Evidence for retaining crosslinked liquid-crystalline order in hydroxypropyl cellulose solid films by polarized microscopy

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Liquid-crystalline solutions of hydroxypropyl cellulose (HPC) in water or alcohols were mixed with *p*-formaldehyde (crosslinking agent) and hydrochloric acid (HCl, catalyst). HPC solid films were cast from those solutions, which were sheared, and fixing of the liquid-crystalline order was tried by chemical crosslinking. The texture of those solutions in the course of casting was observed by polarized microscopy and a solubility test of the resultant HPC cast films in water and alcohol was performed. Those liquid-crystalline solutions with or without *p*-formaldehyde and HCl formed a band texture after cessation of shear. This formation of the band texture is a characteristic of liquid-crystalline solutions. The band texture of aqueous solution decayed rapidly with time and finally changed to a globular texture, whereas the band texture of alcoholic solutions did not decay. The band or globular texture remained in the solid cast films. The HPC solid films cast from liquid-crystalline solutions with *p*-formaldehyde and HCl, which exhibited the band or globular texture, were insoluble in both water and alcohol. Our findings reveal that the liquid-crystalline order is perpetuated in the HPC solid cast films by crosslinking.

(Keywords: hydroxypropyl cellulose; cast film; polarized microscopy; solubility test; texture; cholesteric liquid crystal; crosslinking)

INTRODUCTION

Recently, much attention has been given to cellulosic cholesteric liquid crystals[1–3]. Hydroxypropyl cellulose (HPC) is the most popular cellulose derivative that forms cholesteric liquid crystals. However, HPC is not commercially important due to its high solubility in water[4,5]. In our previous paper[6], we tried to fix the cholesteric order of HPC liquid crystals by chemical crosslinking and reported that the HPC solid films cast from liquid-crystalline solutions in water or alcohols with *p*-formaldehyde and hydrochloric acid (HCl) appeared to be crosslinked. However, there was no direct evidence for fixing the cholesteric liquid-crystalline order in the HPC solid films by crosslinking. HPC is a crystalline polymer[4,7,8], hence, when HPC solid films are quiescently cast from liquid-crystalline solutions, it is difficult from only a polarized microscopic approach to judge whether the texture of the resultant cast films originates from the liquid-crystalline texture or the normal crystalline one.

In this paper, we will offer corroborative evidence for crosslinking of the liquid-crystalline phase of HPC from a polarized microscopic approach. It is well known that liquid crystals form a band texture perpendicular to the shear direction after cessation of shear[9–14], whereas isotropic solutions form no band texture. The band texture is one of the specific features to recognize the liquid-crystalline phase. Therefore, we intend to fix the band texture by chemical crosslinking. When the cast films exhibit the band texture and are insoluble in water or other solvents of HPC, it would be concluded that the resultant cast films retain crosslinked liquid-crystalline order. Then, the liquid-crystalline solutions of HPC in water or alcohols with *p*-formaldehyde and HCl were sheared on a glass plate and the texture formed after cessation of shear was observed using a polarized microscope in the course of casting. In order to compare the texture of liquid-crystalline solutions with *p*-formaldehyde and HCl, the same liquid-crystalline solutions without *p*-formaldehyde were also observed under the polarized microscope.

EXPERIMENTAL

Samples

Commercial reagent-grade HPC (Tokyo Kasei Kogyo Co. Ltd) was used. The weight-average and number-average molecular weights of HPC determined in tetrahydrofuran (THF) at 25°C by g.p.c. were 11.7×10^4 and 5.2×10^4, respectively. The molar substitution of HPC was 4.25 by the n.m.r. technique[15]. Before use, the HPC powder was dried *in vacuo* at 60°C for about 24 h.

Deionized water prepared in our laboratory (hereafter water) and commercial reagent-grade methanol, ethanol, propanol and butanol (Wako Pure Chemical Ind. Ltd) were used as solvents. Commercial reagent-grade *p*-formaldehyde (Kanto Chemical Co. Ltd) and hydrochloric acid (HCl, Wako Pure Chemical Ind. Ltd) were used as a chemical crosslinking agent and as a catalyst, respectively[16]. All samples noted above were used without further purification.

Preparation of single-phase anisotropic solutions

A sample of HPC of 10–20 g was weighed accurately into a glass-stoppered flask and a given amount of water or alcohol was added. The mixtures were stored in a refrigerator (~7°C) for about 5 months. The concen-

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tration of each solution was 45 wt% for water and methanol systems, and 50 wt% for ethanol, propanol and butanol systems; those solutions were single-phase liquid crystals at room temperature (~25°C)[17]. Hereafter, we conveniently define those solutions as starting liquid-crystalline solution (SLCS).

