

Crosslinked Hydroxypropyl Cellulose Films Retaining Cholesteric Liquid Crystalline Order. I. Effects of Cast Conditions and Heat Treatment on the Textures and Order of Films

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SYNOPSIS

To eliminate the shear-induced band texture and wrinkled texture observed on the free surface of cellulosic solid cast films retaining cholesteric liquid crystalline order, we proposed a storing process of the cast solutions: the solution is stored in the same solvent vapor atmosphere as the solution. The effect of cast conditions (the storing time) on those textures and the cholesteric liquid crystalline order was determined using the lyotropic liquid crystalline solution of hydroxypropyl cellulose in methanol with crosslinker. Furthermore, the effect of heat treatment on the liquid crystalline order in the cast films was determined. The resultant crosslinked films were observed with a polarized microscope and a scanning electron microscope, and were investigated with circular dichroism. Our findings showed that the proposed storing process is needed before starting the cast process. During the process the textures vanished, due to the relaxation of the residual stress in the solution, the cholesteric liquid crystalline order became stable, and the cholesteric pitch decreased with increasing storing time. The heat treatment also affected the liquid crystalline order of the films; the peak in the circular dichroism spectrum sharpened and shifted with heat treatment, and the shift in peak seemed to depend on the crosslinker concentration. Furthermore, the crosslinking proceeded with heat treatment. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

We have investigated the preparation of hydroxypropyl cellulose (HPC) solid films retaining cholesteric liquid crystalline order.¹⁻⁵ For preparing the cast films, we chose the solvent with a relatively low boiling point because the residual solvent can be removed from the solid-cast films with relative ease. In the free-surface plane of our cast films, the wrinkled texture or band texture was observed.^{3,5} Those textures have remarkably remained in the cast systems with relatively low boiling-point solvents. To investigate the relation between those textures and the physical properties of the films, we need to control those textures. For the band texture, we tried

to control whether the band texture remained in the films by means of polarized microscopy: when the solidification and crosslinking of cast solutions started, after thoroughly relaxing the stress responsible for the formation of band texture, we could obtain the films with no band texture. However, we need to clarify the inner texture of the films with no band texture. Furthermore, we need to control the wrinkled texture. Charlet et al.⁶ have already shown the effect of cast conditions (mainly, drying rate) on the circular reflectivity for the HPC solid films cast from aqueous solution. Our approach is basically the same as theirs,⁶ however, they showed no details on the free-surface and inner textures of the films by means of optical observation.⁶

In this study, we propose one process to control both band and wrinkled textures by storing the cast solution in the same solvent-vapor atmosphere as the solution system. The lyotropic HPC liquid crys-

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talline solutions in methanol with crosslinker were prepared and were cast under different conditions (mainly the time stored in the solvent-vapor atmosphere); the free-surface textures and cholesteric liquid crystalline order were observed by means of polarized microscopy (POM), scanning electron microscopy (SEM), and circular dichroism (CD); and the effect of the proposed process on the textures and order was discussed. Furthermore, we attempted to find the effect of heat treatment on the order of the cast films.

EXPERIMENTAL

Samples

HPC (Tokyo Kasei Kogyo Co., Ltd., \bar{M}_w : 11.7×10^4 , \bar{M}_n : 5.2×10^4) was the same as that used in our previous papers.^{1,3,5} Reagent-grade methanol (Pure Chemical Co., Ltd.) was used as received. The chemical crosslinkers used in this study were glyoxal and glutaraldehyde (Tokyo Kasei Kogyo Co., Ltd.). Hydrochloric acid (Wako Pure Chemical Ind., Ltd.) was used as catalyzer.

Preparation of Liquid Crystalline Solution

Given amounts of HPC powder and methanol (60 wt %) were mixed and the mixture was vigorously stirred until the powder dissolved. The solution was

allowed to stand in the dark at ca. 10°C for a week. Methanol dissolved HPC powder more easily than water. The solution was single-phase liquid crystal at room temperature.⁷

Preparation of Solid Films

Given amounts of crosslinker and 5 wt % hydrochloric acid were added to the liquid crystalline solution and the mixture was stirred by glass rod for 5 min. The solution was degassed using a centrifuge (1000 rpm, 1 h) and then was allowed to stand in the dark for a week. The bubble-free solution was spread on a glass plate at constant speed (shear rate : ca. 20 sec^{-1}) and the plate was stored in a desiccator saturated with methanol vapor. The storage time in the desiccator was changed in this study. Hereafter, the time is referred to as the "storing time." The methanol vapor saturated in the desiccator prevents the solution from solidifying and ensures the equilibrium of the liquid crystalline order. After storing the plate for a given time (unless otherwise noted, the storing time was 24 h), the plate was transferred to a room atmosphere and was cast for 48 h. The film (thickness was ca. $85 \mu\text{m}$) was peeled from the plate, vacuum-dried at room temperature (ca. 25°C) for 24 h, and stored in a desiccator over silica gel. The preparation processes proposed and parameters for each process are schematically shown in Figure 1.

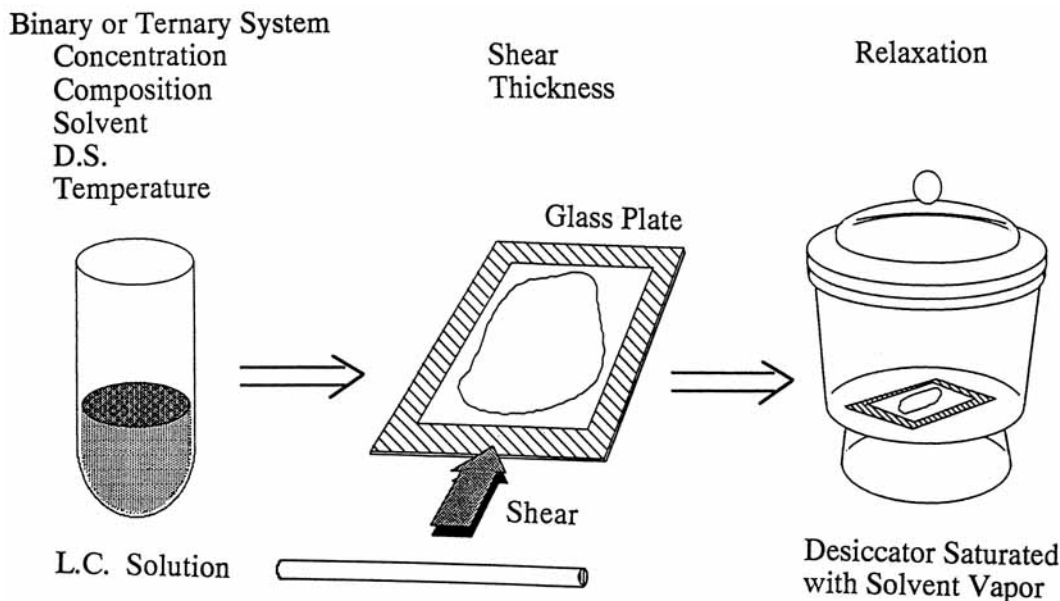


Figure 1 Schematic cast processes proposed in this study and the parameters for each process.

