Swelling Behavior of Crosslinked Hydroxypropyl Cellulose Films Retaining Cholesteric Liquid Crystalline Order. I. Effect of Temperature

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ABSTRACT: Temperature dependence of the swelling behavior in both water and propanol was determined for the crosslinked hydroxypropyl cellulose (HPC) films retaining cholesteric liquid crystalline order (CLCO) and for the crosslinked amorphous HPC films. The dependence of swelling behavior in water for the films retaining CLCO was different from that of the amorphous films. With increasing temperature, the equilibrium swelling ratio (B_e) for the films retaining CLCO decreased, whereas B_e for the amorphous films increased. In propanol, both films exhibited the same temperature dependence. B_e increased with increasing temperature. The increasing rate of the swelling in transient state showed similar temperature dependence on B_e. The increasing rate for the films retaining CLCO decreased with temperature, but that for the amorphous films increased in water; in propanol, the increasing rate for two types of films increased. The difference in the swelling behavior between the two types of films may be due to the difference in the number-average molecular weight between crosslinks. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1015–1022, 1999

Key words: crosslinked hydroxypropyl cellulose films; swelling in solvents; temperature

INTRODUCTION

Our final objective of this work is to develop films that can be applied to the filtration of low-molecular-weight compounds in solvents.

We have prepared crosslinked hydroxypropyl cellulose (HPC) films retaining cholesteric liquid crystalline order (CLCO) according to the cast process[1] and determined the effects of the cast conditions on the equilibrium swelling ratio of the crosslinked films in water.[2,3] Both

determinations of the swelling and circular dichloism studies for such films revealed that the swelling behavior was correlated to the change in the cholesteric pitch.[3] However, details of the swelling behavior for the crosslinked HPC films remained equivocal.

In this study, the temperature dependence of the swellabilities, that is, the transient and equilibrium swelling ratios at different temperatures, for the crosslinked films retaining CLCO were determined in solvents of interest. For comparative purposes, a crosslinked amorphous HPC film was also prepared, and its swellability was determined. The difference in the swellabilities of the crosslinked films retaining CLCO and the

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crosslinked amorphous films was discussed. Water and propanol were chosen as the solvents. It is widely known that the HPC–water system exhibits a cloud point,[4] whereas the HPC–propanol system exhibits no cloud point.

EXPERIMENTAL

Samples

HPC ($\bar{M}_w = 11.7 \times 10^4$, $\bar{M}_n = 5.29 \times 10^4$, molar substitution = 4.25, Tokyo Kasei Kogyo Co. Ltd.), n-propanol, and methanol (Kanto Chemical Co. Ltd.) were used without further purification. Distilled water prepared in our laboratory was also used.

Preparation of Crosslinked Films

The HPC liquid crystalline solution (60 wt %) in methanol was mixed with glutaraldehyde (3 or 5 wt %) as a crosslinker and with hydrochloric acid (3 wt %) as a catalyzer. Unless otherwise noted, the crosslinker concentration used was 5 wt %. The mixed solution was degassed using the centrifuge and was cast on a glass plate according to the previously outlined procedure.[1] The cast crosslinked films retaining CLCO (ca. 350-μm thickness) were dried at room temperature or heat-treated at 60°C in vacuum for 24 h.

As is widely known, it is not easy to find a solvent in which HPC forms no liquid crystals and to prepare the amorphous HPC solid films.[5] However, in principle, we can obtain the crosslinked amorphous HPC films in the following manner: the HPC molecules are crosslinked in preference to the formation of liquid crystalline order. Therefore, the very low polymer and very high crosslinker concentrations of cast solutions are preferable.[6] The crosslinked amorphous HPC film was cast on a glass plate from the isotropic dilute solutions (5 wt %) with the same crosslinker and catalyzer concentrations as those for the crosslinked films retaining CLCO. The glass plate was stored in the dark for a week at room temperature. Polarized microscopical observation and circular dichloism studies ascertained that the resulting film (ca. 200-μm thickness) exhibited no texture and no CLCO and was amorphous.

