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Self-colored crosslinked cholesteric liquid crystalline solid films of hydroxypropyl cellulose

S. SUTO
Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Bunkyou 3, Hirosaki, 036-8561, Japan
E-mail: ssuto@cc.hirosaki-u.ac.jp

S. HASEGAWA
Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonezawa, 992-8510, Japan

Solutions of lyotropic cholesteric liquid crystalline hydroxypropyl cellulose (HPC) in water were self-colored due to the selective reflection of visible light, depending on the solution concentration. It was attempted to apply colored coatings of the liquid crystalline aqueous HPC solutions. HPC solid films were cast from the liquid crystalline solutions at different conditions and the color of the films was controlled. The cast films were chemically crosslinked. The crosslinked cast films were self-colored blue, yellow, or orange, but not red. Circular dichroism study of the cast films revealed that some films exhibited the peak wavelength in the red region of visible light. Scanning electron microscopy also showed that some films had the cholesteric pitch corresponding to the red region of visible light. However, colorimetry of the films indicated that no red films were prepared. This may be due to the highly varied distribution of the pitch. Some problems for applying the HPC liquid crystalline solution as colored coatings still remained open.

1. Introduction

It is widely known that many cellulose derivatives form cholesteric liquid crystals at suitable conditions [1, 2]. The cholesteric liquid crystals are usually characterized by a pitch. Interestingly, when the pitch is within the visible region of light wavelength, the cholesteric liquid crystals are colored blue, yellow, or red, depending on the pitch. In lyotropic cholesteric liquid crystalline solutions, the pitch depends on the solution concentration. Consequently, the color of the liquid crystalline solution could be controlled by changing the solution concentrations [3]. If such colored solutions were cast to form solid films, and if the cholesteric pitch of the solutions were retained, the resulting solid films would be colored, due to the selective light reflection. Such films contain neither dyes nor pigments. Therefore, no mixing process is required before casting and the films have a simple composition and are structually simple.

Cellulose and its derivatives are natually occuring polymers and are abundant and totally biodegradable. Some cellulose derivatives have been used as a lacquer for coatings. However, to the knowledge of the authors, no application of cellulosic liquid crystals as coatings has been tried.

In this study, we attempt to apply the cellulosic liquid crystals as colored coatings. As typical cellulosic cholesteric liquid crystalline solutions, aqueous hydroxypropyl cellulose (HPC) solutions were prepared with different concentrations. The solid films were cast from the liquid crystalline solution with various conditions (initial concentration of the solution, crosslinker type and concentration, casting temperature, and HPC molecular weight) on a glass plate. The pitch of the cast films was determined by means of circular dichroism (CD) and scanning electron microscopy (SEM) and the color of the films was measured by means of colorimetry.

HPC is water-soluble. This is a weak point for applying HPC as coatings. Therefore, the cast films were chemically crosslinked [4, 5].

2. Experimental

2.1. Samples

HPC ($M_w = 11.7 \times 10^4$, $M_n = 5.3 \times 10^4$, molar substitution 4.25, Tokyo Kasei Kogyo Co. Ltd.), glutaraldehyde (GA), p-formaldehyde (PFA) (Tokyo Kasei Kogyo Co. Ltd.), dimethyrolthiourea (DMTU) (Wako Pure Chemical Industry Ltd.), hydrochloric acid (HCl) and sodium hydroxide (NaOH) (Kanto Chemical Co. Ltd.) were used without further purification. Distilled water was prepared in our laboratory.

2.2. Preparation of liquid crystalline solutions

A given weight of HPC was added to distilled water and was mixed with glutaraldehyde as a crosslinker and with hydrochloric acid (2 wt%) as a catalyst for ca. 20 min. at 20°C. The mixed solution was degassed using a centrifuge. The concentrations of the solution were 50–64 wt%. The critical concentration of our aqueous system at which the liquid crystalline phase first forms was 43.3 wt% at 25°C.

2.3. Preparation of solid films

The crosslinked films retaining cholesteric liquid crystalline order were cast on a glass plate mainly at 40°C according to the previously outlined procedure [6]. The cast films were stored in a desiccator over silica gel at room temperature.

2.4. Circular dichroism (CD) study

CD spectra of the crosslinked films were determined with a Jasco J-40S spectropolarimeter (Japan Spectroscopic Co.). The pitch (P) was estimated by using the Equation [7], as follows;

$$\lambda = n \times P \qquad (1)$$

where λ is the peak wavelength, n is an averaged refractive index.

2.5. Scanning electron microscopy (SEM) observation

The fractured planes of crosslinked films were observed with a scanning electron microscope JSM 5300 (Nipon Denshi Detam Ltd.).