Polarized Microscopical Observation of Films

An Olympus polarized microscope (POM) was used to observe and photograph the free-surface texture of films. The magnification was 150 \times .

Circular Dichroism (CD) of Films

CD spectra of the cast films were determined with a Jasco J-40S automatic recording spectropolarimeter (Japan Spectroscopic Co., Ltd.) at room temperature.

Scanning Electron Microphotometry (SEM) of Films

SEM was performed with an S-415 scanning electron microscope (Hitachi Seisakusho, Ltd.). The cast films were freeze-fractured by bending in liquid nitrogen.

Heat Treatment of Films

The cast films (storing time: 24 h) were heat-treated at 60°C or 90°C for given times in a vacuum-oven (ca. 0.18 Pa).

RESULTS AND DISCUSSION

1) Effect of Cast Conditions

Figure 2 shows the polarized microphotographs of free-surface for the cast films crosslinked by glyoxal (10 wt %) and by glutaraldehyde (10 wt %) as a function of the storing time. Clearly, just after the solutions were stored, the typical band texture was still seen. As the storing time increased, however, the band texture vanished regardless of different crosslinker concentrations and systems. This showed that the storing time of 12 hours is enough to relax the stress which induces the band texture for our systems. (Strictly speaking, it took a few minutes to vanish the band texture.^{7,8} After the band texture vanished, the typical liquid crystalline mosaic-like texture for HPC formed⁹⁻¹² and became smaller and smaller with increasing storing time. This suggested that the liquid crystalline domain size decreases with increasing storing time.

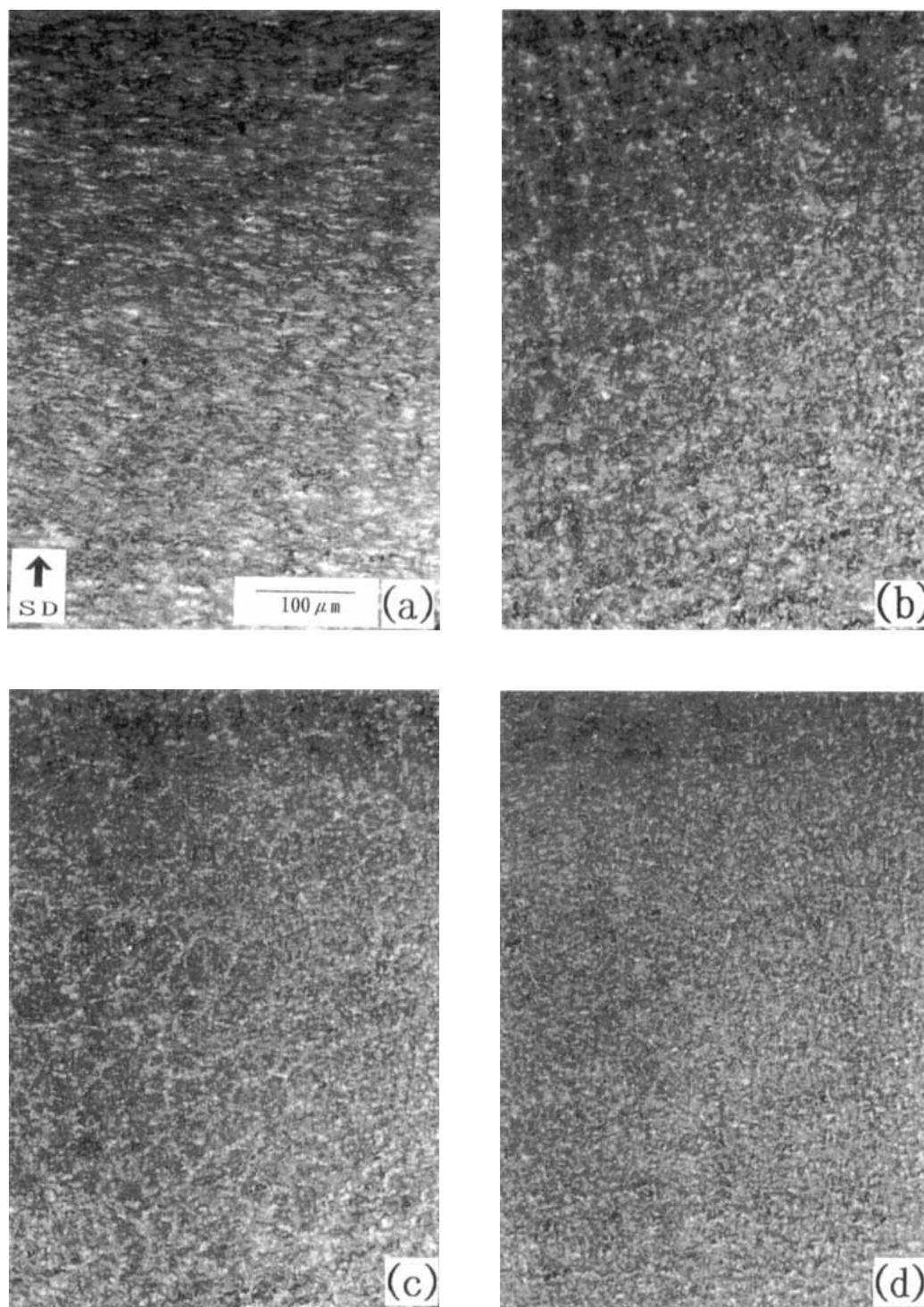
Figure 3 shows the scanning electron microphotographs of fracture and free-surface planes for cast films crosslinked by glutaraldehyde (10 wt %) for each storing time. When we extended the storing time, the free-surface texture became smooth and the wrinkled texture tended to vanish. This was

identical with the findings shown in Figure 2. On the other hand, the effect of the storing time on the texture of fracture plane was not as clear as that on the texture of free-surface. Under higher magnification, the layered texture was observed as shown in Figure 4. The texture seemed to originate from the cholesteric liquid crystalline order.¹³⁻¹⁵ The spacing of the striations shown in Fig. 4(c) was ca. 150 nm. If the striations were related to the cholesteric pitch more or less, the pitch is twice the spacing of striations: ca. 300 nm. This will be discussed below.