Swelling Behavior

A disc having a 1-cm diameter was punched from the cast films. Figure 1 shows the apparatus for
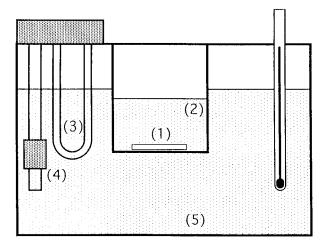

Figure 1   Schematic diagram of apparatus for measuring swelling behavior: (1) disc sample, (2) solvent bath, (3) heater, (4) stirrer, and (5) water bath.

measuring the swelling behavior. The changes in the thickness and diameter (width) of the disc specimen soaked in the solvent bath were measured by means of a travelling microscope through a glass window of the water bath as a function of soaking time at given temperatures. Each experiment was repeated at least two times. The reproducibility was better than 3%. The temperature of the water bath was controlled to a precision of 0.5°C. The swelling behavior in water, propanol, or the mixture of the two solvents at each composition was determined for approximately 40 h. The swelling ratio was defined as the ratio of the difference in dimension to the original dimension.[3]

RESULTS AND DISCUSSION

Crosslinked Film Retaining CLCO

Soaking Time Dependence

Figure 2 shows the typical time dependence of the swelling ratio in water (data for duplicate runs are shown) and in propanol. The film swelled rapidly for both directions (thickness and width) with soaking time and attained an equilibrium value around 400 min in water and around 200 min in propanol. The time to reach the equilibrium state (t_e) depended on the solvent and temperature. The equilibrium swelling ratio (B_e) for the thickness direction was greater than that for the width direction.[3] The transient behavior of the films will be discussed later.
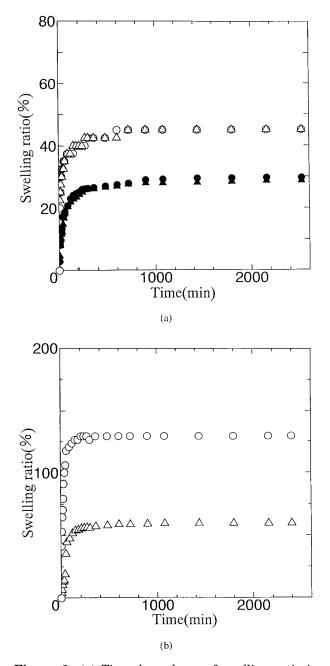
(a)

(b)

Figure 2 (a) Time dependence of swelling ratio in thickness and width directions for crosslinked films retaining CLCO (5 wt % crosslinker) in water at 45°C; open marks indicate thickness, and full marks indicate width. (b) Time dependence of swelling ratio for crosslinked films retaining CLCO (5 wt % crosslinker) in propanol at 25°C: (○) thickness; (△) width.

Effect of Heat Treatment

Figure 3 shows the difference in B_e between the nonheated and heated films at each temperature. B_e for the heat-treated films was smaller than

that for the nonheat-treated films. Hereafter, all data for B_e were for the heat-treated films. This figure also shows the effect of the crosslinker concentration on the swelling ratio. The heat-treatment and the increase in crosslinker concentration reduced the number-average molecular weight between crosslinks ($\bar{M}_c$); For our crosslinked films retaining CLCO, $\bar{M}_c$ was approximately 5×10^2.[2,3]

Temperature Dependence

As shown in Figure 3, B_e in water decreased with increasing temperature in our experimental conditions, irrespective of the crosslinker concentration and of whether or not the crosslinked films were heat-treated. This behavior was not general. It is well known that B_e generally increases with increasing temperature. In fact, B_e in propanol increased with increasing temperature, as shown in Figure 4. In our preliminary studies, the increase in B_e with temperature was also observed both in methanol and in ethanol. The system of HPC–water has a cloud point at around 50°C.[4] Consequently, water was a poor solvent for the relatively hydrophobic HPC around the temperatures we determined. Figure 5 shows the pic-
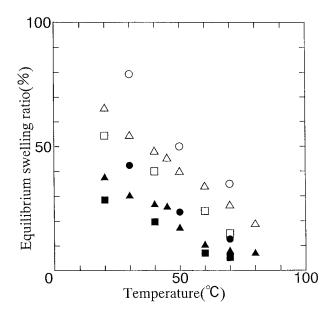

Figure 3 Temperature dependence of equilibrium swelling ratio for crosslinked films retaining CLCO in water. Nonheat-treated films (3 wt % crosslinker): (○) thickness; (●) width. Nonheat-treated films (5 wt % crosslinker): (△) thickness; (▲) width. Heat-treated films (5 wt % crosslinker): (□) thickness; (■) width.
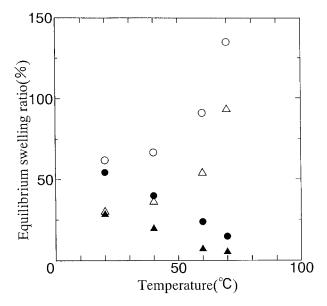
Figure 4 Temperature dependence of equilibrium swelling ratio for crosslinked (heat-treated; 5 wt % crosslinker) films retaining CLCO. In propanol: (○) thickness; (△) width. In water: (●) thickness; (▲) width.