2.6. Colorimetry

The color of the crosslinked films was measured with a spectrophotocolorimeter CM 508i (Minoluta Co. Ltd.) at 20°C and 60% R.H. The light source was type D_{65}. The background for the measurements was a black film ($X: 2.42, Y: 2.54, Z: 2.77$). In our colorimetry, the CIE 1931 color matching functions and CIELAB (L*a*b*) color space were used.

3. Results and discussion

In our crosslinking systems (GA or p-FA with HCl, and DMTU with NaOH), all cast films were insoluble in water and proved to be crosslinked. Strictly speaking, the p-FA or DMTU concentration needed to be over 1.5 wt% to obtain insolubility of the crosslinked films.

3.1. HPC/GA/HCl system

3.1.1. CD study of the films

3.1.1.1. Effect of GA concentration. Fig. 1 shows the CD spectra for the crosslinked HPC films cast from the solution of the initial concentration: 54 wt%. The initial concentration of HPC solution and the concentration of GA are abbreviated as [HPC] and [GA], respectively. Basically, our crosslinked films exhibited a negative peak at a given wavelength (λ). This indicated that our crosslinked films retained a right-handed cholesteric liquid crystalline order. The peak wavelength tended to shift to a longer wavelength with increasing GA concentration. Furthermore, the peak area tended to broaden with increasing GA concentration. Using Equation 1, we can estimate the values of P from the values of λ and n for each crosslinked film. We used the estimated values of n [8]. The estimated values of P will be shown later with the data of P estimated from the SEM observation.

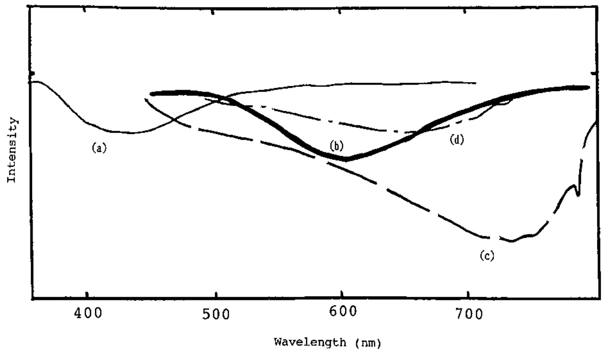


Figure 1 CD spectra for crosslinked HPC solid films cast from system with GA; [HPC] (wt%) : 54, [GA] (wt%) : (a) 8, (b) 10, (c) 12, (d) 14.

Interestingly, a few crosslinked films exhibited a positive peak around the similar wavelength region as the negative peak, irrespective of concentration and type of crosslinkers. In this study, the data for the positive peak were not shown.

3.1.1.2. Effect of HPC initial concentration. The cholesteric pitch depends on the concentration of the liquid crystalline solution; the pitch decreases with increasing concentration. In this study, the crosslinked films were cast using different concentrations of liquid crystalline solutions (here we define the concentrations as initial concentrations). Fig. 2 shows the CD spectra for the crosslinked films cast from the solutions of the 52 and 50 wt% initial concentrations. When those data were compared at the same GA concentration with the data for the films cast from the solutions of the 54 wt% in Fig. 1, the peak wavelength tended to shift to longer wavelength with decreasing initial concentration. The peak area tended to broaden with increasing initial concentration. In Fig. 3, the effects of GA concentration and initial concentration on the peak wavelength were summarized. This figure qualitatively suggested that relatively smaller peak wavelength was obtained at lower GA concentration and lower initial concentration and relatively greater peak wavelength was obtained at higher GA concentration and lower initial concentration.

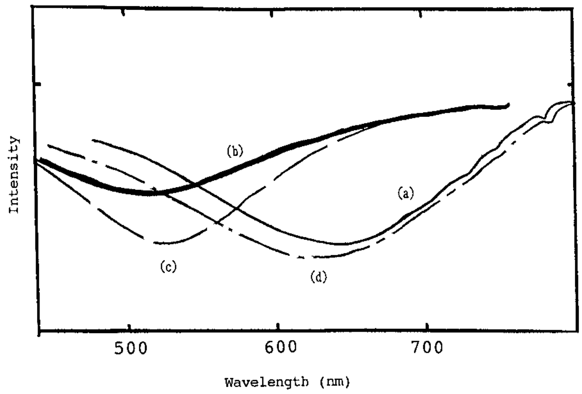


Figure 2 CD spectra for crosslinked HPC solid films cast from system with GA; [HPC] (wt%) : 52 (a, b), 50 wt% (c, d), [GA] (wt%) : (a, c) 10, (b, d) 12.

