# *Crosslinked Hydroxypropyl Cellulose Solid Films Cast from Liquid Crystalline Solutions*

Cellulose and many cellulose derivatives form lyotropic liquid crystal at suitable conditions.[1] Cellulosic solid films exhibiting cholesteric liquid crystalline order could be prepared by casting from lyotropic liquid crystalline solutions.[2-4] From the technological viewpoint, it is more desirable that the cholesteric order in the solid films can be fixed. One of the methods of fixing the cholesteric order is a crosslinking process. There are, in general, two crosslinking processes: one process is $\gamma$- or UV irradiation on liquid crystalline solid films and another one is the use of chemical crosslinking agents. Gray et al.[5] have reported that the cholesteric liquid crystalline acrylic acid ester of hydroxypropyl cellulose could be crosslinked by UV irradiation. However, UV irradiation seems to cause main-chain scission, and the resultant films seem to be too brittle to determine any properties. Hence, we here choose the latter process: crosslinking with chemical crosslinking agents.

Hydroxypropyl cellulose (HPC) has been widely investigated because HPC could form lyotropic and thermotropic liquid crystals in aqueous and nonaqueous solutions and in the bulk.[1] However, liquid crystalline HPC solid films are not so important commercially, because those films are water-soluble.[3] When the crosslinking of the liquid crystalline HPC solid films can be performed with chemical crosslinking agents, the drawback of the HPC solid films can be eliminated.

It is well known that cotton can be crosslinked with formaldehyde (see, for example, Ref. 6) and epichlorohydrin (see, for example, Ref. 7). In this preliminary study, we try to fix the cholesteric liquid crystalline order of the HPC films with those crosslinking agents.

## EXPERIMENTAL

Hydroxypropyl cellulose (HPC) was of commercial reagent grade (Tokyo Kasei Kogyo Co. Ltd.). The weight-average and number-average molecular weights of the HPC determined in THF at 25°C by GPC were $11.7 \times 10^4$ and $5.2 \times 10^4$, respectively. The molar substitution of the HPC was 4.25 by the NMR technique according to the procedure proposed by Ho et al.[8] Before use, HPC powders were dried *in vacuo* at 60°C for about 24 h. All solvents used in this study (summarized in Table I) were of commercial reagent grade (Wako Pure Chemical Ind. Ltd.), except for deionized water (hereafter water), which was prepared in our laboratory. Hydrochloric acid (HCl) and NaOH were of commercial reagent grade (Wako Pure Chemical Ind. Ltd.). Commercial reagent grade *p*-formaldehyde (Kanto Chemical Co. Inc.) and epichlorohydrin (Tokyo Kasei Kogyo Co. Ltd.) were used as chemical crosslinking agents. All samples noted above were used without further purification.

Single anisotropic solutions (above $C_b$)[9] were prepared by storing in a refrigerator (ca. 7°C) for about 5 months and were then mixed with HCl (3.5 wt %) and *p*-formaldehyde (3.5 wt %) or with NaOH (3.5 wt %). The optimum conditions for crosslinking (content of acid or alkali and of crosslinking agent) were not determined here.

HPC solid films were cast from the single anisotropic solutions with both *p*-formaldehyde and HCl or with NaOH; those solutions were poured on a flat Teflon film, and solvent was allowed to evaporate for about 4 days in a laboratory atmosphere. The HPC solid films cast from aqueous alkali liquid crystalline solutions were treated with epichlorohydrin vapor at 80°C for 12 h or 6 days by use of the procedure similar to that proposed by Ferrante[7] ( Fig. 3 in his paper).

A Nikon polarizing optical microscope (POH) was used to observe anisotropic phases in the solutions on a glass plate in the course of casting (from single anisotropic solution through gel to solid film) in a laboratory atmosphere.

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Solubilities of the HPC solid films cast from each liquid crystalline solution (LCS) with *p*-formaldehyde or treated with epichlorohydrin vapor were investigated in both water and each solvent of LCS at room temperature (ca. 25°C). Extraction of the sol fraction of the HPC solid films was performed in boiling water using a Soxhlet apparatus. The extracted HPC films were dried *in vacuo* at 60°C for ca. 24 h, and the gel fraction was taken as the ratio of the weight of the extracted HPC film to the nonextracted one.

