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Crosslinked hydroxypropyl cellulose films retaining cholesteric liquid crystalline order: 2. Anisotropic swelling behaviour in water

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Hydroxypropyl cellulose solid films crosslinked with two kinds of dialdehyde (glyoxal and glutaraldehyde), retaining cholesteric liquid crystalline order, were prepared by casting the liquid crystalline solution in methanol. Effects of crosslinking agent concentration and type, and heat treatment on the swelling behaviour of the crosslinked films in water were determined. The change in cholesteric pitch of crosslinked films during swelling was also determined by means of circular dichroism (c.d.) study. The swelling behaviour and the change in the peak wavelength of the c.d. spectrum were compared, and the anisotropic swelling behaviour of crosslinked films was discussed. The swelling ratio (B) in the film thickness direction was greater than that in width or length direction. B decreased with crosslinking agent concentration and heat treatment. B for the films crosslinked with glyoxal was greater than that for the films crosslinked with glutaraldehyde. The swelling behaviour and the shift in the peak wavelength of the c.d. spectrum as a function of soaking time were almost the same. The shift depended similarly on the concentration and type of the crosslinking agent as the swelling behaviour did. The similarity of the shift in the peak wavelength of the c.d. spectrum and the swelling behaviour clarified that the swelling in the film thickness direction is correlated to the change in the cholesteric pitch of the crosslinked films. Copyright © 1996 Elsevier Science Ltd.

(Keywords: hydroxypropyl cellulose; swelling behaviour; circular dichroism)

INTRODUCTION

The swelling behaviour for the isotropic crosslinked materials has been widely investigated theoretically[1–3] and experimentally[4–6]. However, the systematic studies of swelling behaviour for the anisotropic crosslinked materials were scarce[7,8].

In our previous paper[9], we have reported the swelling behaviour of the chemically crosslinked hydroxypropyl cellulose (HPC) solid films in water. Our main finding was that the equilibrium swelling in the thickness direction is greater than that in the width direction or the length direction. This anisotropic swelling behaviour was also reported by another group[10]. The anisotropic swelling behaviour seemed to correspond to the cholesteric liquid crystalline order retained in the solid films. The swelling in the thickness direction is possibly related to the increase in pitch of the cholesteric liquid crystalline order. The change in pitch can be detected with circular dichroism (c.d.) study. Therefore, the comparison of the swelling behaviour and the c.d. data during the swelling may be expected to reveal new information on the anisotropic swelling behaviour.

In this paper, we determined both transient and equilibrium swelling behaviour of the crosslinked HPC films as a function of crosslinking agent concentration or crosslinking agent type of dialdehyde. The effect of heat treatment on the swelling behaviour was also determined. As the increase in swelling in the thickness direction is expected to induce the increase in pitch of the cholesteric liquid crystalline order, the change in the c.d. spectrum for the crosslinked HPC films during swelling was followed. The transient swelling behaviour and the dependence of the c.d. spectrum on soaking time were compared.

EXPERIMENTAL

Samples and preparation of crosslinked films

Hydroxypropyl cellulose (HPC, Tokyo Kasei Kogyo Co. Ltd.), methanol (Pure Chemical Co. Ltd.), glyoxal and glutaraldehyde (Tokyo Kasei Kogyo Co. Ltd.), and hydrochloric acid (Wako Pure Chemical Industry Ltd.) were the same as those used in our previous paper[9]. The concentration of our liquid crystalline solution was 60 wt%. This clearly showed that the solution is a single-phase liquid crystal and there is no isotropic phase at room temperature. The preparations of free-bubble liquid crystalline solutions with crosslinking agent and catalyzer and of crosslinked films cast from the liquid crystalline solutions were described in more detail elsewhere[9,11], with one exception. The exception is the thickness of the cast crosslinked films; the films of *ca.* 180 μm thickness were used in this study, whereas the films of *ca.* 85 μm were used in our previous study[11]. For