Figure 6 Water content dependence of equilibrium swelling ratio for crosslinked films retaining CLCO in mixed solvent at 40°C: (○) thickness; (△) width.

ture of the swelling disc (viewed from the top) at each temperature. Below 50°C, the disc was transparent; but above 50°C, the disc was colored white. This whitening behavior was reversible; when the white disc was soaked in water at temperature below 50°C, the disc became to be transparent again. This clearly shows that our films retaining CLCO exhibit a phase separation, which is reversible.
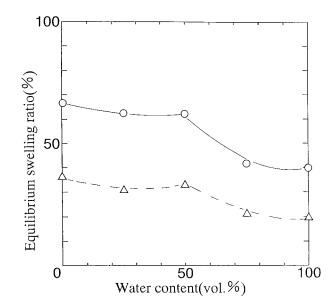
Composition Dependence of Mixture of Water and Propanol

As shown in Figure 4, B_e in water and in propanol depended reversely on temperature. Then, it is interesting to investigate the swelling behavior in the mixture of water and propanol. Figure 6 shows the dependence of B_e in the mixture solvent on water content at 40°C. At less than 50 vol % of water content, the decrease in B_e was very small with respect to the increase in water con-
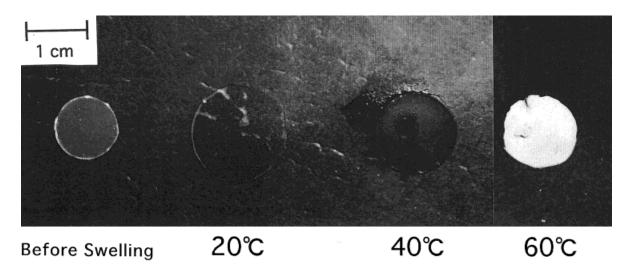

Figure 5 Photographs of the equilibrium swelling ratio for crosslinked films retaining CLCO in water at each temperature.
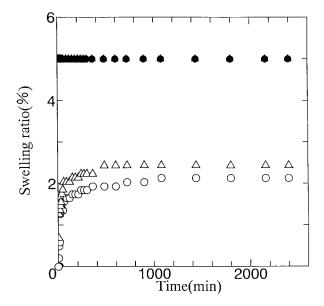
Figure 7 Time dependence of swelling ratio for crosslinked amorphous films in water at 60°C: full marks, thickness; open marks, width.

tent. At over 50 vol % of water content, however, B_e was almost the same as that in pure water. This showed that the swelling behavior in a water-rich mixture solvent was different from that in a propanol-rich one and suggested that the swelling behavior could be controlled by changing the composition of mixed solvents.

Crosslinked Amorphous Film

Figure 7 shows the soaking time dependence of the swelling ratio for the amorphous films in water at 60°C. In this figure, the data for duplicate runs are indicated. The values of t_e for the B_e for the thickness direction and the B_e for width direction were approximately 1 and 400 min, respectively. The most characteristic point was the small value of t_e for the thickness direction. Figure 8 shows the temperature dependence of B_e in water. Data were for duplicated runs. In our experimental range, B_e for thickness direction was almost independent of temperature, and B_e for width direction tended to increase with increasing temperature. Even at 60°C, the disc samples did not change to white. This strongly indicated no phase separation. The temperature dependence of B_e in propanol was the same as that in water. Figure 9 shows the dependence of B_e in the mixture solvent on the water content at 40°C. B_e depended nonlinearly on the water content: B_e seemed to exhibit a maximum at a given water content.
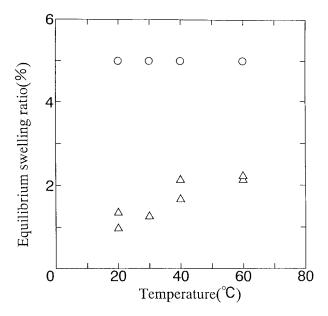

Figure 8 Temperature dependence of equilibrium swelling ratio for crosslinked amorphous films in water: (○) thickness; (△) width.

