

Photoinitiated Crosslinking of Hydroxypropyl Cellulose in the Isotropic and Liquid Crystal States

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SYNOPSIS

The influence of temperature, concentration, and shear rate on the formation of liquid crystal solutions of hydroxypropyl cellulose (HPC) in DMAc and the preservation of the structure by photoinitiated crosslinking were investigated. The rate of changes in the relaxation pattern for the characteristic band texture of HPC liquid crystals after cessation of shear is inversely proportional to the extent of the crosslinking. This shows that the liquid crystalline structure is preserved upon crosslinking. The molecular orientation of the crosslinked films as a function of mesophase organization and concentration during crosslinking was studied.

INTRODUCTION

Hydroxypropyl cellulose (HPC) forms cholesteric liquid crystal solutions when dissolved in water and various organic solvents, as disclosed first by Werbowyj and Gray.¹ Since then, many researchers have reported on the rheological and optical properties of concentrated solutions of HPC as well as the mechanical properties of the films and fibers prepared under various conditions.²⁻⁹ HPC, however, has limited use as a film since it has high solubility in water, alcohols, and many other organic solvents.¹⁰

Due to their good immunological compatibility, mechanical properties, and dimensional stability, hydrophilic HPC liquid crystalline networks have potential applications as column packing materials for gel and biospecific chromatography, semipermeable membranes, and artificial organs. In order to keep a specific organization in the HPC films, we developed a photoinitiated crosslinking method using hexamethoxymethylmelamine as the crosslinker. The advantage of using photoinitiated crosslinking is that one has much better control of the gel formation process, since it can be started long after the crosslinker and catalyst are mixed in. It takes time to get uniform solution and to reach the equilibrium

liquid crystalline organization, and premature crosslinking prevents equilibration. As discussed below, the critical concentration of the formation of liquid crystals is a function of temperature. Much higher concentrations of HPC are needed to get crosslinked liquid crystalline films with heat-activated crosslinking reactions. HPC liquid crystalline solutions have also been crosslinked in our laboratory with other reagents such as diepoxides, diisocyanates, and dimethylolurea. This will be discussed in a separate report.

EXPERIMENTAL

Materials

Food Grade HPC (weight-average molecular weight 95,000) from the Aqualon Co. was used after drying *in vacuo* at 60°C for 24 h. Anhydrous *N,N*-dimethylacetamide (DMAc) (Aldrich) was used as received. Hexamethoxymethylmelamine (HMMM) (Pfaltz & Bauer Inc.), the crosslinking agent, and triphenylpyrylium trifluoromethanesulfonate (TPTS) (Lancaster Synthesis Ltd.), the cationic photocatalyst, were used without further purification.

Preparation of Films

Uncrosslinked films were cast on glass plates at room temperature from HPC/DMAc solutions of differ-

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ent concentrations. The crosslinked films were prepared as follows:

1. A stock solution of photocationic catalyst (4.76 wt %) in DMAc was made and stored in a brown bottle. Crosslinking agent in DMAc solution was made up as needed before use. To make the final solutions, an aliquot of the stock solution was mixed into the crosslinker solution and then mixed with HPC. The final concentration of photoinitiator was 0.65 wt % and the stoichiometric ratio of $\text{OH}/\text{CH}_2\text{OCH}_3$ was 9 in all of the experiments described below.
2. The solution was allowed to stand for 1 h in order to achieve uniformity and to eliminate most of the air bubbles.
3. The solution was then poured onto a Pyrex glass plate with a spacer (0.3 mm) and an upper glass plate was clamped over the lower plate containing the polymer solution.
4. After standing for 30 min, the samples were placed under UV radiation (GE UV lamp, 275 W; sample to lamp distance was kept at about 25 cm) for 4 h at room temperature.
5. The samples were postcured at various temperatures as needed.

Characterization

Viscosity measurements were performed using a Rheometrics RMS 800 dynamic mechanical spectrometer. The fixture used was cone and plate with

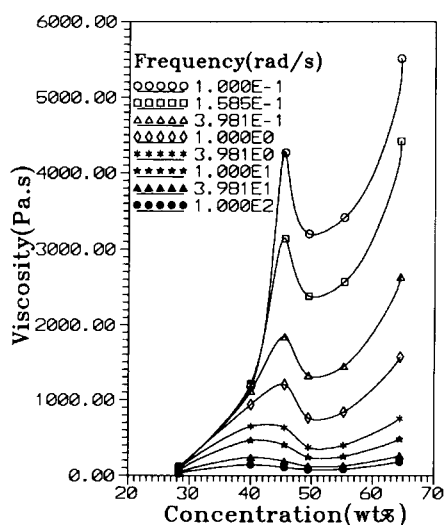


Figure 1 Viscosity vs. concentration at 30°C for HPC/DMAc solutions at various shear rates.

