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Polymer Communication

Change in handedness of cholesteric liquid crystal during swelling in water for crosslinked hydroxypropyl cellulose films filled with cellulose powders

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Abstract

Crosslinked hydroxypropyl cellulose (HPC) films retaining cholesteric liquid crystalline order (CLCO) were filled with cellulose powders. Swellability in water and circular dichroism study during swelling of the films were determined and the effects of cellulose powders on the swellability and CLCO of the films were discussed. The cellulose powders dispersed in the films swelled more greatly and more rapidly than did the matrix HPC and appeared to induce the change in handedness of CLCO of the matrix HPC.

Keywords: Crosslinked filled HPC film; Swelling; Circular dichroism

1. Introduction

We have studied the swelling behavior of the crosslinked hydroxypropyl cellulose (HPC) solid films retaining cholesteric liquid crystalline order (CLCO) in water [1][2]. To increase the stiffness of the swelling crosslinked HPC films, we mixed the HPC liquid crystalline aqueous solution with cellulose powders as a filler and with a crosslinker and prepared the crosslinked HPC cast films in which the cellulose powders were dispersed. The effect of the filler on the swelling behavior of the crosslinked HPC films in water was determined. The swelling process was repeated three times by using the same sample films; after the first run, the sample was dried and followed by the second and third runs. When the circular dichroism (CD) of the crosslinked HPC films during the swelling was determined, an anomalous behavior was observed. In this rapid communication, we report mainly the anomalous behavior of the HPC films observed by means of CD.

2. Experimental

The 50 wt% aqueous liquid crystalline solution of HPC(Tokyo Kasei $\bar{M}w = 11.7 \times 10^4$, $\bar{M}n = 5.29 \times 10^4$ was mixed with 10 wt% cellulose powders (Tokyo Roshi Co., size: ca. 10 μm $\times$ 80 μm), 10 wt% glutaraldehyde (crosslinker) and 3 wt% hydrochloric acid (catalyzer). The mixed solution was degassed using the centrifuge and stored in the dark for 90 h. Two kinds of solid films retaining cholesteric liquid crystalline order were cast from the mixed solution based on our process [3]: one was the crosslinked film filled with the cellulose powders which were impregnated with the crosslinker (film A); another was the crosslinked film filled with the cellulose powders (film B). For comparison, the crosslinked films with no cellulose powders (film C) were also prepared. A disc having a diameter 1 cm was punched from each cast film (thickness: ca. 700 μm). The change in thickness of the disc specimens during swelling in water was measured by means of the travelling microscope through a glass window of a thermostat controlled at 22 $\pm$ 0.5°C. The reproducibilities of CD and swelling data were checked by repeated measurements for independently prepared specimen of films of each type. The reproducibility of the swelling ratio at an equilibrium state for each film was better than 6%. Additionally, the CD spectrum for the films during swelling in water was determined as a function of soaking time and the change in CLCO was evaluated on the basis of the change in the wavelength of the spectrum peak. Reproducibilities of the

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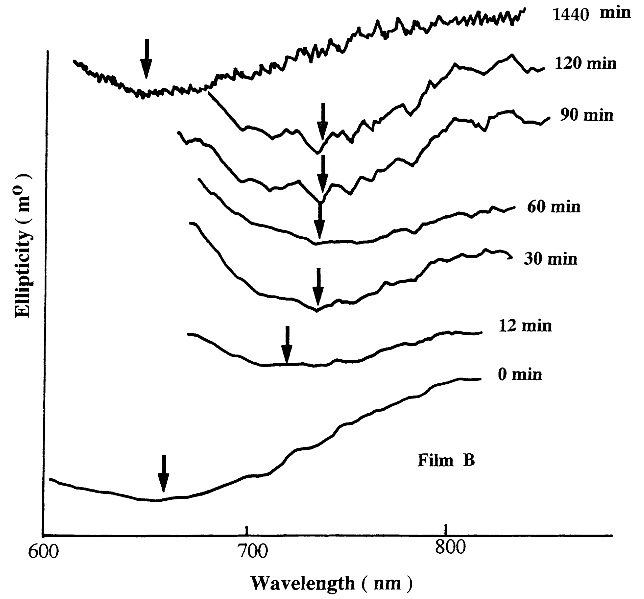

