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Structures of Liquid Crystalline (Hydroxypropyl)cellulose Films Cross-Linked under Shear Flow Fields

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ABSTRACT: (Hydroxypropyl)cellulose (HPC) films cross-linked from different concentration solutions and under various shear conditions have been prepared using a shear-cross-linking device. The HPC films so prepared show a nematic liquid crystal (LC) structure when the solution concentration is above the critical concentration. The molecular chain direction in the nematic LC films is parallel to both the surface of the film and the shear flow direction. The degree of orientation has been quantitatively expressed using Hermans' orientation function. Band texture formation and loss and degree of orientation were interpreted in terms of the competition between orientation and relaxation processes of the rigid-rod polymers. This further clarifies the conflicting reports in the literature regarding the origin of the band texture and its relationship to the orientation.

Introduction

The effects of external fields on polymeric mesophases were investigated by various researchers over the past two decades.[1-9] Many attempts have been made to describe the characteristic optical effect which appears as a banded pattern when polymeric liquid crystals are subjected to external fields, especially simple shear flow fields.[10-19]

Donald and co-workers[20,21] have studied by optical and transmission electron microscopy (TEM) the molecular structure of rigid and semirigid thermotropic polymers oriented under uncontrolled shear conditions. Their specimens for TEM were produced by shearing the polymer in the liquid crystalline state onto a rock salt substrate with a glass slide. The specimen was quenched to room temperature and coated with carbon for TEM observation after dissolution of the rock salt substrate. Their optical microscopy studies indicate that the molecules assume a serpentine sinusoidal orientation pathway, whereas their electron microscopy studies suggest a molecular trajectory more flat than a sine curve. Navard[22] has reported the optical anisotropy of a thermotropic cellulose derivative by quenching it to ambient temperature to freeze the band texture which developed after it was sheared at elevated temperatures.

Marsano et al.[23] used a transparent rheometer to investigate the influence of shear rate and shear strain on band formation in (hydroxypropyl)cellulose (HPC) liquid crystal solutions. They found that there is a critical shear rate below which no band texture appears after cessation of shear and a minimum shear time below which no band texture appears after cessation of shear even if the shear rate is greater than the critical one.

Ernst and Navard[24] extended the work of Marsano using flow and small-angle light scattering and found that no band texture exists during the flow.

Orientation measurements by wide-angle X-ray diffraction (WAXD) have been used for many years to characterize oriented films and fibers,[25-31] mainly crystalline or thermotropic liquid crystalline materials. For lyotropic liquid crystalline polymers, a quantitative measurement of orientation is difficult due to the relaxation of the oriented structures.

We have reported[32] a method to retain the liquid crystalline structure of (hydroxypropyl)cellulose using photoinitiated cross-linking in the mesophase. To correlate the degrees of orientation and shear flow conditions quantitatively, a transparent Couette type shear device was built to prepare cross-linked HPC liquid crystalline films. The shear flow effects on the structures of the films and their optical properties were investigated using WAXD and cross-polarized optical microscopy.

Experimental Section

Materials. Food-grade HPC-LF (weight-average molecular weight 95 000) from Aqualon Co. was used after drying in vacuo at 60 °C for 24 h. Anhydrous *N*,*N*-dimethylacetamide (DMAc) (Aldrich) was used as received. Hexakis(methoxymethyl)-melamine (HMMM) (Pfaltz & Bauer Inc.), the cross-linking agent, and triphenylpyrylium trifluoromethanesulfonate (TPTFS) (Lancaster Synthesis Ltd.), the cationic photocatalyst, were used without further purification. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (Aldrich) was used as received to prevent premature cross-linking of the samples.

Preparation of Films. The HPC solutions for the preparation of cross-linked samples were made according to formulas listed in Table I. HPC films cross-linked under various conditions of shear flow were prepared using a transparent Couette type flow device shown schematically in Figure 1. The shear flow field was induced by rotating the inner cylinder while the outer cylinder was kept stationary by the stop clamps. After the well-mixed solution was poured into a Pyrex tube (outer cylinder of the shear device), the shear apparatus was assembled and allowed to stand for 1 h to eliminate most of the air bubbles and to achieve uniformity. It was kept in darkness during this period. The total UV radiation time (GE sunlamp, 275 W) was 4 h for all the cross-linked samples. The shear rates and flow times were controlled by changing the motor speed and by removing the stop clamps from the Pyrex tube. The samples were postcured within the tube for 0.5 h at 65 °C. The cross-linked films were then taken out of the Pyrex cylinder by cutting the glass using a diamond cutter. The films were immediately immersed in DMAc containing 1 wt % DABCO to stop the cross-linking reaction by neutralization and removal of the acid. After 2 h, the films were rinsed in distilled water several times and finally dried in vacuo at room temperature.

