1714 *Macromolecules* **1995,** *28,* 1714−1716

Polyelectrolyte Hydrogel Swelling in a Concentrated Polymer Solution

Tatiana Budtova† **and Patrick Navard***

Ecole des Mines de Paris, Centre de Mise en Forme
des Matériaux, URA CNRS 1374, BP 207,
F-06904 Sophia−Antipolis Cedex, France

Received July 27, 1994
Revised Manuscript Received November 29, 1994

Introduction

Polyelectrolyte hydrogels are highly swelling polymer networks. They possess many interesting properties. They may swell to hundreds of times their initial volume in water or drastically reduce their size under the influence of external forces or in response to changes in the surrounding media. This makes them a very interesting scientific object of observation and a useful material for practical applications as well. Many published works have dealt with experimental and theoretical studies of hydrogel swelling in low molecular weight water−salt solutions when the pH of the solution and/or the amount of metal ions are changed (see, for example, refs 1−3). A more complicated and less studied system is a polyelectrolyte hydrogel placed in a linear polymer solution. There have been a limited number of papers describing hydrogel collapse in oppositely charged polymer solutions[4,5] or the additional swelling in noncharged polymer solutions.[6] However, all the above investigations describe the results of the gel interactions with different solutions once equilibrium has been attained. Theoretical models and a few experimental data on the kinetics of hydrogel swelling behavior can be found in refs 7−9. They are restricted to the simplest case where the gel is placed in pure water. One reason may be the lack of experimental data concerning polymer concentration changes during hydrogel swelling in low or high molecular weight polymers in aqueous solutions. However, such kinetic studies are very important for understanding and predicting the properties of the whole hydrogel + aqueous solution system in the equilibrium state. The first step in solving this experimental problem is to find a suitable linear polymer solution in which it will be possible to record the swelling of the gel particle and the polymer concentration redistribution that it will induce in the whole system as a function of time.

The aim of this Note is to propose a simple method to measure the swelling rate and the polymer concentration changes around a polyelectrolyte hydrogel particle in an aqueous solution of (hydroxypropyl)cellulose (HPC). It is based on the fact that the local increase in HPC concentration around the swollen particle will induce an isotropic liquid to liquid crystal phase transition which can be evaluated by optical microscopy.

The combination of liquid crystalline order and gels is not new, and many researchers have either prepared liquid crystalline polymer gels[10,11] or studied its deformation.[12] To take advantage of the liquid crystalline phase transition of the surrounding fluid during swelling has apparently not been considered yet.

Experimental Section

The polyelectrolyte hydrogel used in this study was a 75−25 poly(acrylate−acrylic acid) copolymer cross-linked by *N*,*N*′-methylenebisacrylamide, kindly provided by Atochem. The size of dry gel particles was 0.5−1 mm, consisting of 10−20 smaller particles stuck together. The preparation of the aqueous (hydroxypropyl)cellulose (Klucel Type E, molecular weight 6 × 10^4, kindly provided by Aqualon, a Hercules company) solution was performed by a gentle mixing followed by centrifugation to remove bubbles. HPC concentrations are given in weight percent. In water HPC solutions are isotropic below $C^* = 42\%$ and display a transition to a cholesteric liquid crystalline phase above this concentration. Between 42 and 44%, the solution is biphasic, while it is fully anisotropic above $C^{**} = 44\%$.