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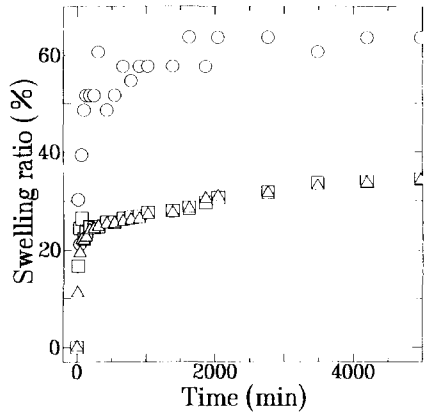

Figure 1 Swelling ratio against soaking time for HPC liquid crystalline films crosslinked with glyoxal (3.0 wt%) at 30°C; (○) thickness, (△) width, (□) length

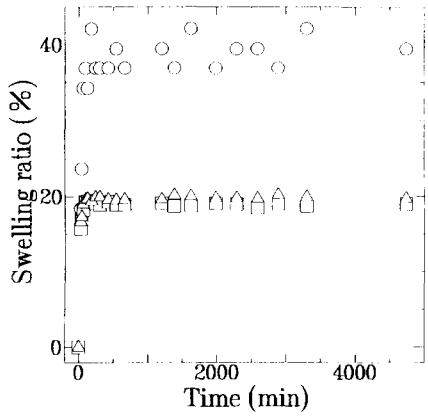

Figure 2 Swelling ratio against soaking time for HPC liquid crystalline films crosslinked with glutaraldehyde (3.0 wt%) at 30°C; (○) thickness, (△) width, (□) length

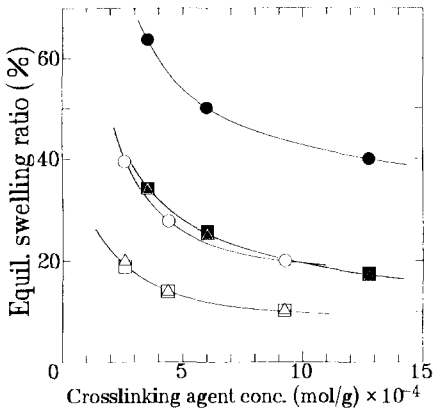

Figure 3 Equilibrium swelling ratio B_e against crosslinking agent concentration for HPC liquid crystalline crosslinked films; (○) thickness, (△) width, (□) length. Closed mark, glyoxal system; open mark, glutaraldehyde system

the test specimen of swelling behaviour in our study, the thicker films are preferable to determine the swelling behaviour with relatively high precision. The difference in the cast film thickness in this and previous studies had qualitatively no effect on the texture of crosslinked films observed with a polarized microscope, because the HPC molecules in the liquid crystalline phase oriented parallel

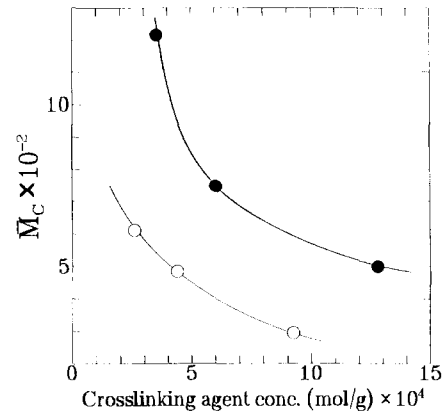

Figure 4 Number-averaged molecular weight between crosslinks ($\bar{M}_c$) against crosslinking agent concentration; (●) glyoxal, (○) glutaraldehyde

to a free-surface and a glass plate surface within *ca.* 200 μm thickness of liquid crystalline phase[12].

Some of the as-cast crosslinked films were heat-treated at 90°C for given times in a vacuum-oven in order to determine the effect of heat treatment on the swelling behaviour[9,11]. The soluble materials of the crosslinked films were extracted in boiling water using a Soxhlet apparatus for 24 h. The extracted films were dried *in vacuo* at 60°C[13–15].