Characterization. A Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer was used to measure the transmittance of HPC solutions which were sealed between two pieces of Pyrex glass sheets with a 0.3-mm spacer. Wide-angle X-ray diffraction patterns of dried, un-cross-linked and cross-linked HPC films were obtained by using a Searle X-ray camera with Cu Kα radiation. Azimuthal diffraction intensity distributions were analyzed by an Optronics P-1000 system densitometer. The measured intensities were corrected for polarization and background. Optical photographs were taken by using a Carl Zeiss microscope equipped with a cross-polarizer. When sheared

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Table I
Formula of HPC Solutions for Cross-Linking

concn, wt %	HPC-LF, g	DMAc, g	HMMM,[a] g	TPTFS,[b] g	DABCO,[c] mg
30	2.00	4.67	0.13	0.065	2.65
40	2.00	3.00	0.13	0.049	2.00
50	2.00	2.00	0.13	0.039	1.59
60	2.00	1.33	0.13	0.033	1.33

[a] Cross-linker: hexakis(methoxymethyl)melamine (HMMM), stoichiometrical ratio of OH/CH_2OCH_3 = 9. [b] Photoinitiator: 2,4,6-Triphenylpyrylium trifluoromethanesulfonate (TPTFS). [c] Base: 1,4-Diazabicyclo[2.2.2]octane (DABCO).

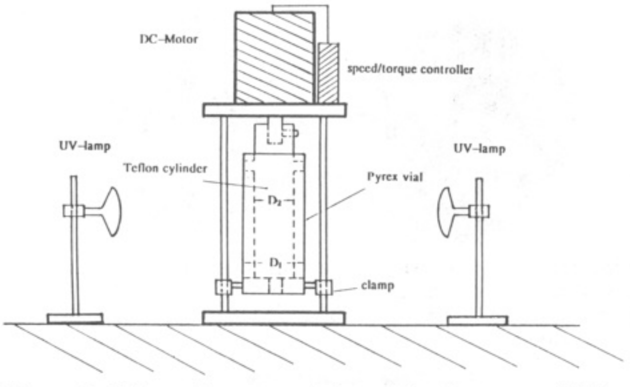

Figure 1. Schematic representation of the shear-cross-linking device with a transparent Pyrex outer cylinder and a Teflon inner cylinder.

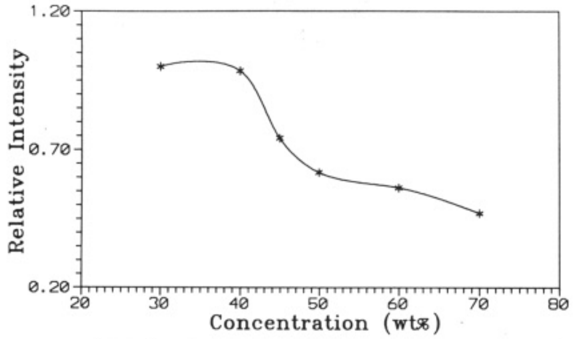

Figure 2. Relative intensity of light (600 nm) transmitted through HPC in DMAc solutions as a function of concentration.

samples were observed, the angle between the flow direction and polarizer was 22.5°.

Results and Discussion

(Hydroxypropyl)cellulose has a semirigid backbone of cellulose with flexible hydroxypropyl side chains. When dissolved in DMAc, HPC solutions change from transparent at low concentrations to opaque at high concentrations. This effect is caused by the establishment of liquid crystalline organization at the higher concentrations which scatter light. Figure 2 shows the normalized transmittance for HPC solutions in DMAc exhibiting a transition at about 45 wt % concentration. Flat-plate wide-angle X-ray diffraction patterns from a dried HPC film cross-linked under shear flow conditions (Figure 3) reveal the oriented structure of the film. Pattern A was taken with the X-ray beam perpendicular to the film surface. Pattern B was obtained with the X-ray beam perpendicular to both the edge of the film and the shear flow direction. Pattern C was obtained with the X-ray beam perpendicular to the edge of the film, but parallel to the shear flow direction. On the basis of the above X-ray diffraction patterns, the film shows a nematic liquid crystal structure. On average, the molecules in the film lie parallel to the film surface in the shear flow direction. Since the molecular chain axis is perpendicular to the X-ray beam, the oriented equatorial reflections from patterns A and B are similar to each other. A ring was found in pattern C showing that the X-ray beam is parallel to the molecular chain axis.