Figure 5 shows the CD spectra for the films crosslinked by glutaraldehyde (5 wt %), with respect to the storing time. Each film exhibited a negative peak around 250 nm. This showed that the films retain the right-handed cholesteric liquid crystalline order. As the storing time increased, the peak spectra became sharp and shifted to a lower wavelength. This trend was similar to that reported by Charlet, et al.⁶; the increase in storing time for our approach was analogous to the lowering drying rate for their approach.⁶ Our results indicate that the cholesteric liquid crystalline order becomes stable and the cholesteric pitch becomes smaller as the storing time is lengthened, within our experimental conditions. This effect of the storing time was similar to that of polymer concentration on the CD peak spectrum for the liquid crystalline solutions,^{10,16} in spite of no marked change in the concentration during our storing process.

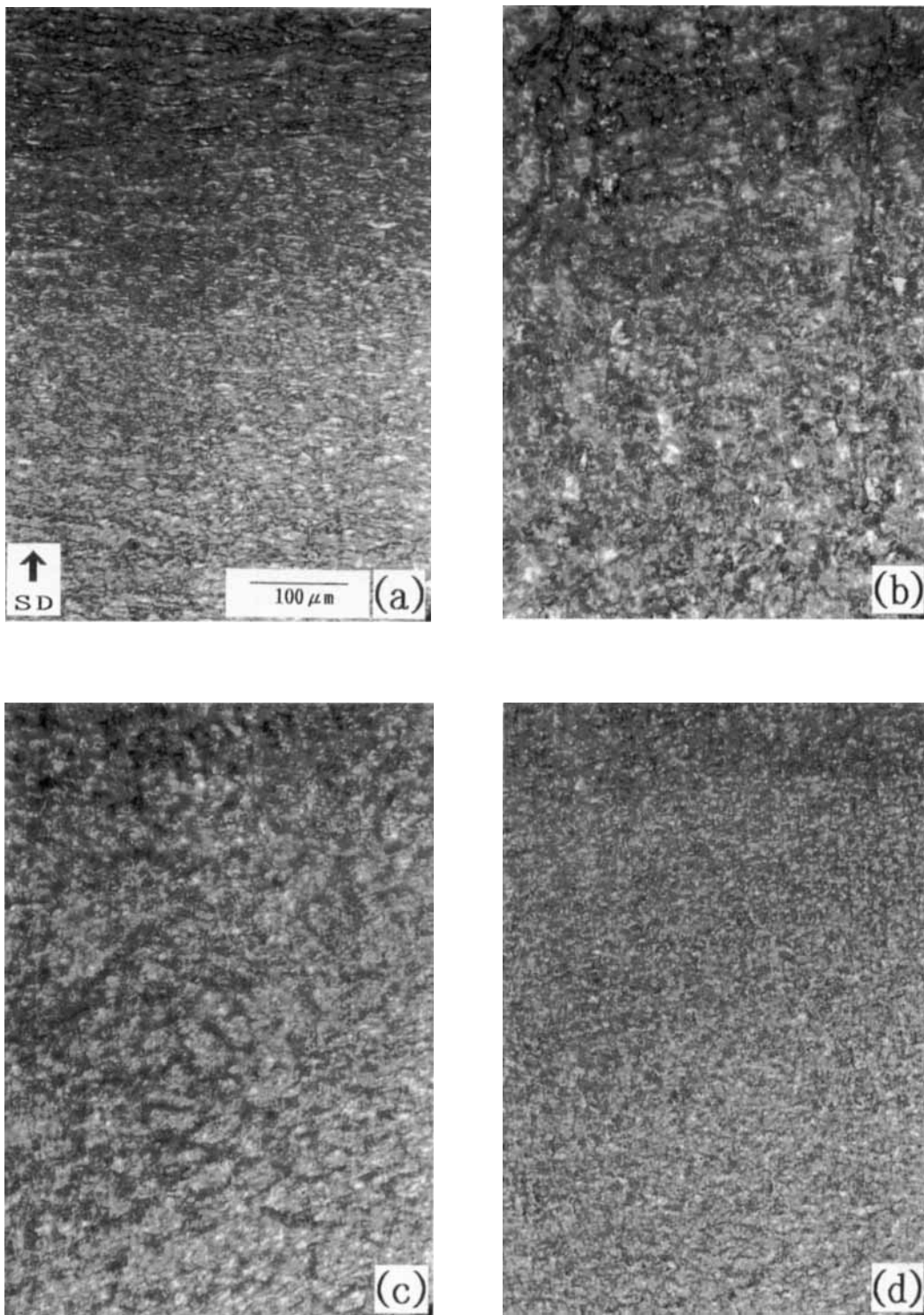
Figure 6 shows the CD spectra for the cast films (storing time: 24 h) as a function of crosslinker concentration. For both crosslinker systems, the peak area in the CD spectrum broadened as the crosslinker concentration increased. The textures of free-surface were vanished for each film, even for the films cast from 10 wt % crosslinker solutions.

Our findings in POM and SEM observations and in CD measurement indicated that the free-surface textures in our films vanish and the cholesteric liquid crystalline order retained in our films becomes stable with increasing storing time. The storing process proposed in this study was key in preparing the HPC solid films retained liquid crystalline order; the basic idea was an infinitesimal drying rate of solvent for a given time to remove the shear-induced band texture and the wrinkled texture. Both to remove the surface textures and to stabilize the cholesteric liquid crystalline order, the storing time in the solvent vapor atmosphere was ca. 24 h for our system, but was dependent on the relaxation time of the liquid crystalline system. The longer storing time is needed, as the relaxation time is long. The relaxation time



(A)

Figure 2 Polarized microphotographs of free-surface for the HPC films crosslinked by 10 wt % glyoxal (A) and for the HPC films by 10 wt % glutaraldehyde (B); storing time (h): (a) 0, (b) 12, (c) 24, (d) 48.