Transient Behavior

As have shown in Figure 2, during a short soaking time, the discs swelled rapidly. Hereinafter, we tried to analyze the rapid swelling behavior by the following form:
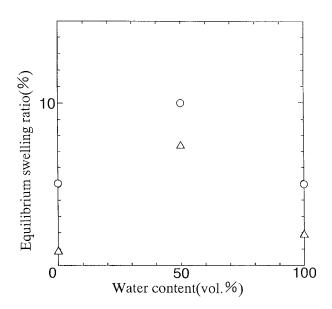
$$\log(\{B(t)/B_e\} \times 100) = \log t^a \qquad (1)$$

Figure 9 Water content dependence of equilibrium swelling ratio for crosslinked amorphous films in mixed solvent at 40°C: (○) thickness; (△) width.
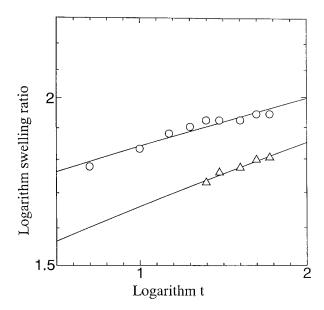
Figure 10 Plots of logarithm of swelling ratio against logarithm of time for crosslinked films retaining CLCO in water at 40°C: (○) thickness; (△) width.

where $B(t)$ is the swelling ratio as a function of soaking time (t) and the exponent a is a constant. For convenience, we define the constant a as a swelling speed.

Figure 10 shows the plots of $\log(\{B(t)/B_e\} \times 100)$ against $\log t$ for the crosslinked films retaining CLCO. Almost a linear relation was obtained, except for the initial and the final regions, and the exponent a could be evaluated from the slope. The greater exponent a means the greater increasing rate in swelling. Figure 11 shows the temperature dependence of the exponent a in water and in propanol for the crosslinked films retaining CLCO. In water, the exponent a decreased with increasing temperature; whereas in propanol, the exponent a tended to increase with temperature. This indicated that our crosslinked films retaining CLCO swelled rapidly at lower temperature in water, and the reverse change was observed in propanol. In a mixture solvent of water and propanol, the exponent a for the crosslinked films retaining CLCO exhibited a minimum at a given water content, as shown in Figure 12. This indicated that more rapid swelling occurred in pure solvent than in the mixed solvent.

Figure 13 shows the dependence of the exponent a on temperature for the amorphous films. In this figure, the swelling data for the thickness direction was omitted because t_e was approximately 1 min, the transient data for the thickness direction were very few, and the exponent a was

not reliable. The exponent a tended to increase with increasing temperature. The exponent a in propanol was greater than that in water. As shown in Figure 13, in the mixture solvent of water and propanol, the exponent a tended to exhibit a minimum with respect to water content. This behavior was similar to that for the crosslinked films retaining CLCO, compared with the data shown in Figure 12.
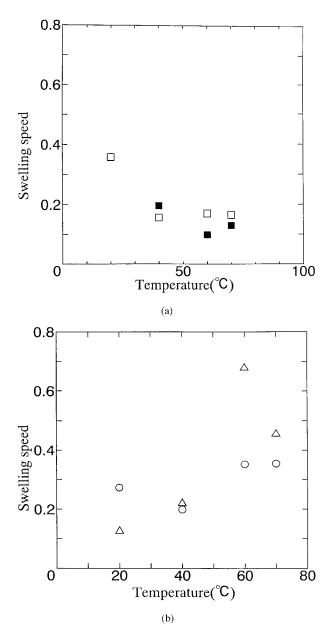

(a)

(b)

Figure 11 (a) Temperature dependence of exponent a (swelling speed) for crosslinked films retaining CLCO in water: (□) thickness; (■) width. (b) Temperature dependence of swelling speed for crosslinked films retaining CLCO in propanol: (○) thickness; (△) width.
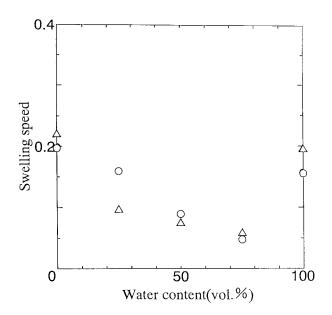
Figure 12 Water content dependence of swelling speed for crosslinked films retaining CLCO in mixed solvent at 40°C: (○) thickness; (△) width.