Preparation of solid films

The SLCS was mixed with *p*-formaldehyde and HCl by using a glass rod for ~10 min; in this process, the solution was contaminated by air bubbles, which were difficult to remove. The mixture was then poured onto a flat Teflon film and the solvent was allowed to evaporate for about 4 days in a laboratory atmosphere (~25°C). The resultant film was peeled from the Teflon film and stored in a desiccator at room temperature in the dark.

Solubility of solid films

Solid cast films of size ~800 μm thick × 1.2 cm wide × 1.2 cm long were soaked in both water and alcohol SLCS for 24 h at room temperature.

Extraction of sol fraction

The sol fraction of the solid films (size ~800 μm thick × 1.2 cm wide × 1.2 cm long) was extracted in boiling water for 24 h using a Soxhlet apparatus. After extraction for 24 h, the gel fraction came to equilibrium. The extracted films were dried *in vacuo* at 60°C for 24 h and the gel fraction was taken as the ratio of the weight of the extracted film to that of the non-extracted one.

Polarized microscopy of band texture

An Olympus microscope equipped with a camera was used to observe the liquid-crystalline texture in the solutions on a glass slide in the course of casting in a laboratory atmosphere (~25°C, relative humidity ~60%). Before use, the glass glides were cleaned with cotton wool soaked in acetone. Each glass slide containing a 60 μm deep cavity was prepared by two adhesive tapes placed parallel to each other on both sides of the glass slide. The sample solution was poured on the glass slide and shear was then applied by sliding a glass rod over the solution. The apparent shear rate was estimated by the ratio of sliding speed of the glass rod to cavity depth: $\sim 54\,s^{-1}$. The sheared solution was stored in a refrigerator (~7°C) and after the elapse of given times the texture of the solution was photographed (magnification × 150). In the water system, the texture was also photographed as soon as the shear had been ceased because the band texture of the water system began to decay and changed into a no-band texture in a few minutes[10,13].

The dried extracted gel films were observed. Furthermore, the solvent of the SLCS was added with a pipette to the dried extracted gel film and the resultant swollen gel film was also observed. For comparison of the band texture of the solution with and without *p*-formaldehyde and HCl, the texture of liquid-crystalline solutions without *p*-formaldehyde and HCl, i.e. SLCS, was also photographed.

RESULTS AND DISCUSSION

Liquid-crystalline solutions with no p*-formaldehyde*

First, we show the change of texture with time for the HPC/water system after cessation of shear. Takahashi *et al.*[9], Horio *et al.*[10] and Navard[13] have reported that the band texture of the HPC/water system has decayed in a few minutes. In fact, as shown in *Figure 1a*, these formed a band texture perpendicular to the shear direction immediately after cessation of shear. The shear direction is shown by the arrow in each figure. However, the band texture distorted with time (*Figure 1b*) and finally changed to a globular texture (*Figure 1c*). The globular texture was reported by other groups[10,13,18–22] and was typical for the liquid-crystalline aqueous solution of HPC. The globular texture of the solid film (*Figure 1d*) was the same as the texture of the liquid-crystalline solution (*Figure 1c*).

Figure 2 shows the band texture after cessation of shear for the HPC/ethanol system in the course of casting in the refrigerator. The arrows indicate the shear direction. All alcohol systems in this study exhibited the band texture clearly and the texture did not decay in our experimental range. The texture of the solid films was the same as that of the liquid-crystalline solutions immediately after cessation of shear. The similarity of the textures for the solid cast films and for the liquid-crystalline solutions clearly indicates that the liquid-crystalline order remains in the solid cast films irrespective of whether the band texture remains or not.

Liquid-crystalline solutions with p*-formaldehyde*

Figure 3 shows the texture after cessation of shear in the course of casting for HPC/water and HPC/alcohol systems with 3.5 wt% *p*-formaldehyde and 3.5 wt% HCl. The arrows show the shear direction. The band texture was formed for HPC/alcohol systems and remained in the solid cast films. Even in the case of the HPC/water system, the band texture was formed momentarily as described in *Figure 1a*. However, the texture disappeared within 1 h in a similar manner as the system without *p*-formaldehyde. In *Figure 3*, *p*-formaldehyde powder and air bubbles were present; however, their presence was not a serious problem for the formation of the band texture.

Comparison of *Figures 1, 2* and *3* reveals that the band texture for the HPC/alcohol systems and the globular texture for the HPC/water system with *p*-formaldehyde and HCl are the same as those for the systems without *p*-formaldehyde and HCl. This finding clearly indicates that the addition of *p*-formaldehyde and HCl to the liquid-crystalline systems has no distinct effect on formation of the band texture in our systems.

