energy associated with the distortion of the gel due to the coexistence of the dry and swollen phases. They showed that this process should scale as the square of the initial size of the dry gel. If the same mechanism is acting for our hydrogel, it may explain for the square dependence of the time of dry phase disappearance on r_0.

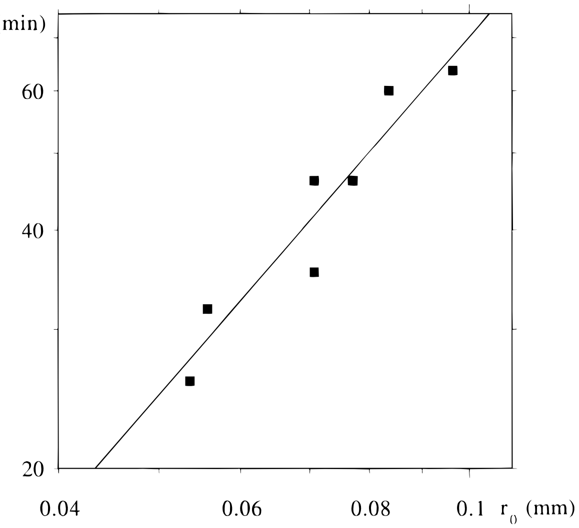

Figure 8. Gel swelling in water: dependence of the characteristic time τ on the initial gel size.

The second mechanism is connected with strong electrostatic interactions which cause additional swelling and result in different scaling laws. Here there is no strong distortion inside the gel, and the approach of Tomari and Doi[8] cannot describe this process.

Master Plot. In the preceding section we were able to identify two successive mechanisms of swelling: the first one scaling with r_0^2, and the subsequent one scaling with r_0. In reality, these two mechanisms are overlapping. This overlap leads to a curve $r/r_{\max} = f(t)$ which can be reasonably well approximated by a single-exponential function

$$\frac{r(r_0,t)}{r_{\max}} = 1 - \exp\left(\frac{t}{\tau}\right) \tag{1}$$

with a single mean characteristic time τ, taking into account both processes. A similar approximation was found to hold for the swelling of a polyelectrolyte gel under load.[12] This may be due to the fact that the equation of motion for all the involved mechanisms can be described as a sum of exponential functions, as pointed out in ref 11.

The dependence of the characteristic time τ on r_0 is shown in Figure 8 for several gel particles of different size. Despite some scattering, the points follow a straight line with the slope 1.5. For a single diffusional mechanism, τ is proportional to the square of the initial size (see, for example, ref 11): $\tau = r_0^2/\pi D$, D being the diffusion coefficient. The lower power law obtained reflects the existence of the two mechanisms described.

With characteristic time reflecting the mean dependence of r on τ, it is tempting to scale kinetic curves for different gel particles as $r/r_{\max} = f(t/\tau)$. This is shown in Figure 9, because the obtained τ values include all the swelling mechanisms.

Trying to decouple the two swelling mechanisms, we calculated a hypothetic characteristic time τ' for the same gels, but as if they had stopped to swell as soon as the dry part had disappeared. In other words, we took t_{dry} as a new hypothetic equilibrium time (with new $r_{\max}' = r(t_{\text{dry}})$) and calculated the values of τ' for the studied gel particles according to eq 1. For the two swelling mechanisms proposed, the value of τ' should correspond to a diffusional mechanism, and thus the exponent in the dependence of τ' on r_0 has to be close to two. The result of calculations gives $\tau' \sim r_0^{1/8}$. This means that the beginning of swelling can be described by the diffusional approach, but the more the gel is swollen, the more important the role the electrostatic interaction mechanism plays, which does not obey the diffusional power law. The two mechanisms are, obviously, overlapping in the middle of swelling; thus, the power law obtained for τ' is lower than 2, but higher than 1.5 found taking into account the whole swelling process.

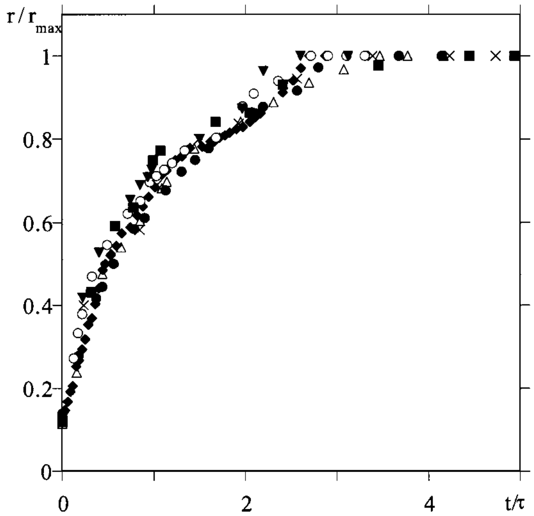

Figure 9. Master plot for the gel particles of different initial size (seven samples) swelling in water.

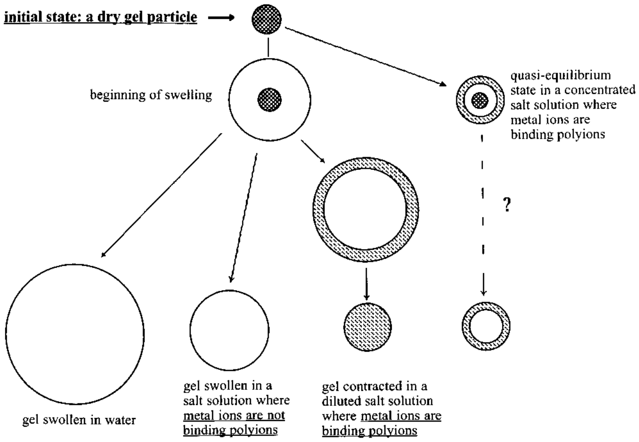

Figure 10. Schematic presentation of the evolution of a dry gel particle immersed in different aqueous salt solutions.

As far as the power laws for the dependences of t_{dry} and $t_{\max}$ on r_0 differ essentially, the diffusion coefficient also differs at the beginning and at the end of the swelling process. A mean diffusion coefficient was calculated from the dependence $\tau = r_0^{1.5}/\pi D$, which gives the value of $(4.4 \pm 0.2) \times 10^{-6}$ cm^2/s.

Coexistence of Phases during Gel Swelling. A summary of how a gel particle swells in different aqueous salt solutions is schematically shown in Figure 10. Three cases are considered: (i) a dry gel particle immersed in water, (ii) in aqueous salt solutions where metal ions are not binding polyions, and (iii) in salt solutions where an insoluble layer is formed on the gel surface. Different equilibrium states can be reached depending on the solvent used.

Conclusions

The kinetics of polyelectrolyte gel swelling in water has two different contributions. While the dry-to-swollen transition can be understood by existing models based on diffusion, the additional swelling that is observed is a new phenomenon that is not yet explained.

The coexistence of several phases in a single gel particle opens ways for structuring gels. For example, if a gel contracted in a dilute salt solution where metal ions have penetrated all over the particle is immersed in an acid solution, the contracted phase will be inside the gel, and a transparent swollen phase will grow on the surface of the particle.[10] This occurs due to replacement of metal ions by hydrogen ions. This could potentially provide a method for obtaining networks with several coexisting layers of various structures and properties.

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