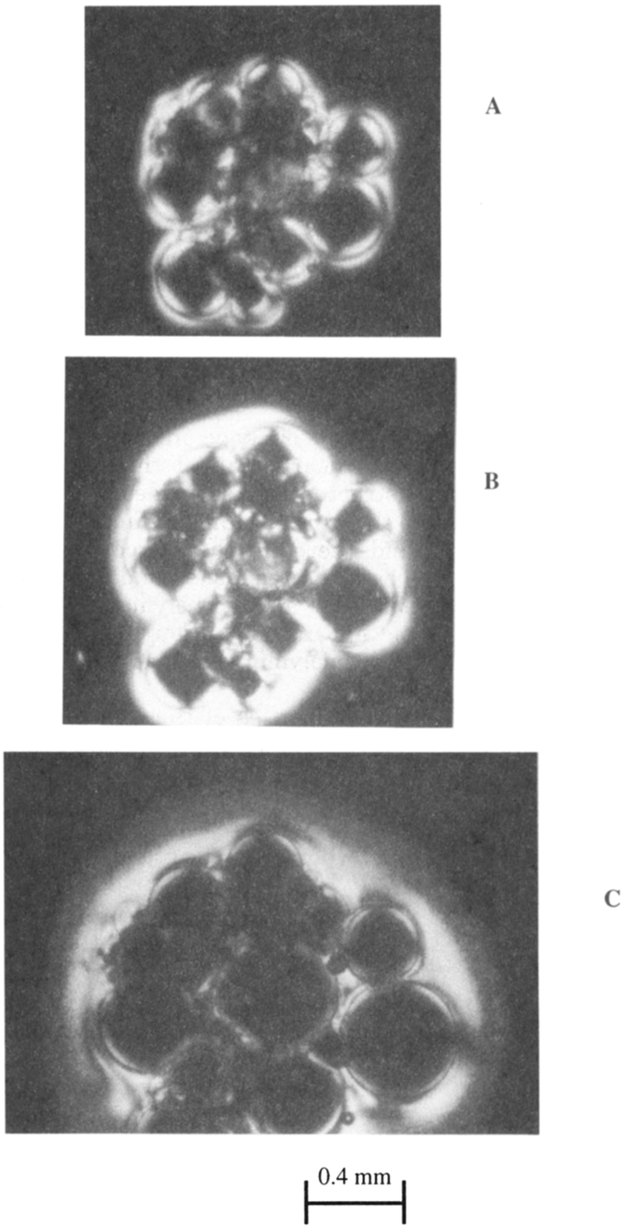

Figure 1. Development of the swelling of a hydrogel particle in a 40% HPC solution: (a) 3 min after contact; (b) 7 min after contact; (c) 55 min after contact. The pictures are taken between crossed polarizers.

One dry hydrogel particle was placed in the HPC solution between two glass slides. The swelling and the development of birefringence around the particle were monitored with a polarizing microscope.

Results and Discussion

When a dry hydrogel particle is placed in a HPC aqueous solution, the particle swells, drawing water

---

† Permanent address: Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi prosp. 31, 199004 St. Petersburg, Russia.

0024-9297/95/2228-1714$09.00/0

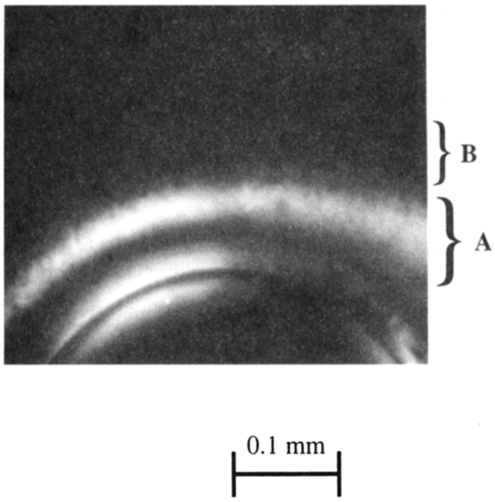

Figure 2. Enlargement of an area of Figure 1. The fully anisotropic area is denoted A and the biphasic one B. The boundary between A and B corresponds to C**, and the boundary between B and darkness corresponds to C*. The dark line in area A is an artifact due to the black-and-white print of the color original.

inside it. As a consequence, there is a local increase in HPC concentration around it. In the present experiment, only one particle is placed in a large amount of HPC solution. When the initial concentration of HPC is less than 20%, the particle swells but no birefringence can be seen around it. When the HPC concentration is larger than 20% and lower than 42%, a birefringent layer develops around the particle, grows, and then decreases in size before completely disappearing. The first signs of birefringence appear very quickly (i.e., a few seconds). The growth and disappearance process can be quick, say a few minutes, when the concentration is around 20% or very slow (a few days) when the concentration is closer to 42%.

Figure 1 is an example of the growth of a birefringent layer around a swelling hydrogel particle in a 40% HPC solution. Two different boundaries can be clearly seen. The first one corresponds to the isotropic–biphasic transition. The biphasic region is composed of bright spots. The second boundary corresponds to the biphasic–fully anisotropic transition. This is more clearly seen in Figure 2, which shows an enlargement of the area around a particle. The fully anisotropic area is denoted A and the biphasic B. The boundaries between A and B, corresponding to C**, and B and darkness, corresponding to C*, are very clear. It is easy to monitor the position of these two concentrations as a function of time. An example of such a result is given in Figure 3. The curve with the right-hand side arrow represents the growth of a 56 μm dry gel particle placed in a large amount of a 40% HPC solution (acting as a reservoir) as a function of time. As previously seen in Figure 1, the gel swells and then keeps a nearly constant size (note that there is a slight increase of size at long times). The curve with the left-hand side arrow is the width of the birefringent (anisotropic) zone (i.e., the distance between the gel surface and the boundary between area B and the isotropic region). The width increases with the swelling of the gel due to the decrease of the water content around the particle. When the particle stops swelling, the HPC concentration decreases and the width of the birefringent zone decreases. It slowly returns to the isotropic 40% concentration. In fact, a small layer of birefringent solution stays around the swollen particle even at very long time. The birefringence which is observed is not due to strain-induced birefringence owing to the very long relaxation times involved. The appearance and disappearance of the birefringence are controlled by the diffusion of water and HPC molecules. The long times which are required to equilibrate the concentration of HPC around the particle are due to the high viscosity of these concentrated solutions (a typical order of magnitude of the viscosity of a 40% HPC solution is 450 Pa·s).

A closer look at the rim of the particle (Figure 2) shows that if the HPC concentration is large enough, colors develop and disappear with time. These colors are connected to the increase of birefringence and/or thickness of the anisotropic layer. The latter parameter can be fixed and the knowledge of the birefringence versus concentration will be used in future studies to give the full concentration profile around the particle.