All films in this study were not soluble in both water and alcohol and the gel content of those films was ~90–100%, which was dependent on the solvent species of the SLCS.

In *Figures 3c, 3e* and *3g* we show the texture of the 100% gel films that were extracted in boiling water and followed by vacuum drying. The texture of gel films was the same as that of non-extracted films. We also show the texture of swollen gel films in *Figures 3f* and *3h*. The swollen gel films retained the band texture and the texture appeared to become rather looser than that for dried gel films. Those findings show that the liquid-crystalline order in the solid cast films is perpetuated by crosslinking. Furthermore, those findings strongly substantiate our previous finding[6] that HPC solid films cast quiescently from liquid-crystalline solutions in water and alcohols can be crosslinked and retain the liquid-crystalline order,

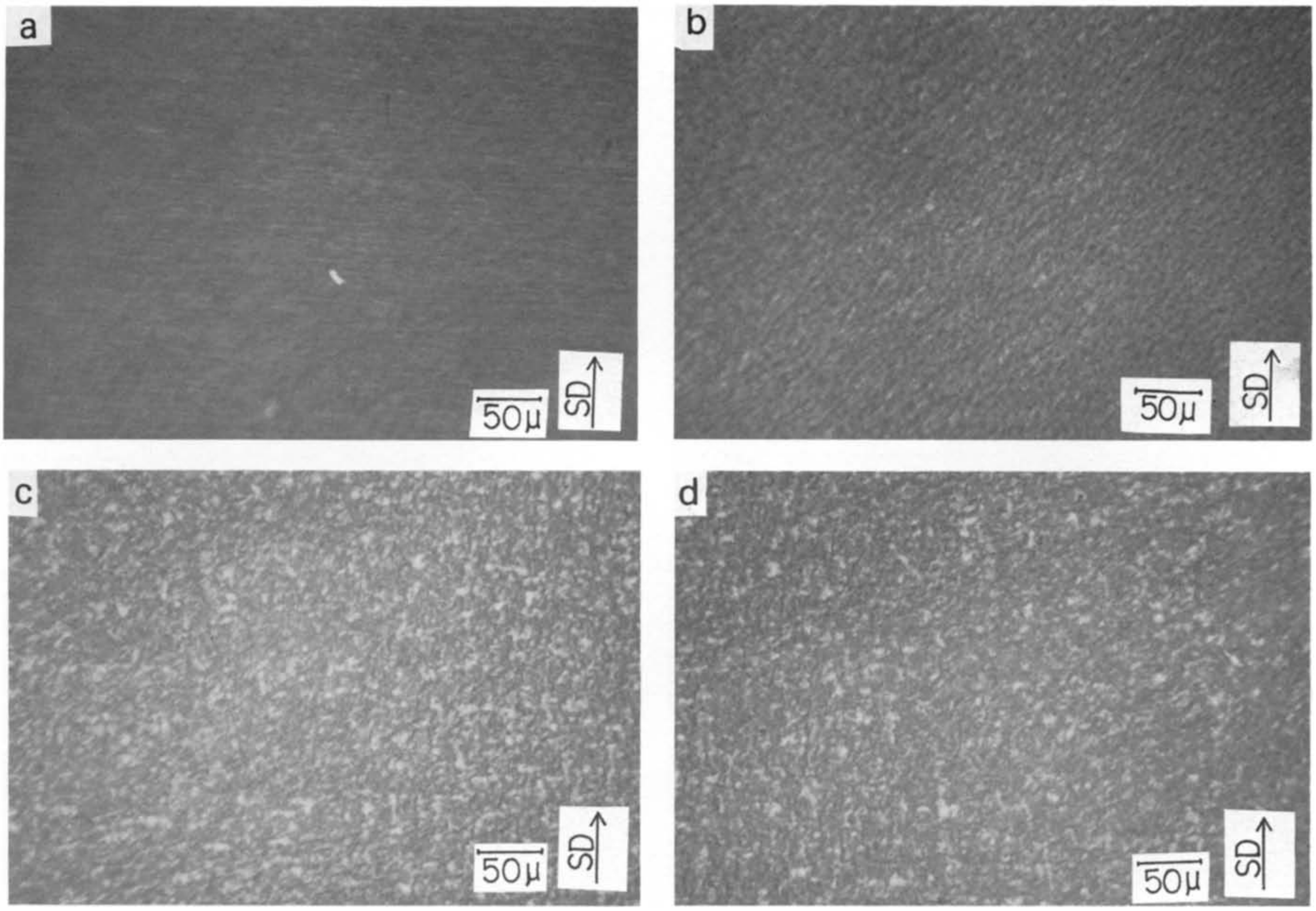

Figure 1 Texture change with time for aqueous liquid-crystalline solution of HPC. Time passed after cessation of shear: (a) 3 s; (b) 3 min; (c) 1 h; (4) 4 days, vacuum dried for 24 h at 60°C (solid film)