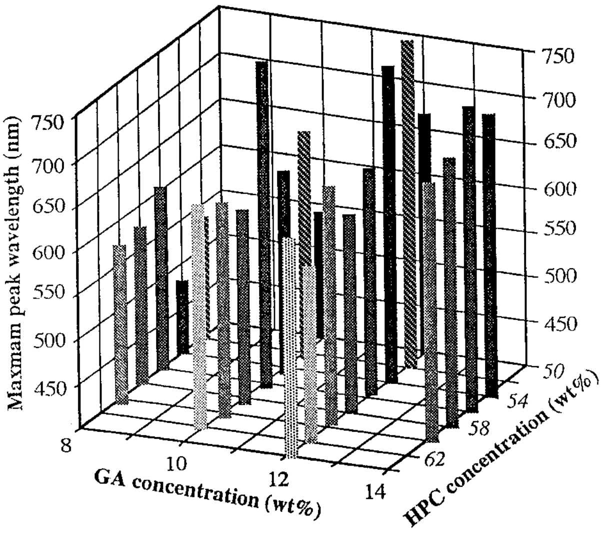


Figure 3 HPC initial concentration and GA concentration dependences of peak wavelength for CD spectrum.

3.1.1.3. Effect of casting temperature. The data shown above were obtained from the films cast at 40°C. The casting temperature was changed to 25 or 8°C. Fig. 4 shows the CD spectra for the crosslinked films cast at 25 or 8°C from the different initial concentrations. Compared with the CD spectra shown in Fig. 2, the peak wavelength tended to shift to lower wavelength with increasing casting temperature, except for the case of the initial concentration, GA concentration, casting temperature (50 wt%, 10 wt%, and 25°C). This suggested that casting at lower temperature was suitable for obtaining crosslinked films with higher peak wavelength in the CD spectrum.

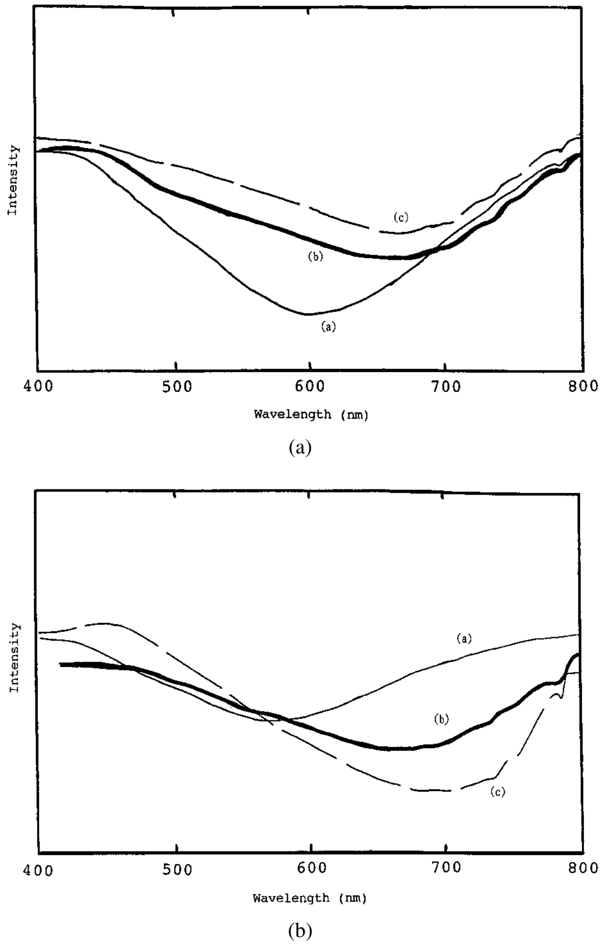


Figure 4 (a) CD spectra for crosslinked HPC solid films cast from system with GA at 25°C; [HPC, GA] (wt%): (a) 50, 10 (b) 50, 12 (c) 50, 14 (d) 52, 14. (b) CD spectra for crosslinked HPC solid films cast from system with GA at 8°C; [HPC, GA] (wt%): (a) 50, 10 (b) 50, 12 (c) 52, 14.