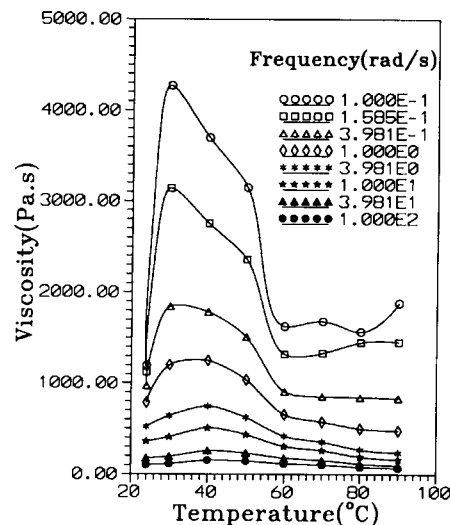


Figure 2 Viscosity of a 45.5 wt % HPC/DMAc solution vs. temperature at different shear rates.

a radius of 25 mm and a cone angle of 0.04 rad. Optical microphotographs were taken using a Carl Zeiss microscope equipped with cross-polarizer. When sheared samples were observed, the angle between the flow direction and polarizer was 45°. Swelling experiments were done at room temperature (about 25°C). Dried films were immersed in the swelling solvents for 48 h before final weight and dimensions were measured.

RESULTS AND DISCUSSION

The effect of temperature and shear rate on the liquid crystal formation of HPC/DMAc solutions at various concentrations was studied using the rheometer in a dynamic mode. Figure 1 shows the change in the viscosity with concentration at various shear rates. All the viscosity curves exhibit a maximum at concentrations between 40 and 50 wt %. The decrease in viscosity at higher concentrations can be attributed to a spontaneous orientation of the macromolecules forming a liquid crystalline phase. Increasing the shear rate lowers the viscosity and shifts the transition peak to lower concentrations, indicating an enhancement of the molecular orientation in the presence of a flow field. A similar tendency is observed in Figure 2 which shows the effect of temperature on viscosity at different shear rates for a solution of 45.5 wt % HPC in DMAc. While still in the mesophase and close to the transition point, the viscosity of the solution increases as the temperature increases. Once the transition temperature

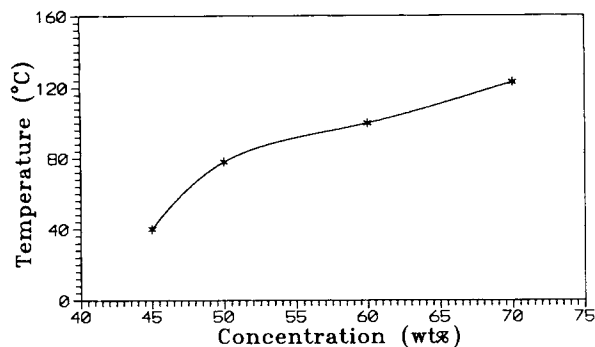


Figure 3 Correlation between critical temperature and concentration for solutions of HPC (MW = 95,000) in DMAc by cross-polarized microscopy.

is reached and the solution becomes isotropic, the viscosity decreases with temperature. In the presence of a flow field the solution retains anisotropy up to higher temperatures. Figures 1 and 2 indicate that at room temperature and low shear rates a solution of 45.5 wt % HPC in DMAc is at least partly in the mesophase. This result is also confirmed by cross-polarized microscopy. The birefringence of a 45.5 wt % solution was found to disappear at about 40°C under no flow conditions. Figure 3 shows the dependence of the critical temperature on concentration for hydroxypropyl cellulose in DMAc solutions.

In order to preserve the liquid crystalline order of the HPC solutions, they were crosslinked using a crosslinking agent (HMMM) and a photocatalyst (TPTS). Figure 4 shows the photographs for a dried film from a 50 wt % polymer solution crosslinked at room temperature. The optical properties remain the same from 30 to 180°C. The pattern darkens slightly when the temperature is raised to 220°C, which might be due to thermal degradation. As a comparison, the birefringence of a dried film cast without crosslinking from a 50 wt % HPC/DMAc solution disappears when the film is heated to 180°C (Fig. 5). Due to the thermotropic properties of HPC,¹¹ a film sheared at 180°C and then cooled to room temperature showed strong birefringence and band texture. The lack of change in optical properties for the cured film from 30 to 180°C demonstrates the fixing of liquid crystalline order by crosslinking.