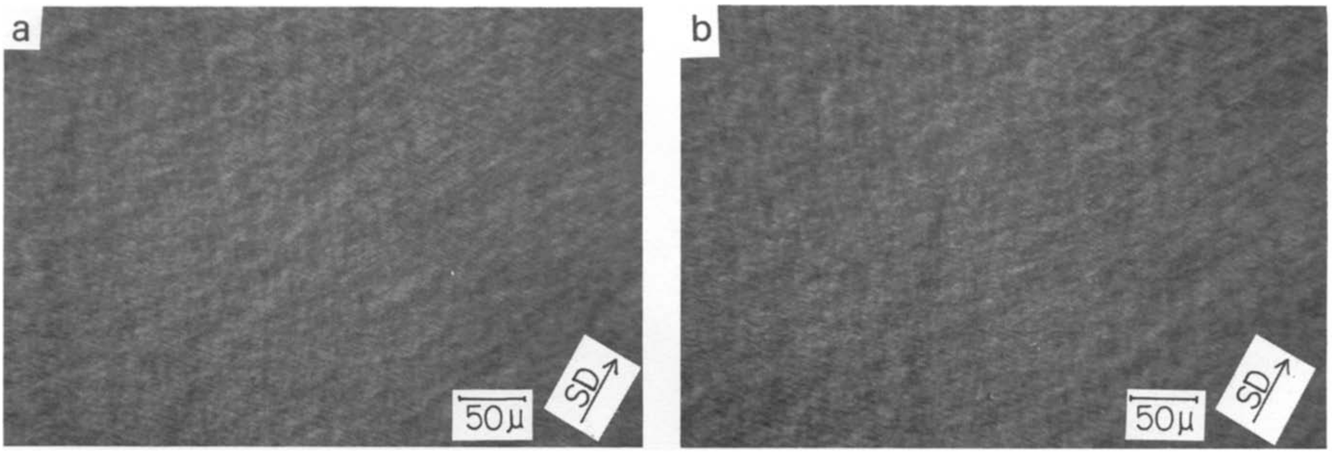

Figure 2 Band texture for liquid-crystalline solutions of HPC in ethanol. Time passed after cessation of shear: (a) 1 h; (b) 4 days, vacuum dried for 24 h at 60°C (solid film)

because the crosslinking reaction would not be affected by shearing; the crosslinking is performed after cessation of shear. In general, crosslinking is not performed in crystalline regions, but only in amorphous ones of crystalline polymers[23]. Liquid crystals are intermediate between crystalline and amorphous states and are not amorphous. However, Tanaka *et al.*[24–26] and Gray *et al.*[27] have already showed that cholesteric liquid crystals of polypeptides and cellulose derivatives were crosslinkable under suitable conditions. Therefore, the results given by us, Tanaka *et al.*[24–26] and Gray *et al.*[27] suggest that liquid crystals can be crosslinked provided an appropriate crosslinking agent or condition is chosen.

Cholesteric liquid-crystalline structure consists of a set of nematic layers, whose individual molecules are continuously twisted from one layer to the next. We just ascertained that the cholesteric liquid crystals of HPC can be crosslinked. However, it is uncertain that the crosslinking occurs at any site of hydroxy groups. Then, we need to make it clear whether intercrosslinking occurs between two adjacent HPC molecules in one layer or between the molecules in two adjacent layers. Further-