(B)

Figure 2 (Continued from the previous page)

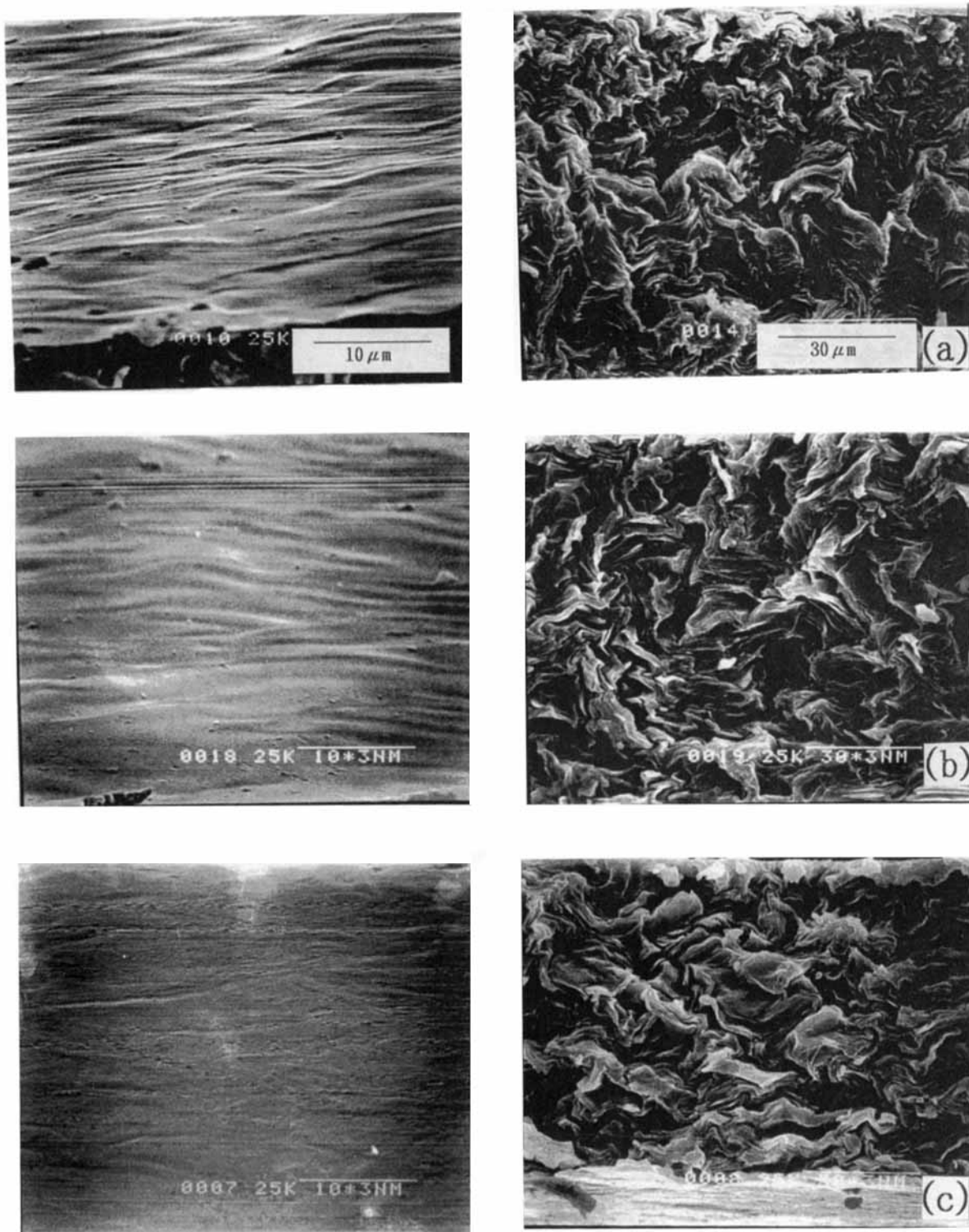


Figure 3 Scanning electron microphotographs of fracture plane (right) and free-surface plane (left) for the HPC films crosslinked by 10 wt % glutaraldehyde; storing time (h): (a) 0, (b) 1, (c) 24.

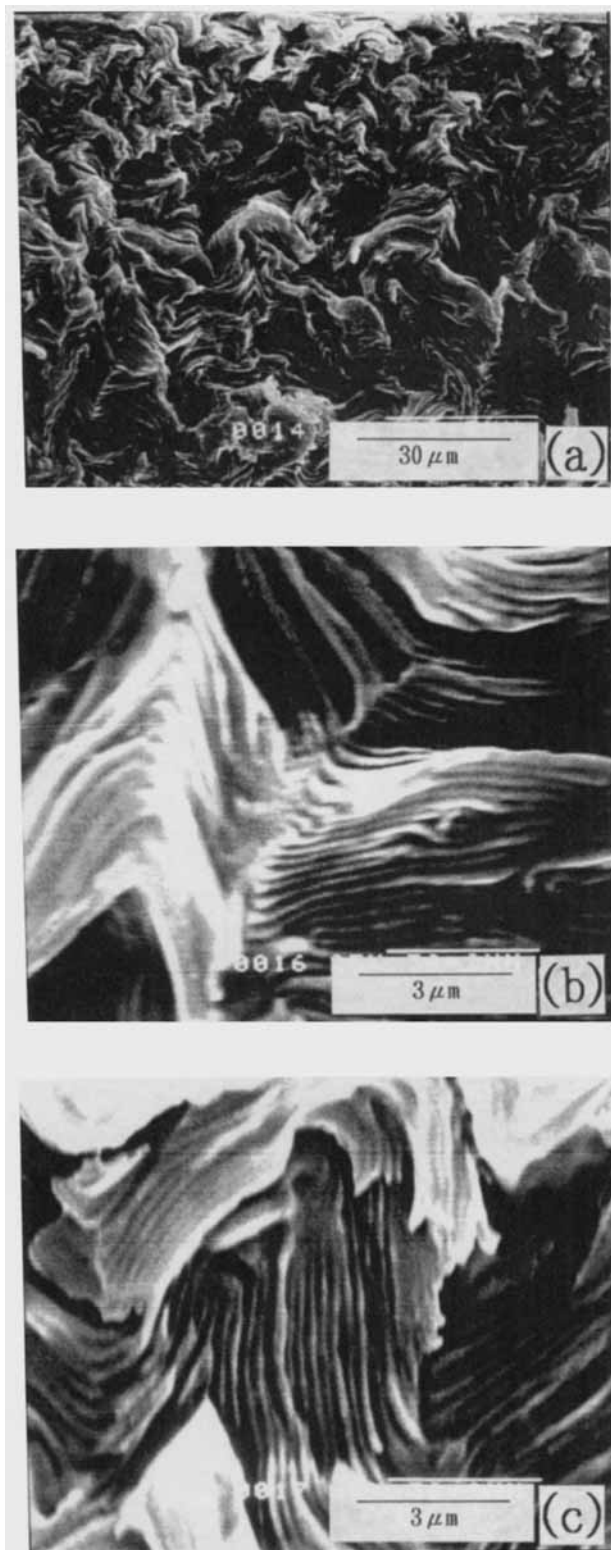


Figure 4 Scanning electron microphotograph of fracture plane for HPC film crosslinked by 10 wt % glutaraldehyde under higher magnification; storing time is 0 h; magnification: (a) 1000 \times , (b) and (c) 15,000 \times .

greatly depended on solution system and concentration.⁷

It is noteworthy that the crosslinker concentration affects the liquid crystalline order as shown in Figure 6. The crosslinking should be performed after the equilibrium liquid crystalline order reformed. However, our findings suggested that the crosslinking occurs more or less before the liquid crystalline order reaches perfect equilibrium for the higher crosslinker concentration (in particular, 10 wt %).