It is well known that one of the characteristics of HPC liquid crystals is the formation of a band texture perpendicular to the shear direction after cessation of shear.^{12,13} For the uncrosslinked sample, the band texture decays rather rapidly into a random texture. Figure 6 shows the relaxation of the shear band texture for a 60 wt % HPC/DMAc solution containing crosslinking agent and photoinitiator which was not exposed to UV radiation. The apparent shear rate was about 40 s⁻¹, estimated from

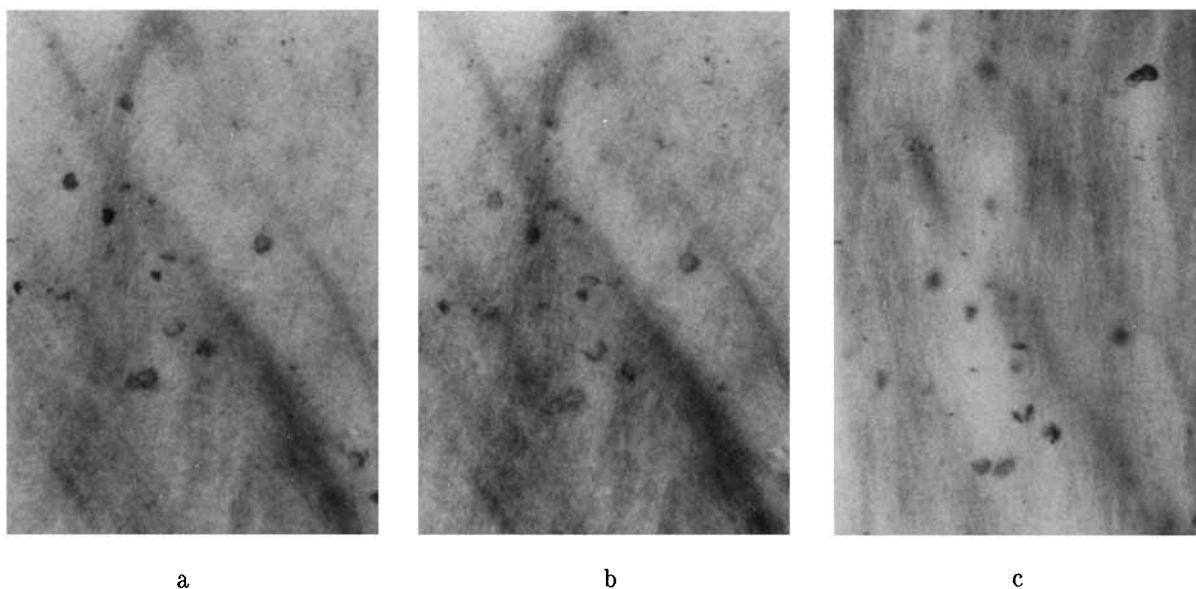


Figure 4 Cross-polarized OM pictures ($\times 110$) of a dried HPC/DMAc crosslinked film with original concentration of 50 wt %. Pictures were taken at: (a) 30°C; (b) 180°C; (c) 220°C.

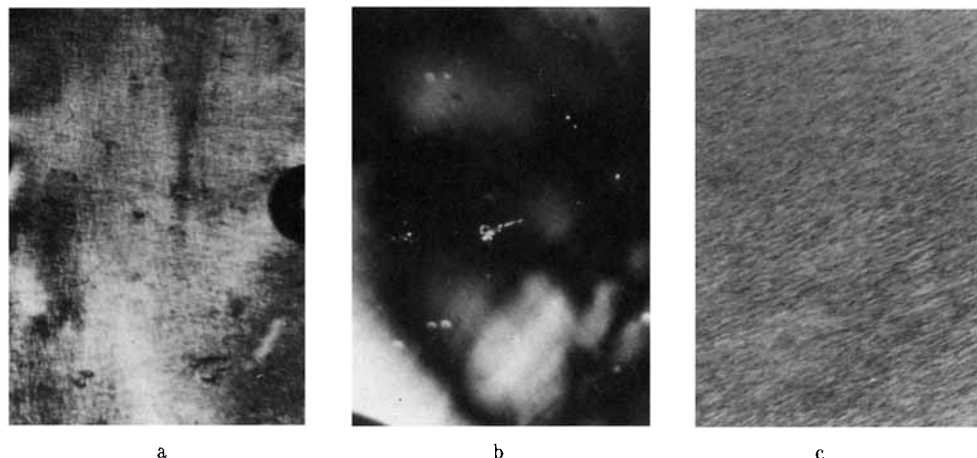


Figure 5 Cross-polarized OM pictures ($\times 110$) of a dried HPC/DMAc uncrosslinked film with original concentration of 50 wt %. Pictures were taken at: (a) 30°C; (b) 180°C; (c) cooled to 30°C.