Swelling behaviour

The square test specimens (size: 1 cm × 1 cm × *ca.* 180 μm) were cut from the cast crosslinked films. When the square specimens were cut, the length direction of the specimens was parallel to the shear direction during casting. However, this precaution for preparing the test specimens was disregarded, because the residual stress in the liquid crystalline solutions relaxed during storing the solutions in a desiccator saturated with methanol vapour[11], and the direction of cutting the test specimens from cast films had no marked effect on the swelling behaviour.

The changes in thickness and length of specimen were measured by means of a travelling micrometer (magnification: 25×) through a glass window of water bath as a function of soaking time; the measurement was *ca.* 7500 min for the glyoxal system and *ca.* 5000 min for the glutaraldehyde system. The temperature was controlled at 30 ± 0.5°C. The swelling ratio (B) was calculated by

$$B(\%) = (L - L_0)/L_0 \times 100 \qquad (1)$$

where L is the thickness or length at a given soaking time and L_0 is the thickness or length at the start of the measurement (the thickness or length at the dry state). For equilibrium swelling data only, we adopted two methods. One is the method of measuring the thickness, width and length as noted above and the other is the method of weighing the specimen film after and before soaking the film.

Circular dichroism (c.d.)

C.d. spectra of the crosslinked films at a dry state and during a swelling state were determined with a Jasco J-40S automatic recording spectropolarimeter (Japan Spectroscopic Co. Ltd.) at room temperature (*ca.* 25°C).

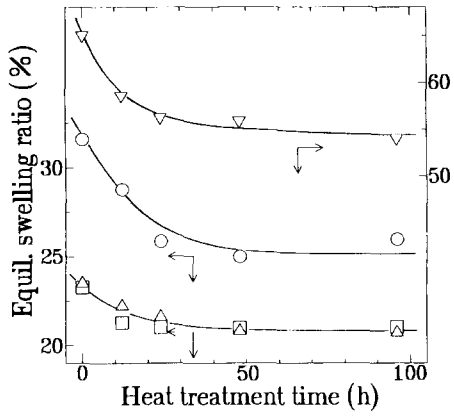

Figure 5 B_e against heat treatment time at 90°C for HPC liquid crystalline films crosslinked with glutaraldehyde (3.0 wt%); (▽) weight, (○) thickness, (△) width, (□) length

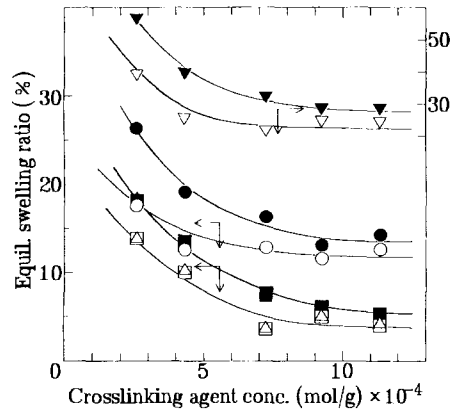

Figure 6 B_e against crosslinking agent concentration for HPC liquid crystalline films crosslinked with glutaraldehyde; (▽) weight, (○) thickness, (△) width, (□) length. Closed symbols, as-cast films; open symbols, heat treated films

The size of the specimen for the c.d. measurement was 1.2 cm × 0.8 cm × *ca.* 180 μm. The specimen was set in a quartz cell with a sponge holder which has a window (size: 1.0 cm × 0.4 cm) at the centre. The films were irradiated with a light through the window of the holder. The crosslinked films exhibited a negative peak. This showed that our crosslinked films retain the right-handed cholesteric liquid crystalline order. The crosslinking agent concentration affected the pitch of the crosslinked films[11]. Hereinafter, we describe simply our crosslinked films as liquid crystalline crosslinked films. When the quartz cell was filled with water, the peak spectrum at dry state (λ_0) shifted to a higher wavelength [$\lambda(t)$] with time. We define the shift in peak wavelength as the difference $\lambda(t) - \lambda_0$. The peak spectrum during the swelling [$\lambda(t)$] was followed as a function of time. The c.d. spectrum only around the peak during the swelling was mainly recorded. The time (t) taken to the peak was evaluated by measuring the horizontal distance of the spectrum curve drawn on the recording paper; the data of the distance from a starting end of the curve to the peak and the recording speed (20 mm min^{-1}) determined the time (t).