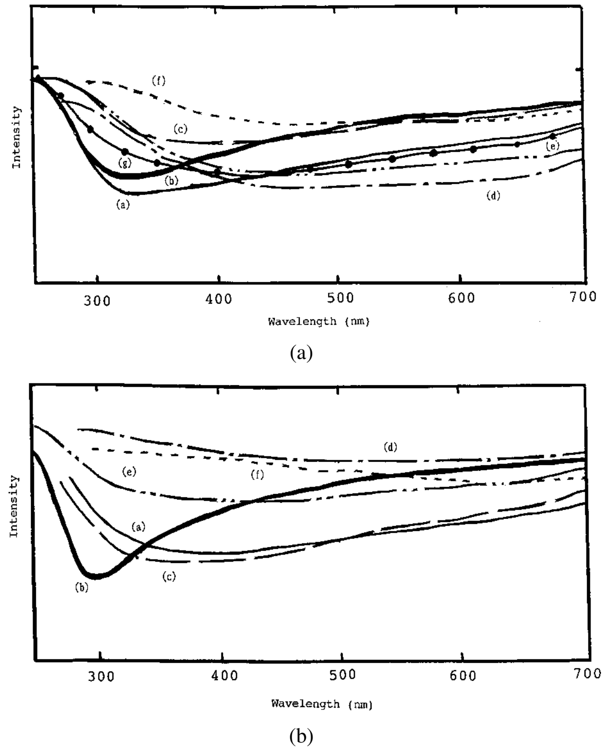


Figure 5 (a) CD spectra for crosslinked HPC solid films cast from system with 10 wt% of GA at 40°C (a, d), 25°C (b, e, g), 8°C (c, f); [HPC] (wt%): 20 (a–f), 10 (g); M_w: 50 × 10^4 (a, b, c, d), 69 × 10^4 (d, e, f). (b) CD spectra for crosslinked HPC films cast from system with 10 wt% GA at 40°C (a, d), 25°C (b, e), 8°C (c, f); [HPC] (wt%) : 30; M_w : 50 × 10^4 (a, b, c), 69 × 10^4 (d, e, f).

3.1.1.4. Effect of HPC molecular weight. The dependence of the pitch on the molecular weight of HPC is not clear experimentally for the cellulosic liquid crystals. However, we can suppose that the pitch decreases with the molecular weight at the same concentration. Here, we used other HPCs with M_w of 50 × 10^4 or 69 × 10^4. Those HPCs were not soluble over 50 wt% with ease and the initial concentrations for those HPC solutions were 10 wt%–30 wt%. Fig. 5 show the CD spectra for the higher molecular weight HPC solutions. The peak for each film was very broad and tended to become broader as the molecular weight increased. When the initial concentration was lower than the critical concentration at which the liquid crystalline order first formed, the liquid crystalline order could not form and remain in the cast films with ease.

3.1.2. SEM observation of the films

Fig. 6 shows a SEM image of a fractured edge of the same crosslinked films as used for determining the CD spectrum. A typical layered texture was observed for the crosslinked films retaining a cholesteric liquid crystalline order. Generally, twice the spacing of the