## RESULTS AND DISCUSSION

First of all, we need to note whether the chemical structure of HPC is altered by adding HCl to the LCSs of HPC or not. Lee and Perlin[10] and Clemett[11] have reported that hydroxypropyl substituent groups of HPC have not been affected by sulfuric acid and HCl treatments. In this study, the solid films cast from the LCSs in water with HCl (with no *p*-formaldehyde) was water-soluble at room temperature. This suggested that HCl (3.5 wt %) had no effect on the chemical structure of HPC. Nevertheless, HPC should be hydrolyzed somewhat with HCl. To check that hydrolysis of HPC with HCl, the 45 wt % aqueous solution of HPC with 10 wt % HCl was prepared and was kept in the refrigerator. By a polarizing microscopy, 3 weeks later, the solution was still liquid crystal; however, 2 months later, the solution was converted from the liquid crystal to isotropic solution. This means that the molecular weight of HPC decreased by the hydrolysis with HCl. Therefore, HCl must be removed from the cast films as possible as quickly after crosslinking is completed.

To the naked eye, the solutions of HPC in all solvents mixed with HCl and *p*-formaldehyde showed still faint iridescent colors. Furthermore, with polarized microscope, those solutions exhibited anisotropic textures. Thus, those clearly imply that the addition of HCl and *p*-formaldehyde into the single anisotropic solutions has little effect on the formation of liquid crystals within our experimental range of conditions.

Colorless HPC solid films could be cast from each LCS and exhibited some structure which seemed to be related to liquid crystalline order under polarized microscope. The key point in this study is whether the cast films are truly crosslinked liquid crystal or not. In what follows, we try to demonstrate that the cast films are liquid crystal first, and next to do that those films are crosslinked. When the LCSs were mixed with HCl and *p*-formaldehyde, the cholesteric structure of the single liquid crystals was temporarily disordered. Furthermore, when the LCSs were poured on the Teflon film, the LCSs were sheared; all LCSs used in this study exhibited a band structure, and the band structure ws gradually transformed into an equilibrium texture.[2,12,13] Thus, crosslinking should be performed after the liquid crystalline structure (the cholesteric one) is reformed.

To observe the liquid crystalline structure in the course of casting, the LCSs with HCl and *p*-formaldehyde were poured on a glass plate (not Teflon film). After couple hours, the aqueous LCS exhibited a globular texture[13] and the other LCSs exhibited a fingerprint-like texture[14]; those textures of the LCSs became fine and the distance between two adjacent fingerprint lines decreased with time, respectively. The ca. 90 wt % solutions (gel-like) exhibited still the fingerprintlike texture which is characteristic of cholesteric liquid crystals. However, the solid films did not exhibit that texture. This is because the distance between the fingerprint lines decreases with time (concentration) and finally becomes to be too narrow to detect by optical microscopy.

As noted above, all systems exhibited textures corresponded to each liquid crystal in the course of casting up to the ca. 90 wt % gel. This strongly suggests that the solid films used in this study are liquid crystal.

Next, we look at crosslinking of the cast films. Solubilities for the HPC solid films cast from each LCS are shown in Table I. In the case of *p*-formaldehyde, the HPC solid films cast from the LCSs in both water and monohydric alcohols were insoluble in both water and each alcohol at room temperature, whereas the HPC films cast from the LCSs in dimethylacetamide, dimethylsulfoxide, *m*-cresol, pyridine, morpholine, and acetic acid were easily soluble in water. The HPC solid films treated with epichlorohydrin vapor for 12 h or 6 days were easily water-soluble. Those findings clearly indicate that *p*-formaldehyde acts as the crosslinking agent in the presence of HCl for HPC/water and HPC/alcohol systems.