We noted that the striations shown in Figure 4(c) possibly originated from the cholesteric pitch. This could be confirmed by CD spectrum data. The negative peak for the film crosslinked by glutaraldehyde (10 wt %) was ca. 350 nm as shown in Figure 6(B). The wavelength (λ) at CD spectrum peak is related to pitch (P) as follows: $\lambda = \bar{n} \cdot P$, where \bar{n} is a mean refractive index. The value of \bar{n} for the solid HPC film was 1.4847.¹⁷ The value for the film cast from an aqueous liquid crystalline solution was 1.4993.¹⁸ Then, the pitch estimated was ca. 230 nm. The estimated value of the pitch was about the same as that estimated from the spacing shown in Figure 4(c).

2) Effect of Heat Treatment

Figure 7 shows the CD spectra for the crosslinked films heat-treated at 90°C for 48 h. Comparisons between the CD spectra in Figures 6 and 7 showed that the negative peak shifts to a longer wavelength and the peak intensity decreases with heat treatment, except for the noncrosslinked films. After the treatment, the films became light brown. As shown in Figure 8, the free-surface texture observed with POM exhibited some black points. Those suggested more or less the thermal degradation of the films. We then changed the heat treatment conditions into rather mild ones, 60°C. Figure 9 show the CD spectra for the films treated at 60°C for 48 h. No difference in color between the films with and without heat treatment was found with the naked eye. The textures observed with POM were almost the same as those in Figure 2, which suggested the elimination of the thermal degradation. Compared results from Figures 6 and 9 show that the peak tended to sharpen with heat treatment. This was the same trend as that reported in our previous paper.¹⁹ The effect of heat treatment on the shift in the CD spectrum peak tended to depend on the crosslinker concentration: for lower concentration, including non-crosslinked films, the peak shifted to a lower wavelength;

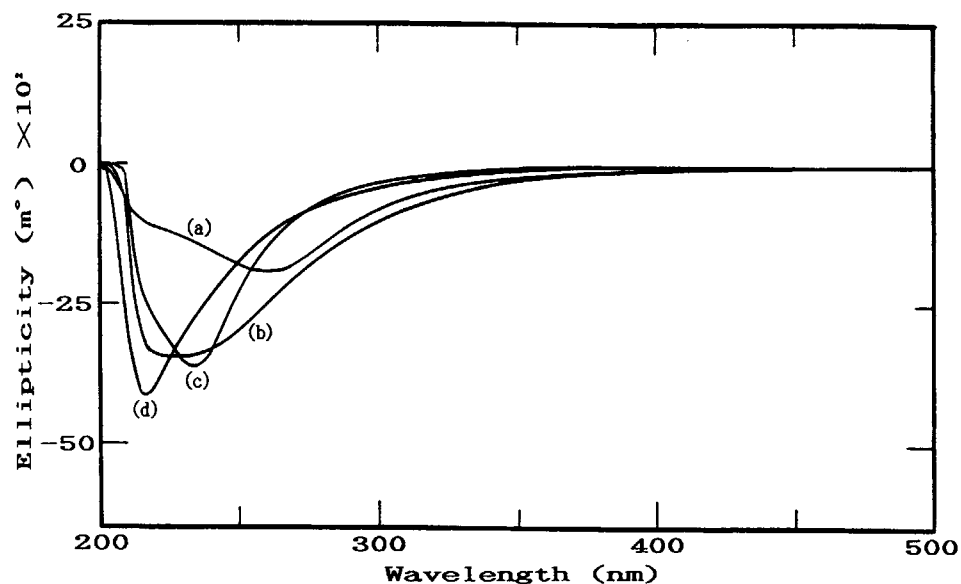


Figure 5 CD spectra for HPC films crosslinked by 5 wt % glutaraldehyde; storing time (h): (a) 0, (b) 12, (c) 24, (d) 48.

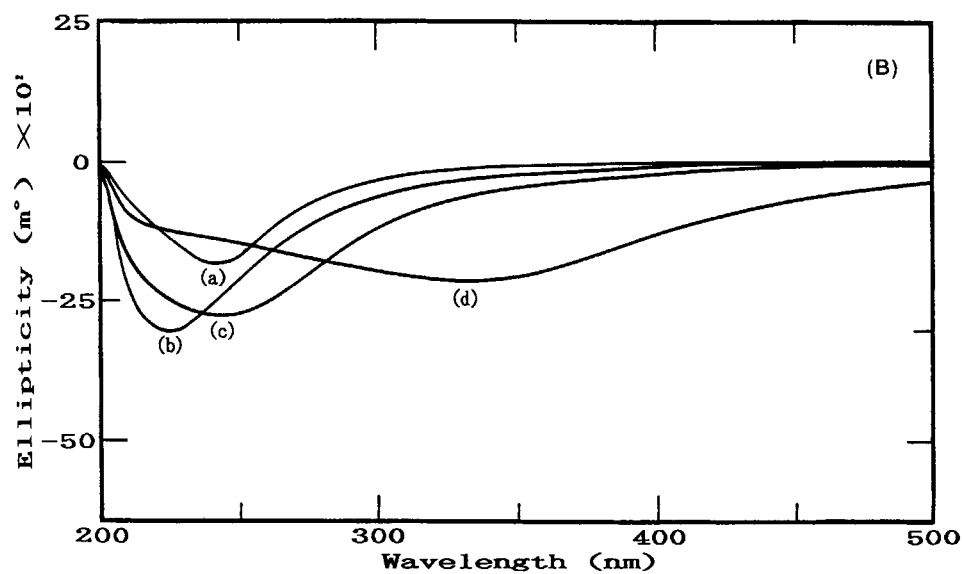
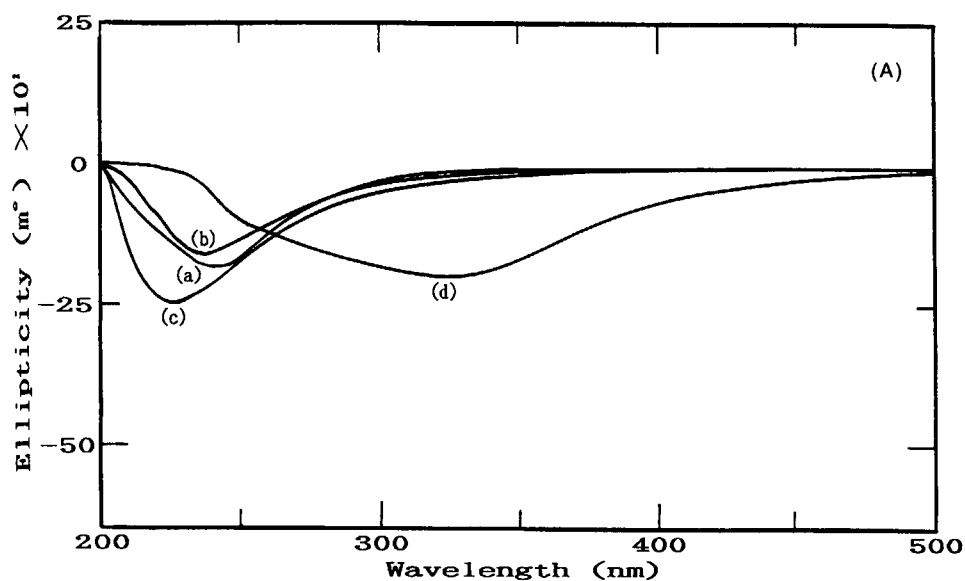