RESULTS AND DISCUSSION

Time dependence of swelling ratio

Figures 1 and *2* show the dependence of swelling ratio for each direction on the soaking time in water for the liquid crystalline films crosslinked with glyoxal and glutaraldehyde, respectively. The swelling behaviour consisted of three parts in our experimental range; a rapid swelling part, a gradual swelling part and an equilibrium part. The rapid swelling was completed in *ca.* 500 min and then the gradual swelling began. Finally the swelling reached the equilibrium state; at this state the swelling ratio is nearly constant and is defined as the equilibrium swelling ratio (B_e). The time to reach the equilibrium state (t_e) depended on the crosslinking agent concentration and type; t_e for the liquid crystalline films crosslinked with the glutaraldehyde system (*ca.* 1000 min) was shorter than that for the films with the glyoxal system (*ca.* 3000 min).

Equilibrium swelling ratio (B_e)

B_e depended greatly on the crosslinking conditions, that is, a crosslinking agent concentration, a crosslinking agent type, and a heat treatment.

Crosslinking agent concentration and crosslinking agent type. *Figure 3* shows the dependence of B_e on the crosslinking agent concentration (the number of moles of crosslinking agent per 1 g of HPC). B_e decreased exponentially with increasing concentration of crosslinking agent. Over the crosslinking agent concentration of 15×10^{-4} mol g^{-1}, the crosslinking agent concentration had no marked effect on B_e for both crosslinking agent systems. When compared at the same concentration, B_e for the liquid crystalline films crosslinked with the glyoxal system was greater than that for the films with glutaraldehyde. Furthermore, B_e in the thickness direction was greater than that in the width or length direction. The swelling behaviour in the width and length directions was the same within our experimental precision. The difference in B_es between thickness direction and width (or length) direction (ΔB_e) depended on the crosslinking agent type: ΔB_e for the liquid crystalline films crosslinked with glyoxal was greater than that for the films with glutaraldehyde. This difference tended to be independent of crosslinking agent concentration. These strongly suggested that the crosslinkability between HPC molecules in the same layer is different from that between HPC molecules in the adjacent layers; the relative frequency of interlayer-crosslinking was lower than that of the intralayer-crosslinking, and the relative frequency of inter-crosslinking with glyoxal was lower than that with glutaraldehyde.

Generally, the swelling behaviour of gels is governed by the number-averaged molecular weight between crosslinks ($\bar{M}_c$). The higher $\bar{M}_c$, the greater B_e. Unfortunately there are no approaches to estimate rigorously $\bar{M}_c$ for the anisotropic gels. Here, for convenience, we estimate $\bar{M}_c$ on the basis of Flory's equation using the equilibrium swelling data in the thickness direction[1]. Flory's equation has been successfully applied to the swelling of isotropic crosslinked materials, but the validity of the equation to our anisotropic crosslinked films appears to be equivocal. Consequently, the values of $\bar{M}_c$ in this study are just a reference. The detailed approach for estimating $\bar{M}_c$ was shown in our previous paper[15].

$\bar{M}_c$ for each liquid crystalline film is shown in *Figure 4*. $\bar{M}_c$ decreased exponentially with increasing concentration of crosslinking agent. $\bar{M}_c$ for the gel crosslinked with