Comparison with Both Types of Films

The swelling behavior of the crosslinked films retaining CLCO was very different from that of the crosslinked amorphous films; B_e for the films retaining CLCO was greater than that for the amorphous films by one order of magnitude, and the values of t_e for the thickness direction for the amorphous films were much smaller than that for the films retaining CLCO. Those differences in the swelling behavior seemed to be due to the difference in $\bar{M}_c$. As noted in the experimental section, both types of films were cast from the following different conditions: the different concentration of HPC solutions and the same concentration of crosslinker. For the amorphous films, the crosslinking reaction undergoes before forming the liquid crystalline order, and the rate of crosslinking reaction is faster than that for the films retaining CLCO. The lower $\bar{M}_c$ for the amorphous films was estimated experimentally from the smaller B_e for the amorphous films based on Flory's equation,[7] provided that the number-average molecular weight, the interaction parameter, and the specific volume of HPC are the same for both types of films.[8]

A further great difference in the swelling behavior in water between the amorphous films and the films retaining CLCO was observed for the dependence of B_e on temperature. With increasing temperature, B_e for the films retaining CLCO

decreased, whereas B_e for the amorphous films did not tend to decrease. The films retaining CLCO changed from transparent to white around 50°C, as shown in Figure 5, whereas the amorphous films did not change to white. This showed that the films retaining CLCO exhibited a phase separation, but the amorphous films did not. This may be due to the difference in $\bar{M}_c$; the films retaining CLCO had a higher $\bar{M}_c$ and could exhibit the phase separation, whereas the amorphous films had a lower $\bar{M}_c$ and could not exhibit phase separation. The anomalous dependence of B_e on temperature in water could not be found in propanol.

As shown in our studies, our films retaining CLCO exhibited an anisotropic swelling behavior: the swelling ratio for the direction of the thickness was greater than that for the direction of width. However, our amorphous films exhibited almost an isotropic swelling behavior; the difference in the swelling ratios for the directions of thickness and width was smaller than that of the films retaining CLCO. This strongly suggested that the crosslinking occurred at random in the amorphous films, whereas the crosslinking occurred anisotropically in the films retaining CLCO; in the films retaining CLCO, the crosslinking between HPC molecules in the same cholesteric layer occurred preferentially rather than the crosslinking between HPC molecules in the adjacent layers.
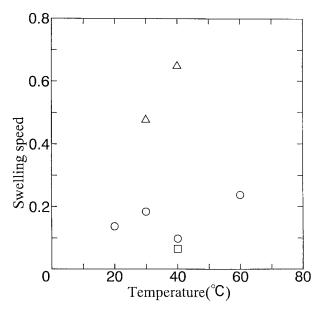

Figure 13 Temperature dependence of swelling speed for crosslinked amorphous films: in (○) water, (△) propanol, and (□) mixed solvent (50/50).

Finally, the exponent a for the amorphous films was almost the same as that for the films retaining CLCO in water and was greater than in propanol. The difference in the temperature dependence of the exponent a for both type films was similar to that in the temperature dependence of B_e. The exponent represents the sensitivity of the films to the change in temperature in water. Our data suggested that the effect of the CLCO on the sensitivity was not great. Poly(N-isopropylacrylamide)[9] and cellulose derivatives[10] were known to have a potential application as a thermosensitive switching device for aqueous systems. The behavior of HPC in water was similar to that of poly(N-isopropylacrylamide). Consequently, our films also had the same applications as that polymer.

CONCLUSIONS

B_e for the crosslinked films retaining CLCO decreased with increasing temperature in water and increased with temperature in propanol. B_e for the crosslinked amorphous films increased with temperature in both water and propanol. In the transient state, the increasing rate in swelling for the films retaining CLCO decreased with temperature in water and increased in propanol. The increasing rate for the amorphous films increased with temperature in water and in propanol. The increasing rate was greater in pure solvent than in the mixed solvent. The difference in swelling behavior between our crosslinked films retaining CLCO and amorphous films was due to the difference in $\bar{M}_c$; our amorphous films had a lower $\bar{M}_c$ than our films retaining CLCO.

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