Fig. 1. CD spectra during swelling for film B in the first run. The soaking time is indicated in the figure.

peak wavelength at the dry state and at equilibrium state for each film were better than 5 and 8%, respectively. After the first run, the disc specimen was dried under vacuum at room temperature for a week and then was stored in a desiccator over silica gels for a week. Further details of the determination have been described elsewhere [2].

3. Results and discussion

3.1. Swelling behavior in water

All films swelled rapidly with increasing soaking time and attained an equilibrium state at a given time (T_{eq}). T_{eq} was dependent on the type of films; T_{eq} for film B $< T_{eq}$ for film A $< T_{eq}$). T_{eq} was dependent on the type of films; T_{eq} for film B $< T_{eq}$ for film C. The equilibrium swelling ratio (B_e) also depended on the type of films; B_e for film B was greatest and that for film C was the smallest. The dependence of B_e on the type of films was the inverse order of that of T_{eq}. These behaviors showed that the filled films swelled more rapidly and to a greater extent than the unfilled film. This was due to the rapid and great swelling of the cellulose powders dispersed in the HPC matrix. The great swelling of the cellulose powders was confirmed by microscopic observation. Furthermore, the swelling ratio of the cellulose powders dispersed in the film B was greater that than in film A. This suggested the intra-crosslinking in a cellulose powder dispersed in film A. The difference in the swelling ratio of each cellulose powder resulted in the difference in the total swelling ratio of the filled films (film A and film B).

3.2. CD study

Fig. 1 shows the typical CD spectra for film B in the first run, as a function of soaking time. Arrows in this figure indicate the peak wavelength. In the first run, the spectrum for each film exhibited a negative peak at a given wavelength. This was general for the crosslinked HPC films [2]. With increasing soaking time, the peak wavelength first increased, then decreased, and finally became constant. The half-value width of the peak and peak height tended to behave as similarly as peak wavelength with increasing soaking time. The peak was significant, even at the longest soaking time.

Compared with the constant peak wavelength for each film, film C showed the highest wavelength. The peak is