Figure 6 Effect of crosslinker concentration on CD spectrum for HPC films crosslinked by glyoxal (A) and by glutaraldehyde (B); crosslinker concentration (wt %): (a) 0, (b) 3.0, (c) 5.0, (d) 10.0.

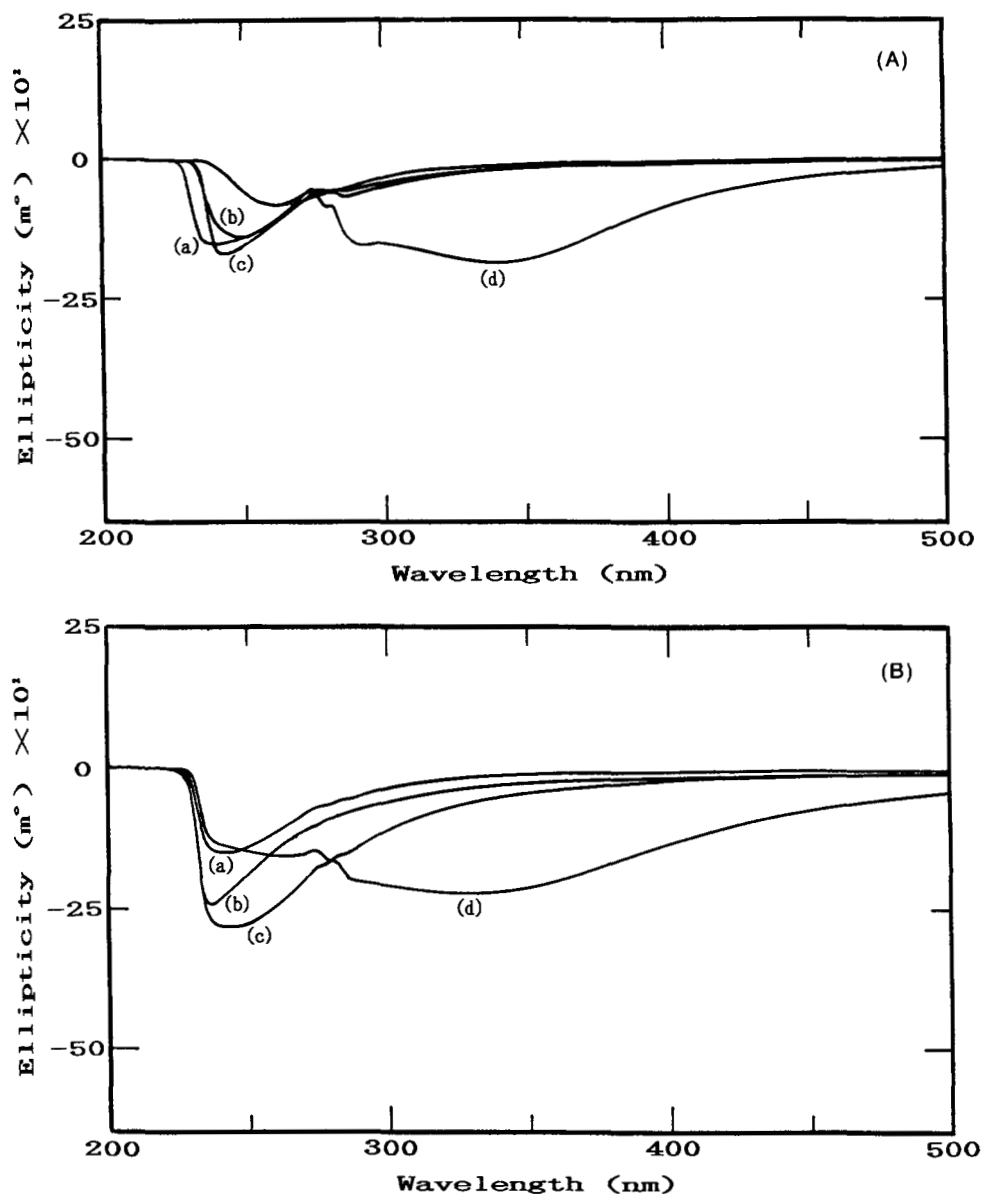


Figure 7 Effect of heat treatment at 90°C for 48 h on CD spectrum for HPC films crosslinked by glyoxal (A) and by glutaraldehyde (B); crosslinker concentration (wt %): (a) 0, (b) 3.0, (c) 5.0, (d) 10.0.

whereas for the higher concentration, the peak shifted to a higher wavelength. In our systems, the 5 wt % of crosslinker concentration seemed to be critical.