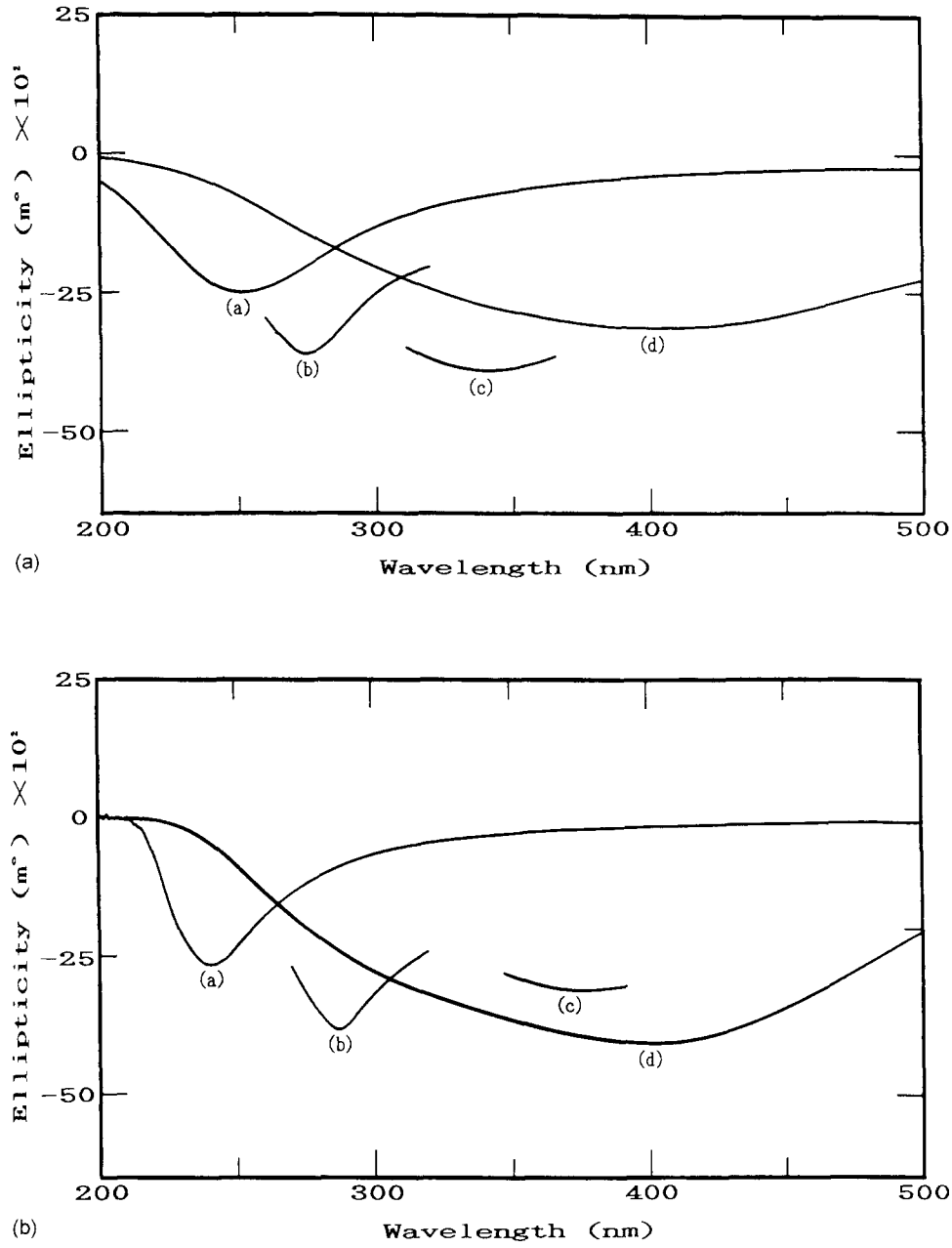

Figure 7 (a) C.d. spectra of HPC liquid crystalline films crosslinked with glyoxal (3.0 wt%); swelling time in water (min): (a) 0, (b) 4, (c) 9, and (d) 4320. (b) C.d. spectra of HPC liquid crystalline films crosslinked with glutaraldehyde (3.0 wt%); swelling time in water (min): (a) 0, (b) 4, (c) 9, (d) 4320

glyoxal was greater than that for the gel with glutaraldehyde in our experimental range. This suggested that the gel crosslinked with glyoxal has a looser texture than the gel crosslinked with glutaraldehyde. The order of $\bar{M}_c$ was *ca.* 5×10^2 for our gels. The order was almost the same as that reported by us[14,15] and by Mitchell *et al.*[16], but was much smaller than that reported by Mark *et al.*[17,18].