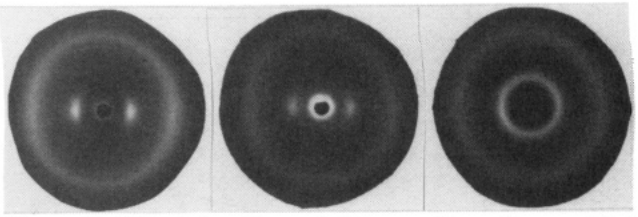

Figure 3. Flat-plate wide-angle X-ray patterns from a dried HPC film cross-linked under shear: (A) X-ray beam perpendicular to the film surface; (B) X-ray beam perpendicular to both the edge of the film and the shear flow direction; (C) X-ray beam perpendicular to the edge of the film and parallel to the shear flow direction.

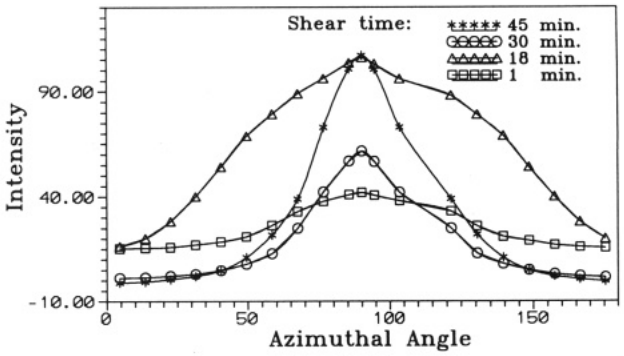

Figure 4. Azimuthal scans of the equatorial diffraction of HPC films cross-linked under various shear times from 60 wt % solutions.

The oriented equatorial diffraction, (100) as indexed by Samuels,[33] can be used to calculate the molecular orientations in films cross-linked under various shear flow conditions. Hermans' order parameter, *f*,[26,34-36] was used to correlate the average orientation of the molecules in the films with respect to the flow direction. Azimuthal scans of the equatorial diffraction intensities were recorded by using a densitometer and are shown in Figure 4. ϕ is the angle between the flow direction and the vector $S - S_0$, where S and S_0 are unit vectors in the direction of the incident and diffracted beams, respectively, as described by Wilchinsky.[28] After background and polarization corrections, the orientation parameter $\langle\cos^2\phi\rangle$ was calculated using a computer integration method according to the following equation:

$$\langle\cos^2\phi\rangle = \frac{\int_0^{90} I(\phi)\cos^2\phi\sin\phi\,d\phi}{\int_0^{90} I(\phi)\sin\phi\,d\phi}$$

where $I(\phi)$ is the intensity of the diffraction peak at an angle ϕ to the flow direction. $\langle\cos\phi\rangle$ is restricted to values between 0 and $^1/_3$, where 0 means complete orientation and $^1/_3$ shows randomness. Values greater than $^1/_3$ imply orientation perpendicular to the flow direction.

Considering the symmetric structure of HPC molecules, Samuels[33] calculated the average molecular chain orientation by

$$\langle\cos^2\gamma\rangle = 1 - 2\langle\cos^2\phi\rangle$$

For a random orientation, the parameter $\langle\cos^2\gamma\rangle$ equals $^1/_3$. For molecules which are parallel to the flow direction,

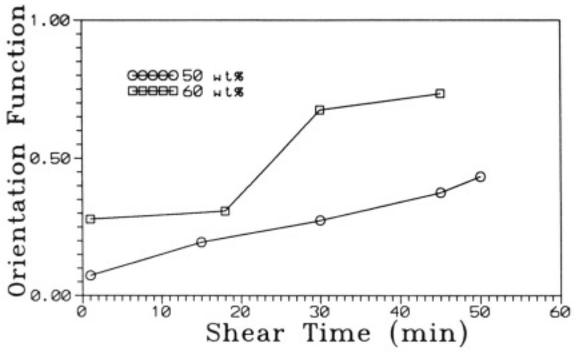

Figure 5. Orientation function for films cross-linked under shearing at 6.36 s^{-1} versus shearing time.