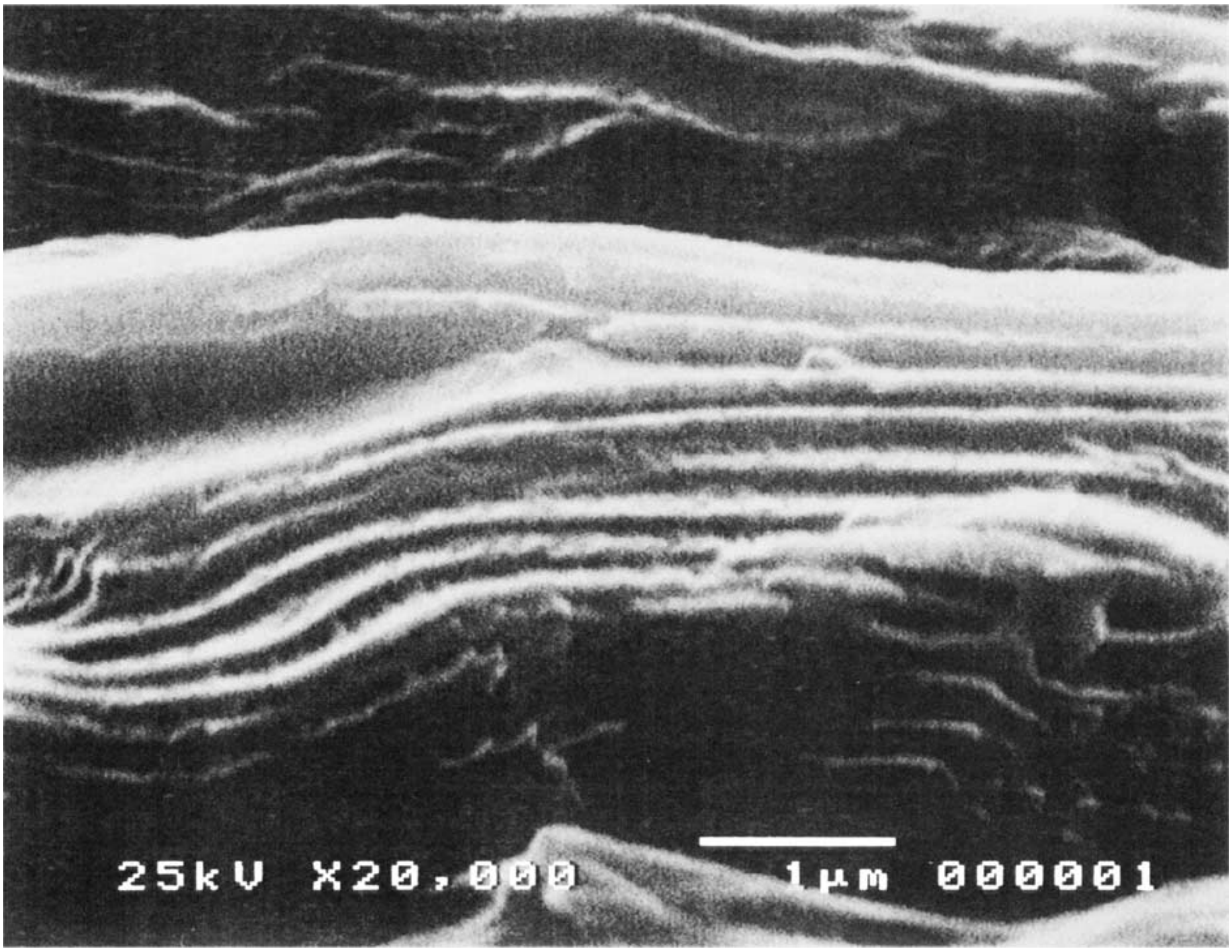


Figure 6 Scanning electron microphotograph of the fracture plane for crosslinked HPC film.

TABLE I The values of cholesteric pitch from CD study and SEM observation

[HPC] (wt%)	[GA] (wt%)	*P* (nm) CD	*P* (nm) SEM
54	10	434	395
56	10	528	418
	12	450	443
58	12	428	425
	14	484	460

striations is the pitch. This was confirmed by comparing the data for the pitch determined by means of the CD study and SEM observation in Table I. The pitches estimated by CD study were somewhat greater than those by SEM observation. As clearly shown in Fig. 6, the laminated striations were bent and were heterogeneous. This corresponded to the broad peak area of the CD spectra shown in Figs 1–5.

3.1.3. Colorimetry of the films

Fig. 7 show the *XYZ* and L*a*b* chromaticity diagrams for the crosslinked HPC films. Dots in figures show our films. Our films had a blue, a yellow, or an orange color. Expressed in terms of color tone, our films were dull. Although the films were cast with various conditions (temperature, etc.), the color and tone of the resulting films were similar with those shown in Fig. 7. As described above, the peak wavelength of the CD spectrum for some films tended towards the red portion of the visible region. However, our colorimetry data indicated that we could not prepare red colored crosslinked films.

3.2. HPC/PFA/HCl system

HPC could be crosslinked with PFA under an acid condition [4, 5]. Fig. 8 shows the CD spectra for the crosslinked films. The trends observed for the PFA system were almost the same as those observed for the GA system. Comparing the data for the GA and PFA systems, the peak wavelength for the GA system tended to be greater than that for the PFA system. Colorimetry revealed that the crosslinked films with PFA were duller than the films with GA as shown in Fig. 9.

3.3. HPC/DMTU/NaOH system

The crosslinked films cast from this system exhibited similar trends for the CD spectrum to those from the other two (GA, PFA). The chromaticity diagram suggested that the dullness of the films cast from the DMTU system was almost the same as that of the films cast from the PFA system.

4. Our proposals for coating application

4.1. Long relaxation process

One of the most intrinsic features for polymeric liquid crystals is the very long relaxation time [9]. During the relaxation process, polymeric liquid crystals exhibit a so-called band texture [10–12]. Therefore, when we intend to apply an equiliburium texture of the cholesteric liquid crystals as a coating, a major problem in the coating process is how to settle the long relaxation time.

In our previous paper [6], we determined the relationship between the texture of HPC crosslinked cast film and the casting conditions and proposed a storing process for the liquid crystalline solution before starting the casting process; the liquid crystalline solution was sheared on the glass plate and the sheared solution was stored in the same solvent-atmosphere as the solution system for a given time. With increasing storing time, the cast films exhibited a sharp CD peak and a short wavelength for the the CD peak. Our finding suggested that we need at least 24 h for the cast film to retain the equilibrium cholesteric liquid crystalline order.