Heat treatment. Another factor affecting B_e is the heat treatment[9,11]. *Figure 5* shows the dependence of B_e on heat treatment for the liquid crystalline films crosslinked with glutaraldehyde. B_e decreased with treatment time and reached the constant value after a definite time of treatment (t'_e). Our data showed that t'_e at 90°C depends on the crosslinking agent type; t'_e for the liquid crystalline films crosslinked with glutaraldehyde was longer than that for the films with glyoxal. Interestingly, t'_e depended on the swelling direction; t'_e for the swelling in the thickness direction was greater than that for the swelling in the width or length direction. The heat treatment affected markedly B_e in the thickness direction more than B_e in the width or length direction. The heat treatment induces the supplemental crosslinking[9,11]. Consequently, the supplementation preferred the interlayer-crosslinking to the intralayer-crosslinking. Furthermore, B_e evaluated by the weighing method had almost the same t'_e as that in the width or length direction, exhibited a different trend from B_e in the thickness direction, and was greater than B_e evaluated by our other method. This suggested that the weighing method does not reflect exactly the true swelling behaviour of our crosslinked liquid crystalline films. *Figure 6* shows the dependence of B_e on crosslinking agent concentration as a function of heat treatment. Heat treatment (at

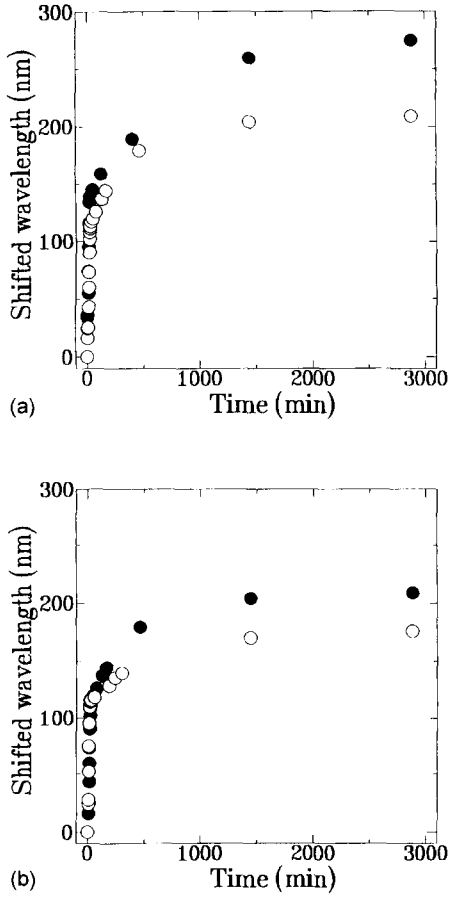

Figure 8 (a) Shifted wavelength of c.d. spectrum peak againt swelling time for HPC liquid crystalline crosslinked films: (●) glyoxal (3.0 wt%), (○) glutaraldehyde (3.0 wt%). (b) Shifted wavelength of c.d. spectrum peak against swelling time for HPC liquid crystalline films crosslinked with glutaraldehyde; glutaraldehyde concentration (wt%): (●) 3.0, (○) 5.0

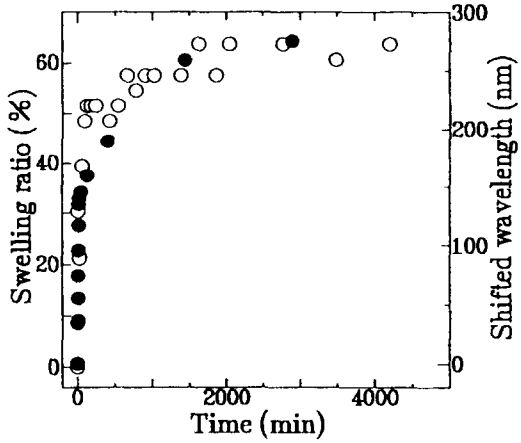

Figure 9 Swelling ratio (○) and shifted wavelength of c.d. spectrum peak (●) against swelling time for HPC liquid crystalline films crosslinked with glyoxal (3.0 wt%)