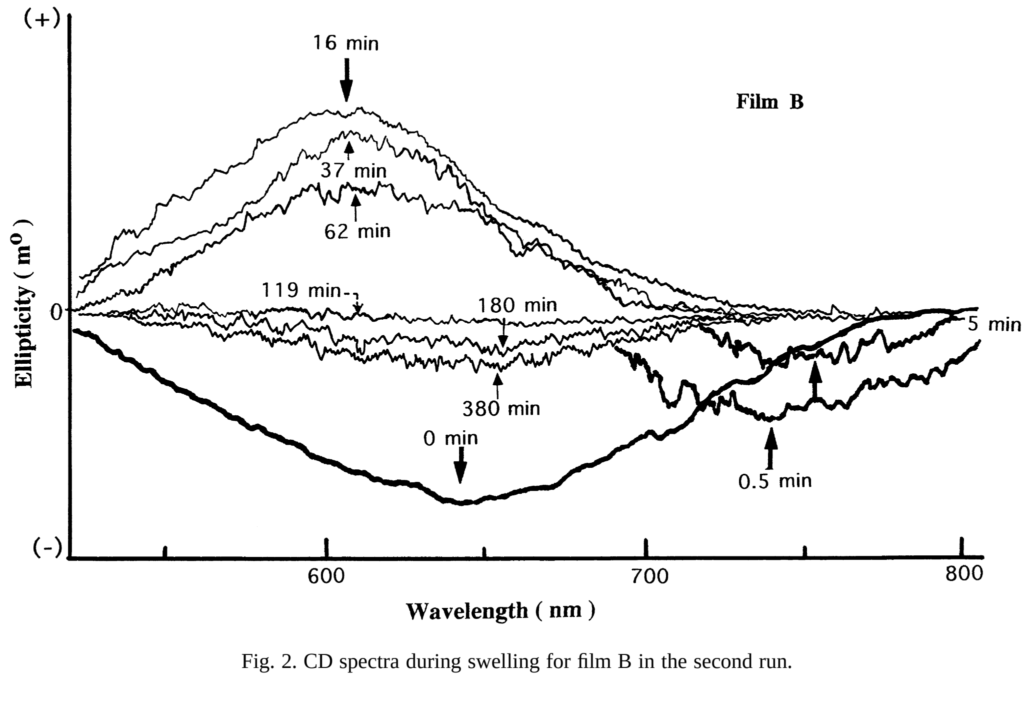

Fig. 2. CD spectra during swelling for film B in the second run.

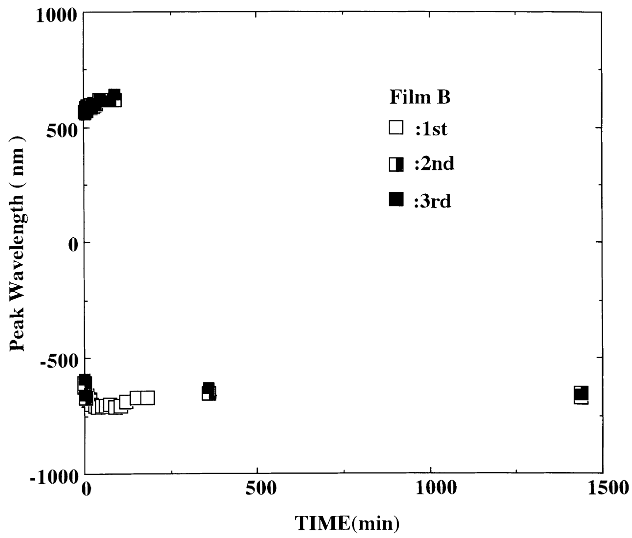

Fig. 3. Soaking time dependence of peak wavelength during swelling for film B; □: first run, ◨: second run, and ■: third run.

related to the pitch of CLCO. Therefore, our findings suggest that the swelling of the cellulose powders reduced the cholesteric pitch of the matrix HPC. In the second run, the most interesting behavior was found for films A and B. The sign of the peak changed with soaking time, as shown in Fig. 2. First, the peak was negative. Suddenly, the peak sign changed to positive at a given soaking time (ca. 5 min) and reverted to the original one after a given period (ca. 150 min). Before changing its sign from positive to negative again, the peak could not be regarded as significant within our experimental precision; i.e. the CD spectrum at 119 min in Fig. 2. This change in sign also occurred in the third run for films A and B, but was never observed for film C. The CD data during swelling are summarized in Fig. 3. The trends of the change in the CD sign for films A and B were almost the same; the change in sign (from negative to positive, or from positive to negative) for film B tended to occur at a shorter soaking time than that for film A.

The negative or positive peak generally corresponded to the right- or left-handedness of the cholesteric liquid crystalline order, respectively. Consequently, the change in sign refers to the change in handedness; the righthanded order changed into the lefthanded one and finally reverted to the righthanded one. Strictly speaking, the origin of the change is still unclear. However, based on the phenomenological data: the rapid and great swelling of the cellulose powders, and no change for the unfilled film, we supposed that the change in sign was induced by the swelling of the cellulose powders dispersed in the films. When the irregularly oriented cellulose powders swelled, the CLCO of the HPC molecules was stressed and was successively changed. After the relaxation of the stress, CLCO returned to the original one. No change occurred in the first run. This may be because the inter-crosslinking between the cellulose powders and the matrix HPC molecules was still strong and the stress was not enough to change the sign. After the first run, the intercrosslinking weakened and the cellulose powders stressed the liquid crystallline order more strongly.

In conclusion, the change in handedness of CLCO occurred for the crosslinked HPC films filled with cellulose powders. The cellulose powders appeared to induce the change in handedness of CLCO during swelling.

References

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