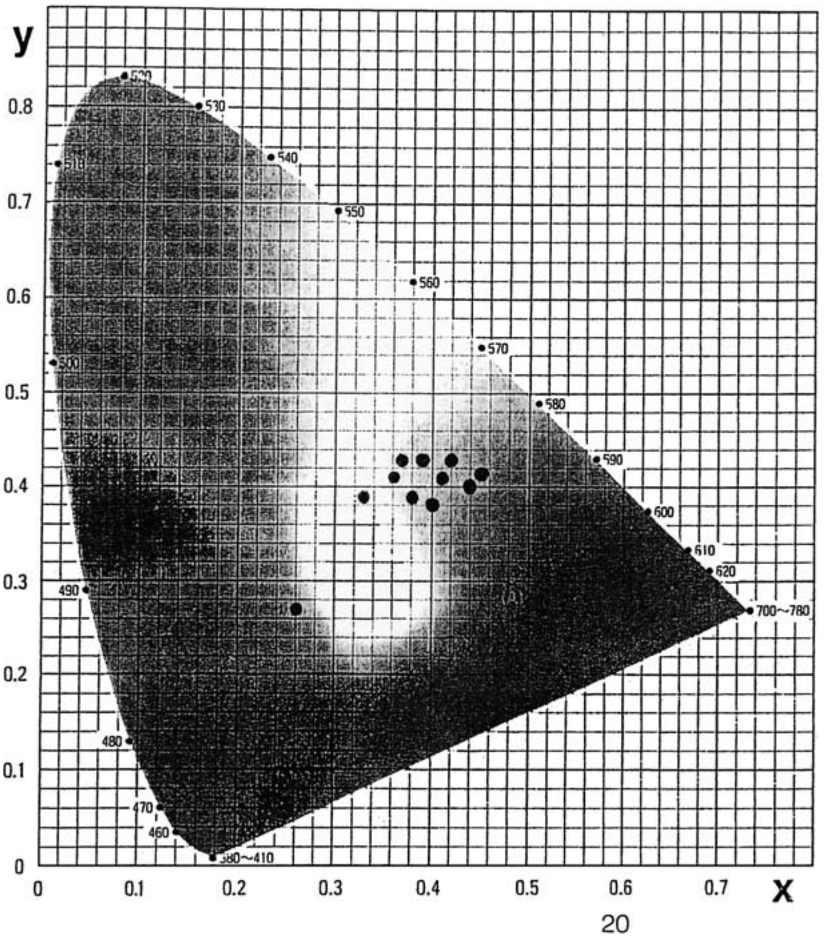
In another paper [13], however, we determined that the HPC cholesteric liquid crystalline solutions do not have as long a relaxation time as previously supposed; the relaxation times for the liquid crystalline solutions were of the order of several hundred seconds. The band texture formation or disappearance takes a significant time. The latter time depended on the shear rate and decreased with increasing shear rate. The time at relatively high shear rates was of the order of several 10s of seconds.

Our findings suggested that the relaxation times of cellulosic cholesteric liquid crystalline solutions were not as long as generally accepted and the relaxation greatly depended on the casting conditions (solution concentration, solvent, and shearrate). More or less, the storing process of the liquid crystalline solution after shearing was needed.