90°C for 48 h) reduced B_e. Clearly, the pronounced effect of heat treatment on B_e in the thickness direction was found, as the crosslinking agent concentration decreased. As shown in *Figure 3*, B_e for the as-cast films was almost constant over the crosslinking agent concentration of 15×10^{-4} mol g^{-1}. However, B_e for the heat-treated films became constant over 10×10^{-4} mol g^{-1}.

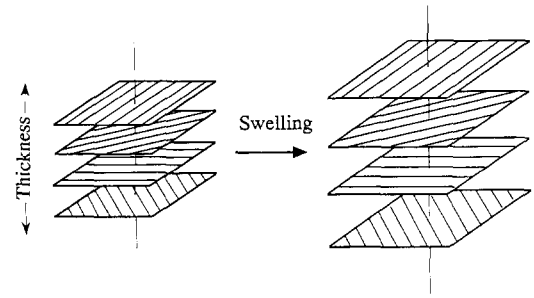

Figure 10 Swelling model of HPC liquid crystalline crosslinked films

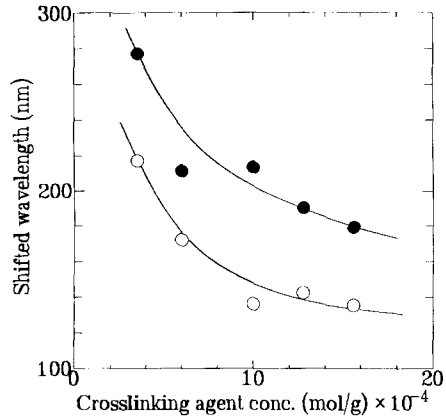

Figure 11 Equilibrium shifted wavelength of c.d. spectrum peak against crosslinking agent concentration for HPC liquid crystalline films crosslinked with glyoxal (●) and with glutaraldehyde (○)

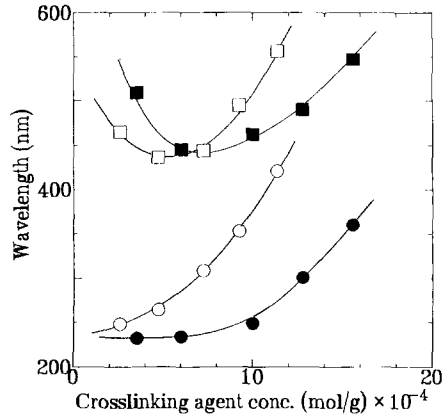

Figure 12 Wavelength of c.d. spectrum peak against crosslinking agent concentration for HPC liquid crystalline crosslinked films; (○) before swelling, (□) after swelling. Closed symbols, glyoxal system; open symbols, glutaraldehyde system

C.d. measurement

Figure 7 shows the typical c.d. spectra for the liquid crystalline films crosslinked with glyoxal or glutaraldehyde. As noted in the Experimental section, only the wavelength around the negative peak was mainly shown for some cases. The peak wavelength shifted to a higher one with increasing time. The shift in peak $[\lambda(t) - \lambda_0]$ for each film is shown as a function of time in *Figure 8*. The curve comprised a rapid increasing part, a gradual increasing part, and a nearly constant (equilibrium) part. This was very similar to the swelling behaviour shown in *Figures 1* and *2*. The time to reach the equilibrium shift depended on the crosslinking agent concentration and