the distance between the glass sheets and the speed of movement. Within 10 min, the pattern lost most of its band structure features and after 2 h no band structure remained. Samples with the same composition were exposed to UV for various times prior to shearing. Figure 7 shows the relaxation patterns for a sample exposed to UV radiation for 2 min. The relaxation process is much slower than that of the unirradiated sample. Even after 2 h, some band texture was retained. For a sample irradiated for 4 min, (Fig. 8) the band texture was preserved even 24 h after shearing. This further demonstrates the fact that the liquid crystalline structure is stabilized by the crosslinking. A sample exposed to UV light for

5 min prior to shearing showed much weaker shear band structure due to partial gelation of the solution.

For a given HPC liquid crystal solution, there is a critical temperature above which the organization disappears. The same sample can therefore be crosslinked in either the isotropic or mesophase by changing the curing temperature. Figure 9 shows cross-polarized photomicrographs for samples cured at room temperature and at 100°C from solutions with an initial concentration of 50 wt % HPC. The sample cured at room temperature shows birefringence, whereas the one crosslinked at 100°C does not, since the transition temperature at this concentration is about 80°C (Fig. 3). The isotropic

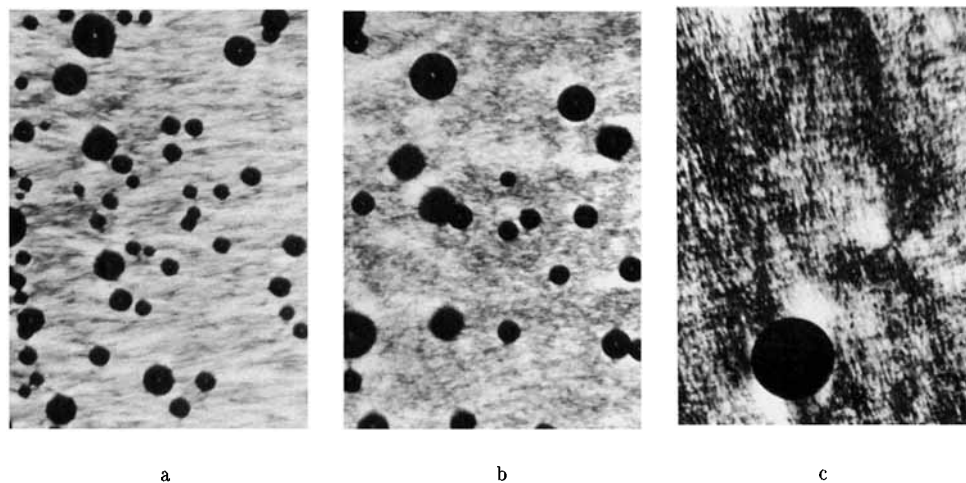


Figure 6 Cross-polarized OM pictures ($\times 110$) of 60 wt % HPC/DMAc solution at 0 min UV irradiation. Time after shearing: (a) 5 s; (b) 10 min; (c) 2 h.