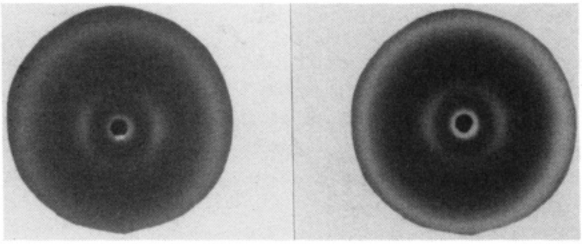

Figure 6. Flat-plate wide-angle X-ray patterns from dried HPC films cross-linked under shear from solutions with various concentrations: (A) 30 wt %; (B) 40 wt %. The applied shear rate was 6.36 s^{-1}.

$\langle \cos^2 \gamma \rangle$ is larger than $^1/_3$. For molecules which are perpendicular to the flow direction, $\langle \cos^2 \gamma \rangle$ is smaller than $^1/_3$. Finally, the Hermans' order parameter f can be derived from

$$f = \frac{3\langle \cos^2 \gamma \rangle - 1}{2}$$

For random molecular orientation, f is equal to 0. For molecular chains perpendicular to the flow direction, f is smaller than 0 but larger than −0.5. For molecular chains parallel to the flow direction, f is larger than 0 but smaller than 1.

Two series of HPC films cross-linked under shear from 50 and 60 wt % solutions in DMAc were prepared using the shear-cross-linking apparatus described above. Both HPC solutions were above the critical concentration. The orientation degree increases with the time of cross-linking under shear, as shown in Figure 5. For the samples cross-linked from 50 wt % solutions, f increases almost linearly with the shear time until the solutions approach the gel point (about 50 min under the conditions described above). For the samples cross-linked from 60 wt % solutions, the orientation degree is always larger than that for the corresponding samples from the 50 wt % solutions. The orientation degree tends to equilibrate at longer shear times, probably due to local relaxations in the already highly oriented very viscous 60 wt % solutions. Samples cross-linked under shear from 30 and 40 wt % HPC solutions (below the critical concentration) show only a slight orientation (Figure 6), indicating that the relatively low shear flow field even with the increasing viscosity due to cross-linking has little effect on the formation of a liquid crystalline phase.

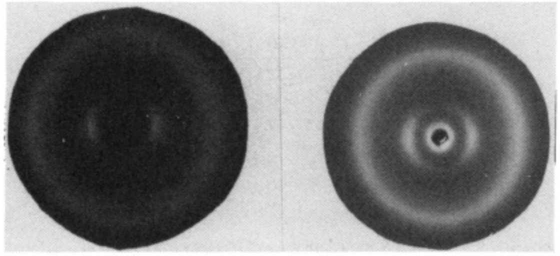

Figure 7. Flat-plate wide-angle X-ray patterns from dried HPC films cross-linked from 50 wt % solutions at various shear rates: (A) 6.36 s^{-1} (f = 0.43); (B) 93.3 s^{-1} (f= 0.42).

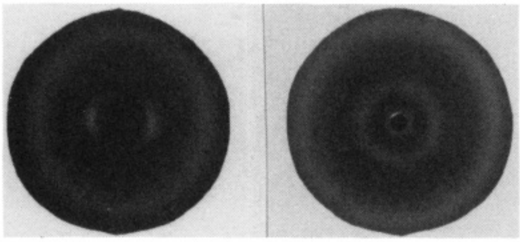

Figure 8. Flat-plate wide-angle X-ray patterns from dried HPC film cross-linked at the same shear strain of 1.91×10^4: (A) shear rate = 6.36 s^{-1}, shear time = 50 min; (B) shear rate = 93.3 s^{-1}, shear time = 3.4 min.