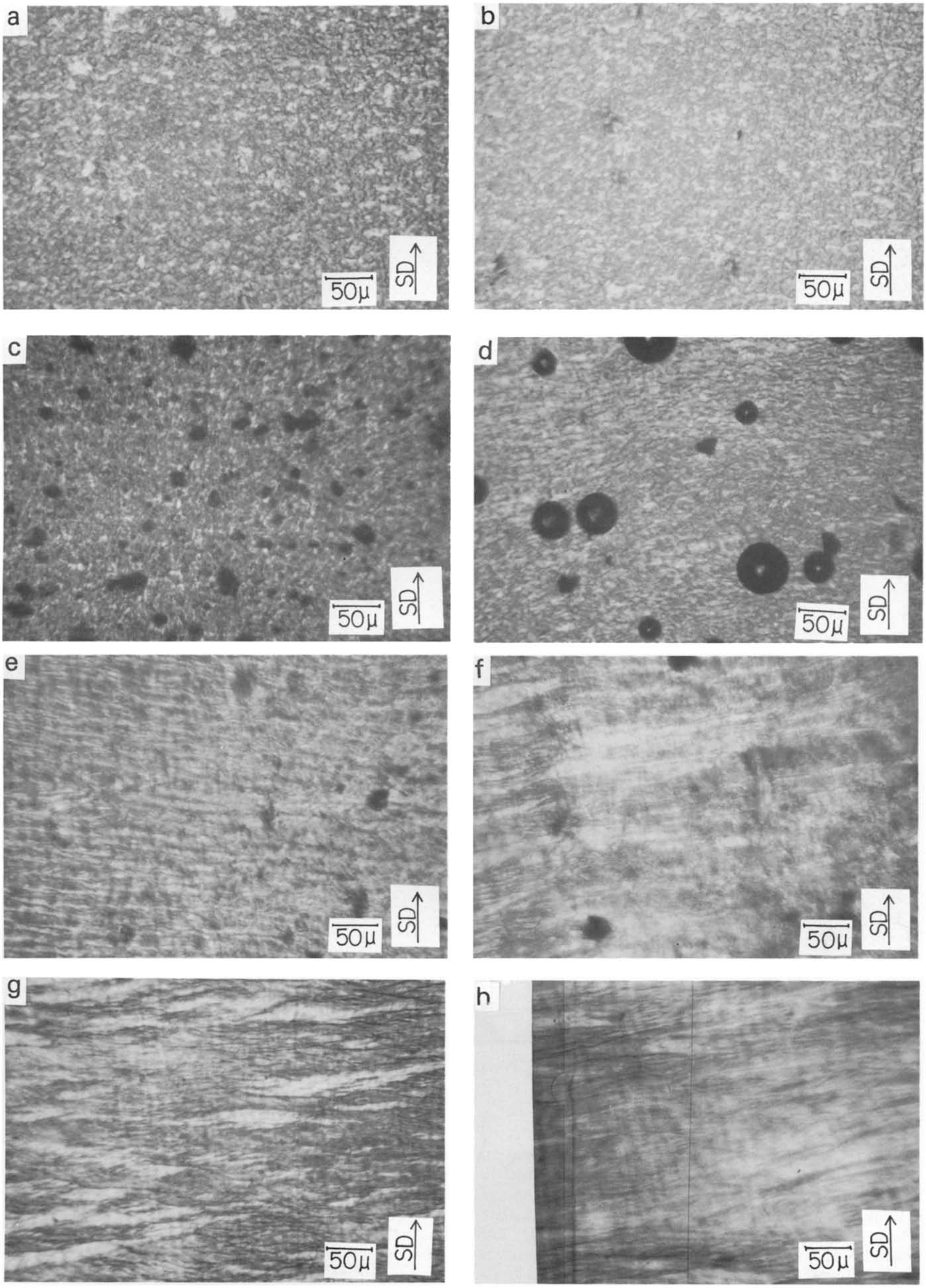

Figure 3 Texture for liquid-crystalline solutions of HPC in water and alcohols with 3.5 wt% *p*-formaldehyde and 3.5 wt% HCl. Solvent: (a)–(c) water; (d)–(f) ethanol; (g), (h) butanol. Time passed after cessation of shear: (a), (d), 1 h; (b) 4 days, vacuum dried for 25 h at 60°C (solid film); (c), (e), (g) extracted gel film, vacuum dried for 24 h at 60°C; (f), (h) swollen gel film

more, it must be noted that there is one problem for our crosslinked solid films to be improved. As shown in *Figure 3*, *p*-formaldehyde powder remains in the crosslinked gel. Nevertheless the gel was extracted in boiling water for 24 h. *p*-Formaldehyde powder acts as a contaminant when the films are applied to end use. Therefore, the powder must be removed from the films. To solve this problem, we are undertaking a solubility test of *p*-formaldehyde.

CONCLUSIONS

Liquid-crystallline solutions of HPC in water and alcohols with and without *p*-formaldehyde and HCl exhibited the band texture after cessation of shear. The solid films cast from alcohol systems retained the band texture, whereas the film cast from the waters system exhibited a globular texture. The texture of the solid films was the same as that of liquid-crystalline solutions. This means that those cast solid films retain the liquid-crystalline order. The solid films cast from water and alcohol systems with *p*-formaldehyde and HCl were insoluble in both water and alcohol. Those findings reveal that liquid-crystalline order in our films is perpetuated by crosslinking.

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