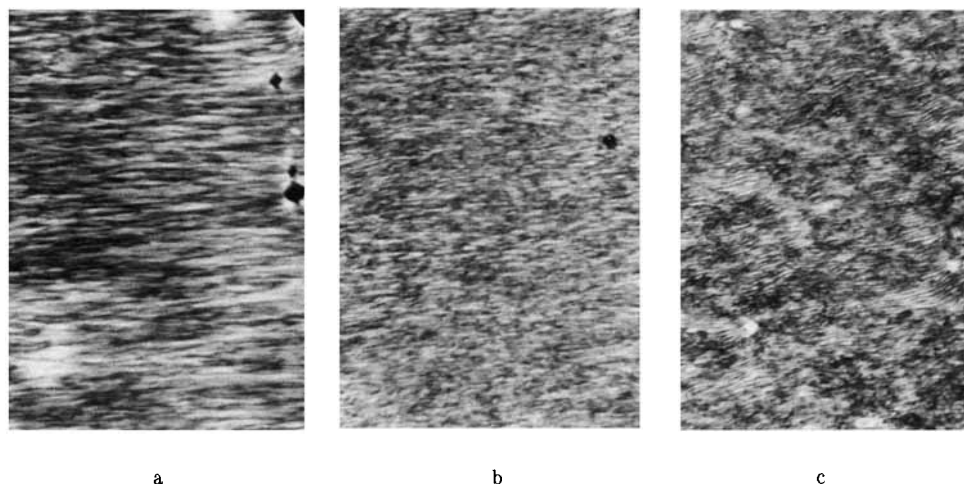


Figure 7 Cross-polarized OM pictures ($\times 110$) of 60 wt % HPC/DMAc solution after 2 min UV irradiation. Time after shearing: (a) 5 s; (b) 10 min; (c) 2 h.

structure at 100°C was retained by crosslinking; the cured film did not reform a mesophase at room temperature. Even after drying, the sample was transparent and showed no birefringence.

We wished to understand the effect of concentration on the molecular orientation of the HPC. Since crosslinked samples must retain their original organization, we could use differential swelling of the films as a measure of average orientation. The samples for the swelling experiments were postcured at 65°C for 24 h, following the initial room temperature curing reaction. They were then immersed in a solution of 1% triethylene diamine in DMAc for 24 h to remove the acid catalyst, rinsed with water

and finally dried under vacuum at 75°C for 24 h. Table I summarizes the swelling results in water for the films crosslinked from HPC solutions of various concentrations.

The swelling properties of the films cured under different conditions reflect their structures. All films swell anisotropically, except the films crosslinked from a 45 wt % HPC in DMAc solution. It was mentioned before that the critical concentration for the onset of the isotropic to mesophase transition at low shear rates and room temperature is about 45 wt %. However, the 45 wt % samples lost their birefringence upon crosslinking. Only films prepared from 50% or higher HPC solutions exhibited birefringence

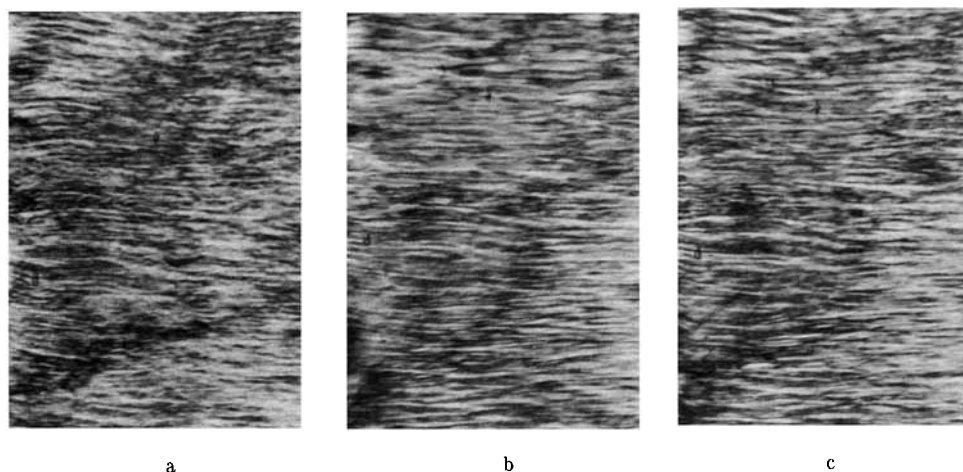


Figure 8 Cross-polarized OM pictures ($\times 110$) of 60 wt % HPC/DMAc solution after 4 min UV irradiation. Time after shearing: (a) 5 s; (b) 30 min; (c) 24 h.