4.2. Clearly colored coating

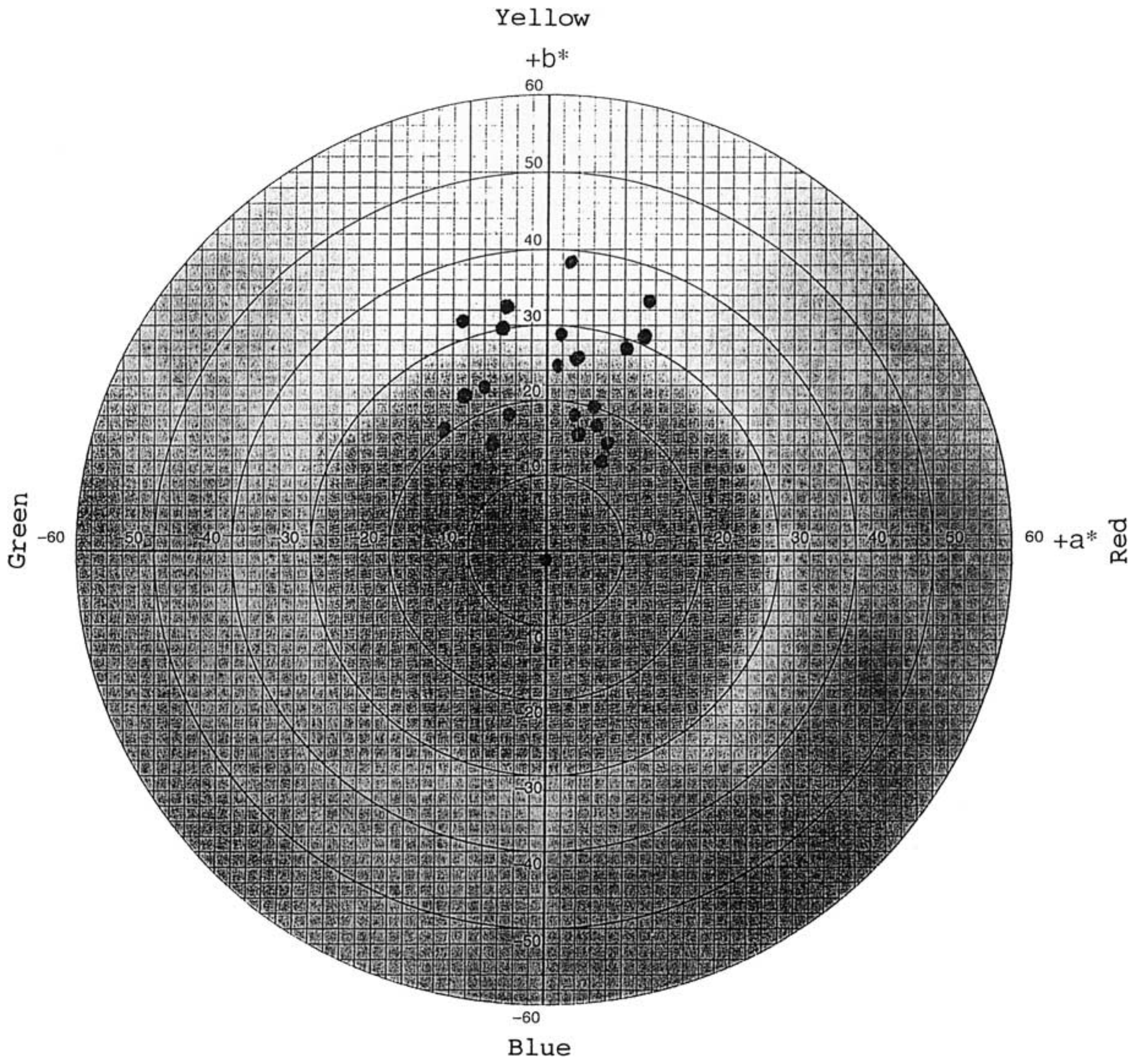
In this study, we could obtain no clear red films. This clearly showed that we could not control the pitch within the red region of light wavelength. Some cast films exhibited the CD peak wavelength in the red region. However, the color of such films was orange, judging from the colorimetry data. This may be due to the broad CD peak area. One of the causes for the broad area is attributed to the great molecular weight distribution of the HPC sample used in this study. The ratio of M_w/M_n for our HPC was about 2.2. After fractionating the HPC sample, we should be able to obtain cast films which exhibit a sharp CD peak.

Another cause for the broad CD peak is the heterogeneity of the pitch, clearly observed by means of SEM, as shown in Fig. 6. When we can cast films which



(a)

Figure 7 (a) *XYZ* chromaticity diagram for crosslinked HPC films cast from system with GA. Dots in figure show our films. (b) L*a*b* chromaticity diagram for crosslinked HPC films cast from system with GA. Dots in figure show our films. (*Continued.*)



(b)

Figure 7 (*Continued*).

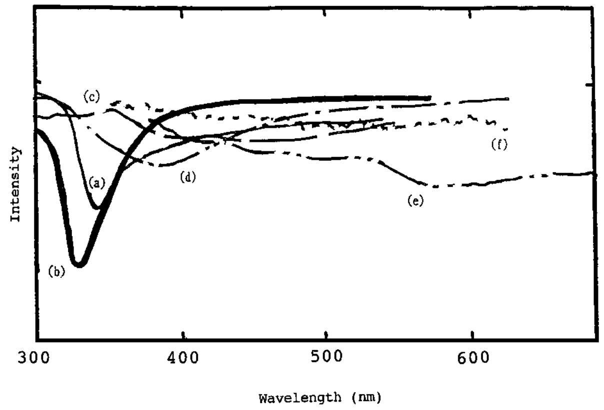


Figure 8 CD spectra for crosslinked HPC films cast from system with PFA at 40°C; [HPC] (wt%) : 50 (a–d), 55(e, f); [PFA] (wt%) : (a, b) 1, (c, d, e) 1.5, (f) 2.

exhibit clear laminated striations with no bending, we can obtain films with a sharp CD peak. The resulting films are expected to have not only controlled hue, but also the value and chroma.