type; the time for the liquid crystalline films crosslinked with glyoxal was greater than that for the films crosslinked with glutaraldehyde and the time decreased with increasing concentration of crosslinking agent. The trends of the dependence of the time on the crosslinking agent concentration and type were the same as those of the dependence of swelling ratio. *Figure 9* shows the comparison of the shift in the wavelength of the c.d. peak and the swelling behaviour in the thickness direction. Clearly, both characteristics behaved synchronously. This confirmed our expectation: the swelling in the thickness direction is strongly correlated to the change in pitch of the cholesteric liquid crystalline order. Consequently, we propose a model for the swelling of our crosslinked films as shown in *Figure 10*. The cholesteric pitch for our crosslinked films was *ca.* 3500 Å[11]. The diameter of the HPC molecules was *ca.* 10 Å according to Conio *et al.*[19,20]. Therefore, the number of layers per pitch for our crosslinked films was estimated as *ca.* 350. When water is introduced between layers, the distance of adjacent layers becomes greater and the shift in peak wavelength increases.

Another finding from the c.d. measurement shown in *Figure 7* was that the peak area of the c.d. spectrum broadens with increasing time, i.e., with increasing swelling ratio. This indicated that the distribution of the cholesteric pitch increases with increasing swelling ratio. This distribution of the pitch can be explained using our model as follows. The introduction of water in the neighbourhood of interlayer-crosslinks (junctions) is restricted more or less; however, the introduction of water becomes easier, as the position becomes further from the crosslinks (junctions). Consequently, the distance of adjacent layers has the distribution along the length direction of HPC molecules (it is widely known that the HPC molecules are semi-rigid). As $\bar{M}_c$ decreases, the introduction of water is restricted and B_e decreases. This was similar to our results shown in *Figure 4*.

The equilibrium shift, the shift in the peak after *ca.* 3000 min, is plotted against crosslinking agent concentration in *Figure 11*. The equilibrium shift decreased exponentially with increasing concentration of crosslinking agent. The decrease in the equilibrium shift for the liquid crystalline films crosslinked with glyoxal was greater than that for the films with glutaraldehyde. These data showed that the interlayer-crosslinking increases with increasing concentration of crosslinking agent and glyoxal is a more effective crosslinking agent than glutaraldehyde. The dependence of the equilibrium shift on the crosslinking agent concentration was analogous to that of B_e in the thickness direction shown in *Figure 6* and to that of $\bar{M}_c$ shown in *Figure 4*. Over the crosslinking agent concentration of *ca.* 15×10^{-4} mol g^{-1}, the equilibrium shift became constant. These seemingly suggested that the interlayer-crosslinking terminates around this crosslinking agent concentration; OH groups in HPC molecules are finished to consume the crosslinking. However, this was not true. *Figure 12* shows the c.d. peak wavelengths before and after swelling of the liquid crystalline crosslinked films as a function of crosslinking agent concentration. For the dry liquid crystalline films (before swelling), the curves for the films crosslinked with glyoxal and glutaraldehyde were concave upward. However, for the swelling liquid crystalline films (after swelling), the curves exhibited a minimum. These curves did not become constant around the crosslinking agent concentration of 15×10^{-4} mol g^{-1}, as expected from *Figure 11*. Irrespective of whether or not the liquid crystalline crosslinked films were dry, the c.d. peak wavelength increased even over the crosslinking agent concentration of 15×10^{-4} mol g^{-1}, although the difference in the c.d. peak wavelengths before and after swelling was nearly constant as shown in *Figure 11*.

CONCLUSIONS

The swelling ratio in the thickness direction was greater than that in the width or length direction. The swelling ratio for the films crosslinked with glutaraldehyde was smaller than that for the films with glyoxal. The swelling ratio decreased with increasing concentration of crosslinking agent and heat treatment time. The c.d. spectrum for the crosslinked films during swelling exhibited a negative peak. The peak shifted to longer wavelength with increasing swelling ratio. The dependence of the peak shift on the crosslinking agent concentration and type was the same as that of the swelling ratio.

These findings revealed that the swelling ratio in the thickness direction is correlated to the change in the cholesteric pitch.

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