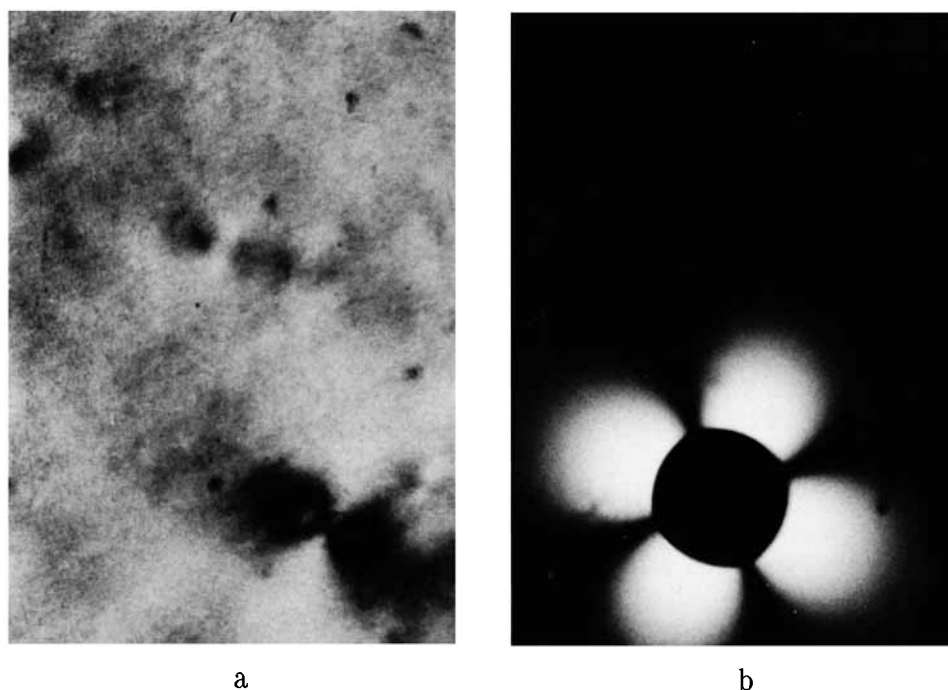


Figure 9 Cross-polarized OM pictures ($\times 110$) of dried HPC/DMAc crosslinked films, initial concentration 50 wt %. Crosslinking temperature: (a) 30°C; (b) 100°C.

after crosslinking. (Further investigation showed that the critical concentration changes with the crosslinker concentration and crosslinking density.¹⁴) Samples prepared from solutions below the critical concentration show a certain degree of preferred direction of swelling which may result from a slight orientation of the molecules during the film preparation. The films from 50 and 60 wt % HPC solutions have strong preferred swelling in the thickness direction. This indicates that at concentrations above the critical point, the HPC molecules form nematic, possibly locally cholesteric liquid

crystals, with layers of molecules aligned parallel to the film surface but with the orientation varying from one layer to the other. In such an organization with multiple crosslinking of the HPC molecules, the preferred swelling direction of the crosslinked samples will be the direction perpendicular to the layers; that is, the thickness direction. The final HPC concentrations of the swollen films crosslinked in isotropic state are even higher than the initial concentrations. This may be due to the difference of solvent power as indicated by the results in Tables I and II. In DMAc those swollen films reach almost

Table I Swelling Properties in Water of Dried HPC Crosslinked Films

Initial Concn (%)		Final Concn Volume (%) ^a	Increase in Thickness (%) ^a	Increase in Width (%) ^a	Increase in Length (%) ^a
Weight	Volume				
30	26	33 ± 2.6	39 ± 4.5	49 ± 6.7	47 ± 2.1
40	35	39 ± 2.4	31 ± 2.2	43 ± 3.3	37 ± 5.0
45	40	39 ± 1.5	36 ± 2.0	36 ± 6.2	36 ± 2.1
50	45	44 ± 1.9	44 ± 1.6	29 ± 3.9	22 ± 2.2
60	55	49 ± 1.4	64 ± 2.6	12 ± 3.6	12 ± 0.4

^a The values given are averages of four samples.

Table II Swelling Properties in DMAc of Dried HPC Crosslinked Films

Weight	Initial Conc'n (%)		Final Conc'n Volume (%)
	Weight	Volume	
30	26		28
40	35		36
45	40		36
50	45		43
60	55		47

the original volumes. As one would expect, DMAc is a better solvent than water for hydroxypropyl cellulose.

The differential swelling of the films shows that the molecules cured in the liquid crystalline state resist further expansion in the directions parallel to the layers, possibly because the rigid molecules prevent stretching. However, the films can swell further in the third direction after reaching the original volume because the molecules are linked through flexible hydroxypropyl appendages in that direction.

SUMMARY AND CONCLUSIONS

The formation of liquid crystalline solutions of HPC in DMAc is influenced by temperature, concentration, and shear rate. These factors could be varied independently in our study by using a latent UV activated catalyst for the crosslinking. The relaxation rates for the band texture in sheared HPC/DMAc solutions decreased as the crosslinking extent increased. Both isotropic and liquid crystalline crosslinked films can be prepared either by changing the HPC concentration in DMAc or by changing

the curing temperature. The films with birefringence show strong preferred swelling in the thickness direction and thus have molecular orientation parallel to the film surface.

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