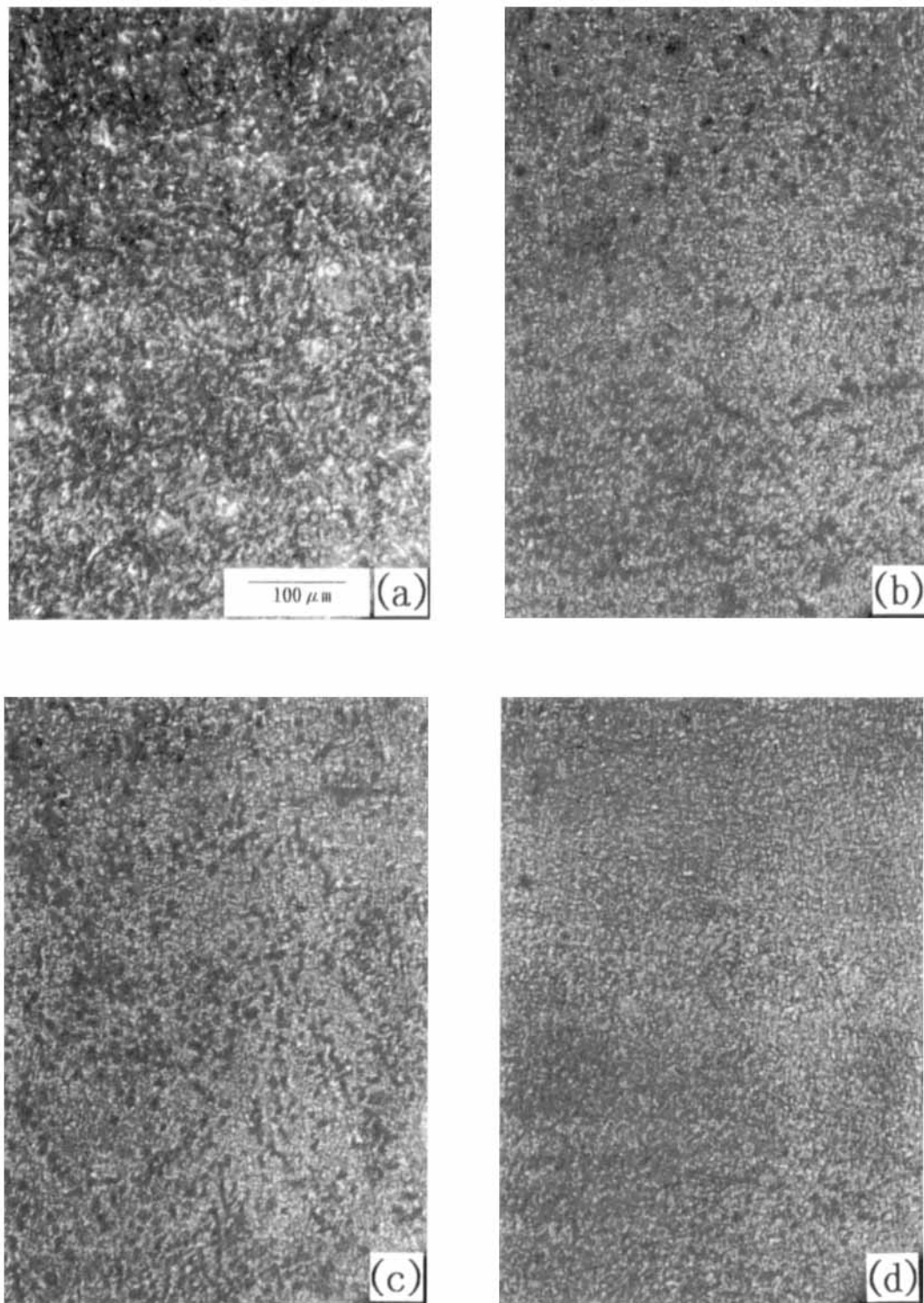
Table I shows the effect of heat treatment on the gel content of the cast films. For each film, the gel content increased by ca. 3% with heat treatment. This showed that the heat treatment enhances the crosslinking.

Consequently, the heat treatment increased the cholesteric liquid crystalline order and enforced the crosslinking for the films cast from lower crosslinker

concentration systems, but not always for the higher crosslinker concentrations. This implied that the additional crosslinking due to the heat treatment increases the order for the relatively higher liquid crystalline order, but decreases for the relatively lower order.

