Atomic Force Microscopy and High-Resolution Scanning Electron Microscopy Study of the Banded Surface Morphology of Hydroxypropylcellulose Thin Films

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Introduction. The banded texture is a commonly observed microstructure when liquid crystalline polymers sheared in the mesophase are viewed with a polarizing microscope.[1-5] This texture consists of alternating bright and dark bands perpendicular to the shear direction that appear due to a periodic oscillation of the optic axis.[2] The total width of a bright and dark band is determined by the wavelength of the oscillation. Recent investigations have found that these bands are formed due to an associated change in the molecular orientation.[1-7] Relaxation of the director orientation after cessation of flow induces a periodic (banded) morphology, where the local molecular orientation varies periodically about the shear direction.

The bands which are transient in the mesophase can be vitrified by cooling below T_g and therefore can be observed in thin films. The mechanical and optical anisotropy of the films have been found to depend on the wavelength of these bands.[5] In order to optimize these properties in sheared liquid crystalline polymers, a better understanding of the origin of the shear bands and the conditions that promote their formation is needed. One of the important aspects of such an understanding is a detailed knowledge of the associated morphology.

In this paper we report on the use of low-voltage high-resolution scanning electron microscopy (LVHRSEM) and atomic force microscopy (AFM) in characterizing the surface morphology of hydroxypropylcellulose (HPC) thin films. HRSEM and AFM were used in a complementary fashion. LVHRSEM has many advantages compared to conventional scanning electron microscopy. The use of low accelerating voltages gives rise to lower electron beam penetration and also eliminates the need for thick conductive coatings typically required for insulating specimens. Both of these factors are important in enhancing surface contrast and resolution. The greater depth of field provided by LVHRSEM as compared to TEM was very useful for imaging the out-of-plane component of the shear bands. AFM was used to provide detailed quantitative measurements of the topographical features.

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Experimental Procedure. Sheared films of the polymer were prepared from 37 wt % solutions of HPC (KLUCEL L; 95 000 molecular weight) in glacial acetic acid.[5,8] The films were cast and sheared simultaneously by moving a casting knife (supplied by Gardner Laboratory) at a controlled shear rate of 2000 s^{-1}. The films which were cast on a rigid flat glass plate coated with a fluorocarbon polymer were prepared at 85 °C and dried overnight at the same temperature, followed by further storage at room temperature for another 72 h to yield dried films. Dried films with a thickness of 20 μm were prepared, and their thicknesses were measured using a Mitutoyo digital micrometer. Photomicrographs were taken after observing the films with crossed polars on a Nikon microscope. Scanning microscopy was performed using a Hitachi S-900 LVHRSEM operating at 1.0-keV accelerating voltage. The samples were coated with 2 nm of tungsten using a VCR dual ion beam coater. Along with reducing charging effects by increasing the surface conductivity of the insulating specimens, the thin metal coating was also useful in improving the resolution by enhancing the image contrast at edges.

The AFM images were taken in air using a Park Scientific SFM-BD2 scanning force microscope. A silicon nitride pyrimidal tip of a 40 nm radius of curvature and an effective force constant of 0.032 N/m was used, and the AFM was operated in the repulsive mode using forces on the order of 10^{-9} N. For better resolution, a piezoelectric scanner with a $10 \times 10\ \mu m^2$ scan area was used.

Results and Discussion. LVHR Scanning Electron Microscopy. Figure 1 shows the free surface of a sheared HPC film, with the shear bands perpendicular to the shearing direction. A fibrillar morphology was observed, with the fibrils (which are considered to be made of oriented HPC molecules) running sinusoidally about the shearing direction with wavelengths ranging from 5.0 to 6.5 μm. Some of the initial studies assumed that the fibrils were restricted to the plane of the film, although later studies[3,4,6] indicated that an out-of-plane component was present. In the present study we have attempted to quantify this out-of-plane component of the fibrillar trajectory.