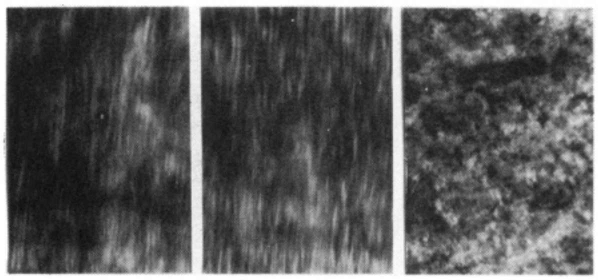

Figure 9. Cross-polarized optical micrographs of dried HPC films cross-linked from 60 wt % solutions under various shear times: (A) 5 min; (B) 15 min; (C) 45 min. The applied shear rate was 25.4 s^{-1}. Original magnification ×440; the micrographs have been reduced to 40% of their original size for publication purposes.

The influence of shear rate and shear strain on the degree of orientation of the samples was investigated by changing the motor speed and the shearing time. Figure 7 shows the flat-plate wide-angle X-ray diffraction patterns from dried HPC films obtained from 50 wt % solutions cross-linked under shear for 50 min. The shear rate was 6.36 s^{-1} for pattern A and 93.3 s^{-1} for pattern B. The orientation function, f, is almost the same for both samples. The degree of orientation for the shear-cross-linking systems depends only on the original solution concentration and the shear time. Due to the very high viscosity of the solutions near the gel point, the applied shear stresses are high enough even at low shear rates that no minimum critical shear rate was found in our experiment. The degree of orientation seems to be mainly dependent on the cross-linking time under shear and not the applied shear strain, as shown in Figure 8. Pattern A was taken from a dried HPC film cross-linked at a shear rate of 6.36 s^{-1} and shear time of 50 min, and pattern B was taken from a dried HPC film cross-linked at a shear rate of 93.3 s^{-1} and shear time of 3.4 min. The total applied shear strain for both samples was identical. It is clear that pattern A shows a much higher degree of orientation than pattern B. The oriented nematic structure under shear can relax back toward the original cholesteric structure if the shearing is stopped while the viscosity of the solution is still relatively low.

Although several research groups[14,18,37] have described the origin of the band patterns in liquid crystalline solutions, there are still conflicting reports on the experimental observations of whether the texture appears during shearing[38] or during the shear relaxation.[14,18] Our results support the latter conclusion. As shown in Figure 9, the films sheared for 5 or 15 min while being cross-linked by UV irradiation and then UV irradiated continuously until gelation without shearing give a clear band texture under

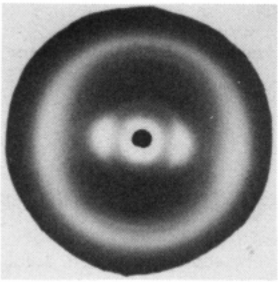

Figure 10. Flat-plate wide-angle X-ray pattern from a dried HPC film cross-linked from a 60 wt % solution under shear for 45 min. The shear rate was 25.4 s^{-1}. The X-ray beam is perpendicular to the film surface.

the cross-polarized microscope; by comparison, the film cross-linked under shear up to gelation shows no band texture at all. The flat-plate X-ray diffraction pattern from the film without band texture, Figure 10, shows a strong orientation. Therefore the nematic liquid crystalline structure was present in this case and the orientation was locked in by cross-linking. The lack of a band texture is therefore explained, since the "gelled" polymer chains cannot relax.

Summary and Conclusions

(Hydroxypropyl)cellulose films cross-linked under shear from liquid crystalline HPC/DMAc solutions show a nematic mesophase structure. The molecular chains are parallel to the film surface and to the shear flow direction.

Hermans' orientation function was used to describe the degree of orientation of the films. For films cross-linked from 50 wt % solutions of HPC in DMAc, the orientation increases almost linearly with the shear time whereas the orientation of the films cross-linked from 60 wt % solutions tends toward an equilibrium value at longer shear times due to local multisegmental relaxations in the highly viscous oriented solutions. For the shear-cross-linking systems, no critical shear rate has been detected, due to the very high viscosity near the gel point. The major factor which influences the orientation degree is the cross-linking time under shear. The films cross-linked under shear from solutions below the critical concentration showed only a very low degree of orientation.

The technique of cross-linking under shear proved that the shear band texture is mainly the result of a relaxation phenomenon. No band textures were found in the films cross-linked under shear up to the gel point, although the films still showed a very high degree of orientation by wide-angle X-ray diffraction. When the shearing was stopped before gelation, films with a well-developed band structure were obtained.

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Registry No. (HPC)(HMMM) (copolymer), 133945-66-1.