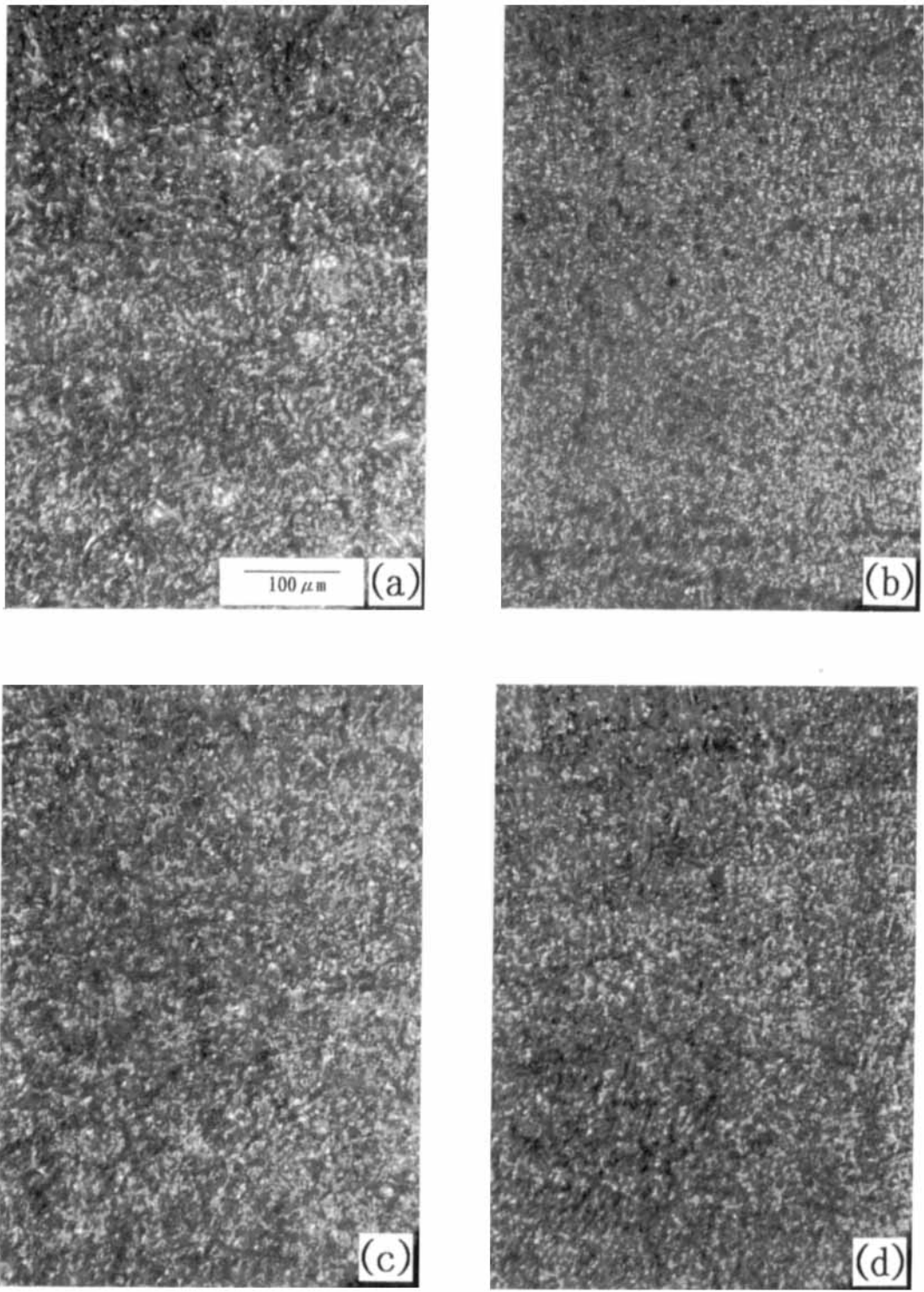
CONCLUSIONS

On the basis of POM and SEM observations and CD measurement, the process proposed in this study



(A)

Figure 8 Effect of heat treatment at 90°C for 48 h on textures of free surface of HPC films crosslinked by glyoxal (A) and by glutaraldehyde (B); crosslinker concentration (wt %): (a) 0, (b) 3.0, (c) 5.0, (d) 10.0.



(B)

Figure 8 (Continued from the previous page)

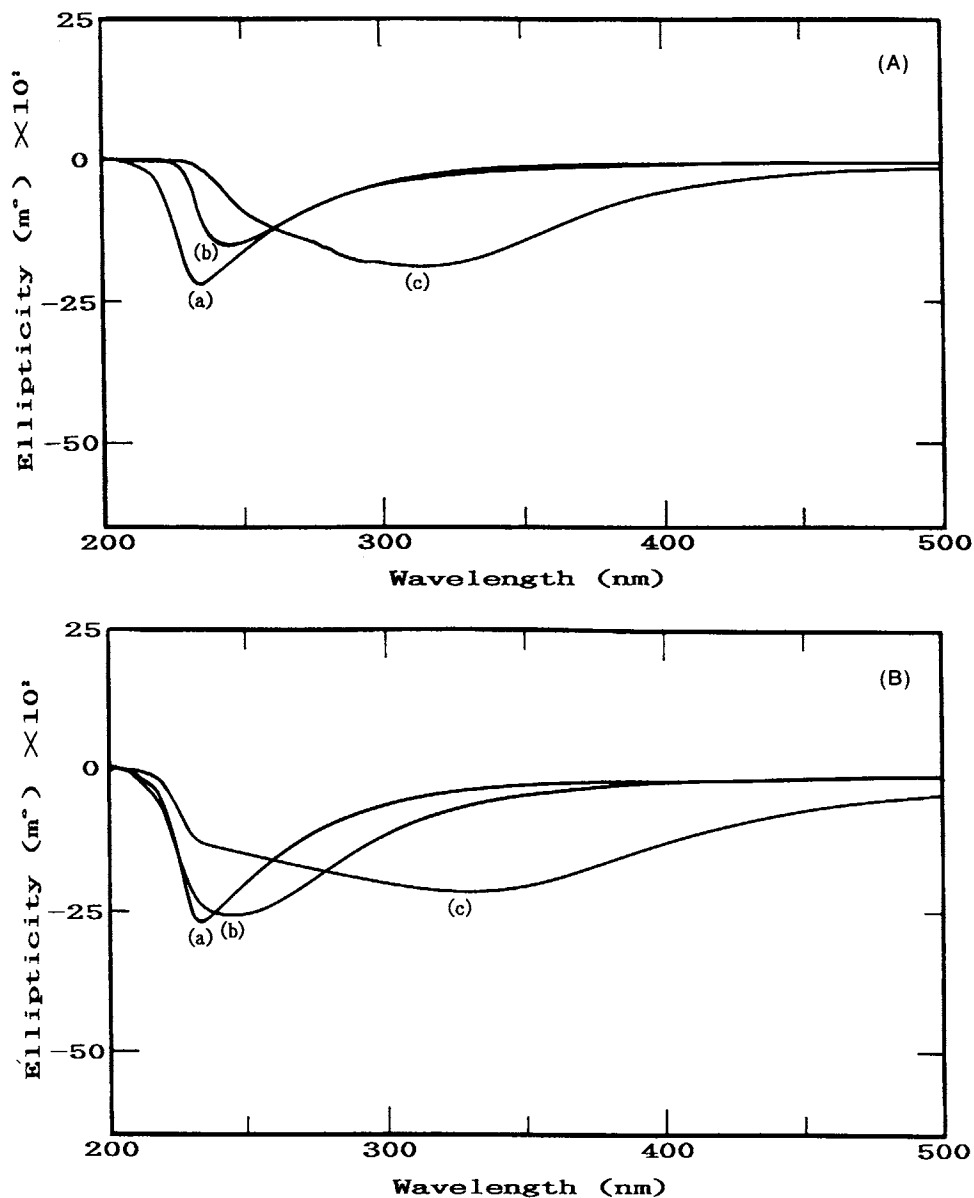


Figure 9 CD spectra for HPC films heat-treated at 60°C for 48 h, crosslinked by glyoxal (A) and by glutaraldehyde (B); crosslinker concentration (wt %): (a) 3.0, (b) 5.0, (c) 10.0.

Table I Gel Fraction for Crosslinked HPC Films

Crosslinker	Conc.		Gel Fraction (%)	
	(wt %)	(mol/g) × 10 ⁻⁴	As-cast	Heat Treatment
Glyoxal	3.0	3.53	91.1	95.0
	5.0	6.01	93.4	96.9
	10.0	12.76	94.7	98.0
Glutaraldehyde	3.0	2.57	89.5	92.8
	5.0	4.37	91.1	94.4
	10.0	9.25	93.0	96.3

was key for casting hydroxypropyl cellulose solid films retaining cholesteric liquid crystalline order. Before starting the cast process for preparing the solid films, we needed to store the cast solution in the same solvent-vapor atmosphere as the solution system for a given time. With increased storing time, the shear-induced band texture and wrinkled texture vanished and the cholesteric liquid crystalline order became stable. When the resultant cast films were heat-treated, the liquid crystalline order increased and the crosslinking proceeded. The effect of heat treatment on the liquid crystalline order seemed to depend on the crosslinker concentration.

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Received April 11, 1994

Accepted July 20, 1994