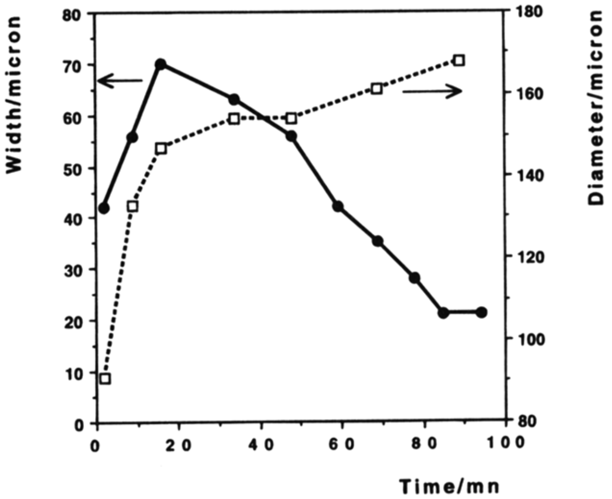

Figure 3. Concentration changes and particle growth as a function of time of a 40% HPC in water solution. (☐) Diameter of the particle (scale on right-hand side). The curve represents the growth of a 56 μm dry gel particle placed in a large amount of a 40% HPC solution as a function of time. (●) Width of the birefringent zone (scale on left-hand side). The curve is the width of the birefringent (anisotropic) zone (i.e., the distance between the gel surface and the boundary between area B and the isotropic region).

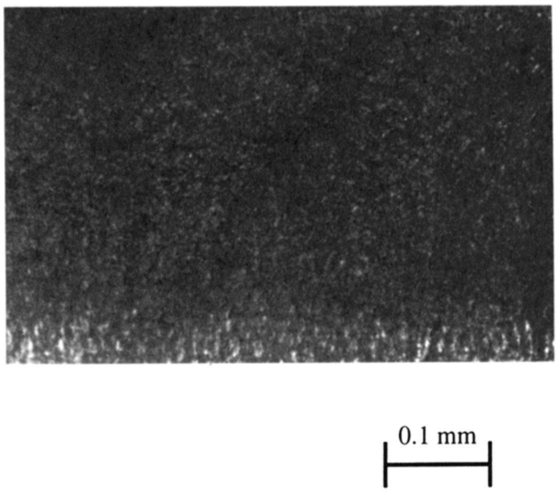

Figure 4. Optical micrograph of a fully anisotropic region of an HPC solution, obtained from an initially isotropic solution allowed to dry in the air, between two glass slides. The grainy aspect is very typical of such solutions and due to a complex director field.

The structure of the fully anisotropic region around the particle is another point of interest. It is a well-known fact that aqueous anisotropic HPC solutions at rest are characterized by the presence of many orientational defects, typical of liquid crystals.[13] This gives the aspect of a domain-like structure[14] like the one shown in Figure 4, obtained by leaving an isotropic HPC solution placed between two glass slides to dry in the air. On the contrary, the anisotropic region around the gel particle does not contain defects. This is a most unusual fact that cannot be explained. It may be related to the rapid concentration change associated with some flow due to the swelling.

Conclusion

The use of a polymer having an isotropic-to-anisotropic phase transition can provide a simple way to study the evolution of the polymer concentration around a swelling particle. This was demonstrated using an HPC solution. The defect-free structure of the anisotropic region is very intriguing and will require further investigations.

References and Notes

(1) Ricka, J.; Tanaka, T. *Macromolecules* **1984**, *17*, 2916.
(2) Vasilevskaya, V. V.; Khokhov, A. R. *Vysokomol. Soedin.* **1986**, *A28*, 316.
(3) Budtova, T. V.; Belnikevich, N. G.; Suleimenov, I. E.; Frenkel, S. Ya. *Polymer* **1993**, *34*, 5154.
(4) Vasilevskaya, V. V.; Khokholv, A. R. *Macromolecules* **1992**, *25*, 384.
(5) Kabanov, V. A.; Zezin, A. B.; Rogacheva, V. B.; Litmanovich, E. A. *Dokl. Akad. Nauk SSSR* **1986**, *288*, 1408.
(6) Budtova, T.; Suleimenov, I.; Frenkel, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 281.
(7) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.
(8) Peters, A.; Candau, S. J. *Macromolecules* **1988**, *21*, 2278.
(9) Komori, T.; Sakamoto, R. *Colloid Polym. Sci.* **1989**, *267*, 179.
(10) Aharoni, S. M.; Edwards, S. F. *Polym. Bull.* **1992**, *29*, 675.
(11) Matsuoka, Y.; Kishi, R.; Sisido, M. *Polym. J.* **1993**, *25*, 919.
(12) Kyu, T.; Jen-Cheng Yang; Cheng, S. Z. D.; Hsu, S. L. C.; Harris, F. W. *Macromolecules* **1994**, *27*, 1861.
(13) Kléman, M. *Points, Lines and Walls*; Wiley-Interscience: Chichester, 1983.
(14) Meeten, G. H.; Navard, P. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 413.

MA941257I