4.3. Adhesion of the liquid crystals coating to glass

We have not determined quantitatively the adhesion between the HPC films and glasses or metals. After our casting process, the crosslinked HPC films have to be peeled from the glass plate. The peeling was not easy and needed some skills. This means that the HPC films can not peel spontaneously from the glass even with no pretreatments. HPC is widely known to be soluble in great many types of solvents [1]. When coating the liquid crystalline system on a given metal, the solvent is chosen which shows a suitable surface tension for the metal.

4.4. Removal of acid

In our chemical crosslinking process, hydrochloric acid was mainly used as a catalyzer. When we apply our crosslinked HPC films to coatings on metals, the metals will readily corrode with the acid included in the films. We can remove the acid from the HPC crosslinked films on the metals by soaking in water for a couple of hours.

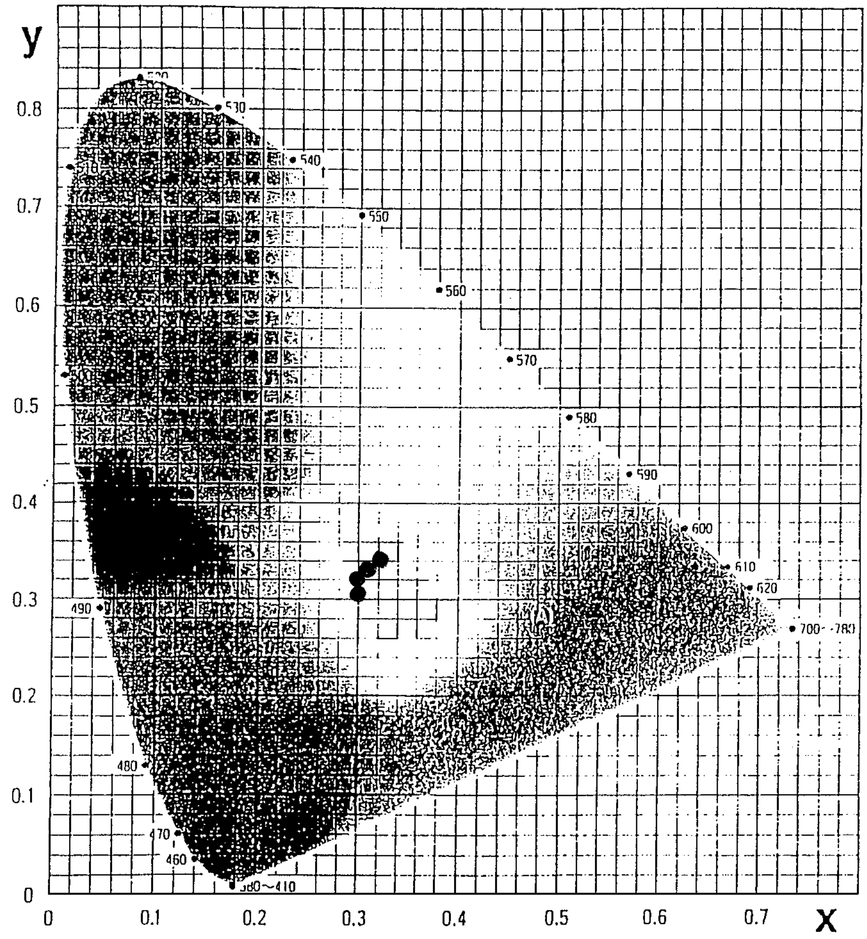


Figure 9 *XYZ* chromaticity diagram for crosslinked HPC films cast from system with PFA. Dots in figure show our films.

The acidic films can be neutralized in alkaline solvents. However, it must be kept in mind that such alkaline treatment for a long period breaks the crosslinking and results in the dissolution of the films [14].

5. Conclusions

The crosslinked cast films could be colored blue, yellow, and orange, by controlling the initial concentration of liquid crystalline solution, the crosslinker type and concentration, the casting temperature, etc, but not red. The CD study of the cast films revealed that some films exhibited the peak wavelength in the red region of the light wavelength. SEM observation also showed that some films had the cholesteric pitch corresponding to the red region of the light wavelength. However, the colorimetry of the films indicated that we could not prepare red colored films, because the CD peak was broad and the pitch distribution was wide. Some problems for applying our systems to the colored coatings still remained open: long relaxation time, dullness of the films, adhesion to metals, and removal of the acid catalyzer.

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