The ca. 90 wt % gels for HPC/water, HPC/methanol, HPC/ethanol, and HPC/benzyl-alcohol systems, which were liquid crystal as noted above, were peeled from the glass plate and were

TABLE I
Solubilities of Hydroxypropyl Cellulose Solid Films Cast from Each Liquid Crystalline Solution

| Crosslinking agent | Liquid crystalline solution | | Solubility[a] | |
|---|---|---|---|---|
| | Solvent | Concentration (wt %) | Water | Solvent[b] |
| *p*-Formaldehyde | Water | 45 | Insoluble | |
| | Methanol | 45 | Insoluble | Insoluble |
| | Ethanol | 50 | Insoluble | Insoluble |
| | Propanol | 50 | Insoluble | Insoluble |
| | Butanol | 50 | Insoluble | Insoluble |
| | Pentanol | 55 | Insoluble | Insoluble |
| | Benzylalcohol[c] | 40 | Insoluble | Insoluble |
| | Dimethylacetamide | 50 | Soluble | — |
| | Dimethylsulfoxide | 50 | Soluble | Soluble |
| | *m*-Cresol | 40 | Soluble | Soluble |
| | Pyridine | 40 | Soluble | — |
| | Morpholine | 40 | Soluble | — |
| | Acetic acid | 50 | Soluble | Soluble |
| Epichlorohydrin | Water | 45 | Soluble | |

[a]At room temperature (ca. 25°C).
[b]Solvent in each liquid crystalline solution.
[c]*p*-Formaldehyde concentration: 10 wt %.

determined those solubilities in water at room temperature; those gels could not dissolve. This clearly means that those gels are liquid crystal and crosslinked. Therefore, this is one of the strongest pieces of evidence supporting the crosslinked liquid crystalline structure of the solid films cast from LCSs in water and alcohols. However, there was no direct evidence for the crosslinked liquid crystalline solid films, and we must seek an unambiguous evidence.

Figure 1 shows the gel fraction for the HPC solid films cast from water and alcohol systems.

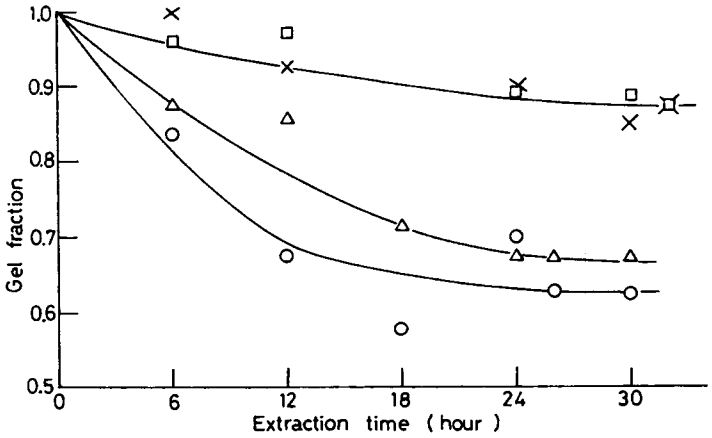


Fig. 1. Gel fraction vs. extraction time in boiling water for hydroxypropyl cellulose solid films cast from liquid crystalline solutions in water and alcohols; solvent in liquid crystalline solution: (○) water; (△) methanol; (□) butanol; (×) pentanol.

The gel fraction decreased with an increase in extraction time and finally levelled off. The levelled-off values of the gel fraction were 0.65–0.9 and were dependent on the solvent in the LCS. The gel fraction needed about 24 h to come to equilibrium. The extracted films were not so brittle, and we can determine the mechanical and other properties.

The mechanism of the crosslinking was not clear now, but was presumed to be similar to that for cotton.[6]

## CONCLUSIONS

From our observation by polarizing microscopy and our determination of solubilities of the HPC solid films cast from the LCSs with the crosslinking agent, the following have to be emphasized: (1) *p*-formaldehyde acted as the crosslinking agent in the presence of HCl for HPC/water and HPC/alcohol systems; however, epichlorohydrin did not in the presence of NaOH; (2) the gel fraction of the solid films needed about 24 h to come to equilibrium; (3) there is no direct evidence; however, HPC solid films cast from LCSs in water and alcohols with *p*-formaldehyde and HCl appeared to be crosslinked cholesteric liquid crystal.

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