By comparing the SEM micrographs with the optical micrographs obtained with crossed polars, a correlation between the optical director and the fibrillar trajectory can be established. The optical micrographs show a set of primary bands running perpendicular to the shear direction and a set of secondary bands inclined to the shear direction (Figure 2). The primary bands can be explained as a direct consequence of the sinusoidal variation in the fibrillar trajectory. When the polarizer is parallel to the shear direction, bright areas are observed where the fibril is at an angle to the shear direction, and dark areas are observed at the peaks and valleys of the sinusoidal trajectory of the fibril where the fibril is parallel to the shear direction. Thus, when large numbers of fibrils are stacked together, a banded structure is observed, with the bands running normal to the direction of shear. Bright bands are separated by dark lines which are observed where the peaks and valleys of adjacent fibrils are in register. The secondary bands which are called "torsads" are believed to be produced as a consequence of the hydrodynamics of solvent evaporation.[8] A detailed study relating the tilt angle of the optic axis as observed in the optical

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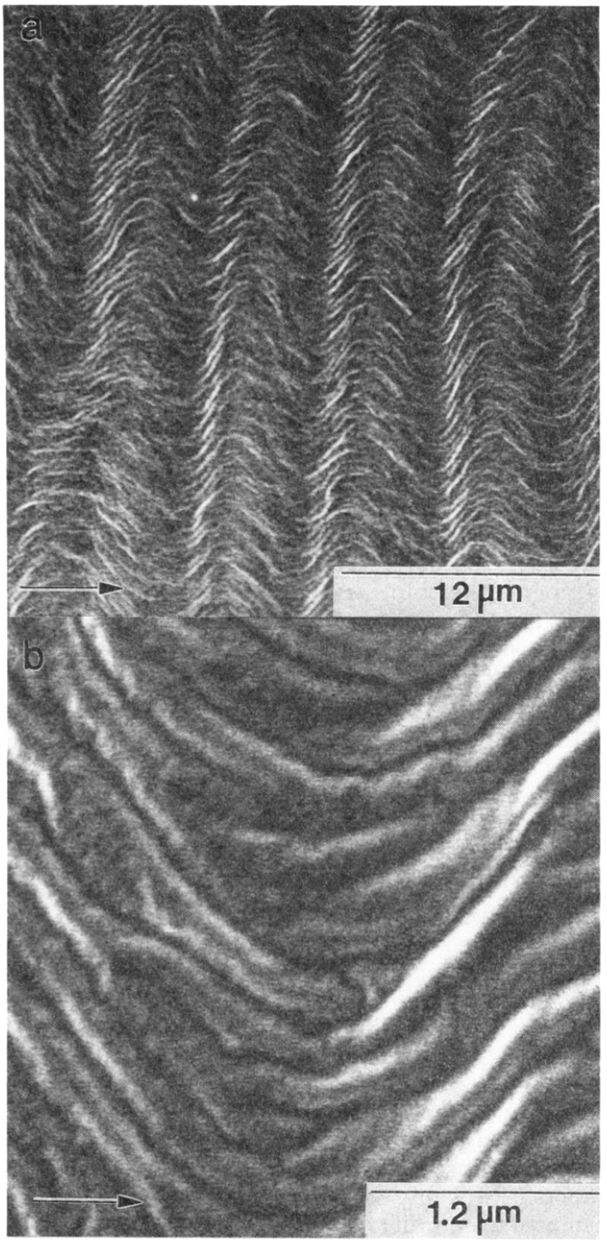

Figure 1. LVHRSEM micrographs of a sheared film of HPC taken at different magnifications. Arrows indicate the direction of shear.

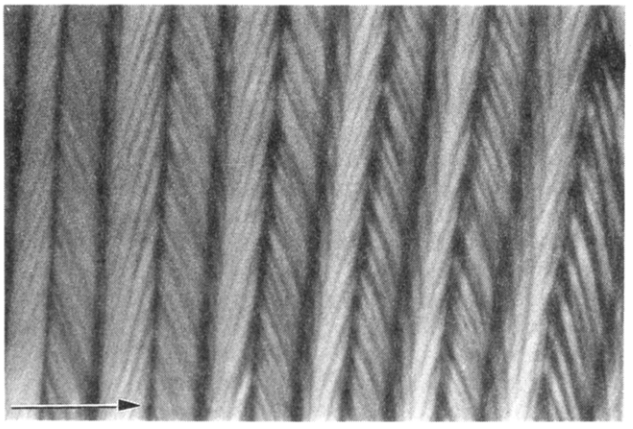

Figure 2. Polarizing micrograph of a sheared film of HPC. The arrow indicates the direction of shear.

micrographs and the fibrillar trajectory as observed in the SEM micrographs needs to be done to establish a direct correlation between the torsads and the microstructure.

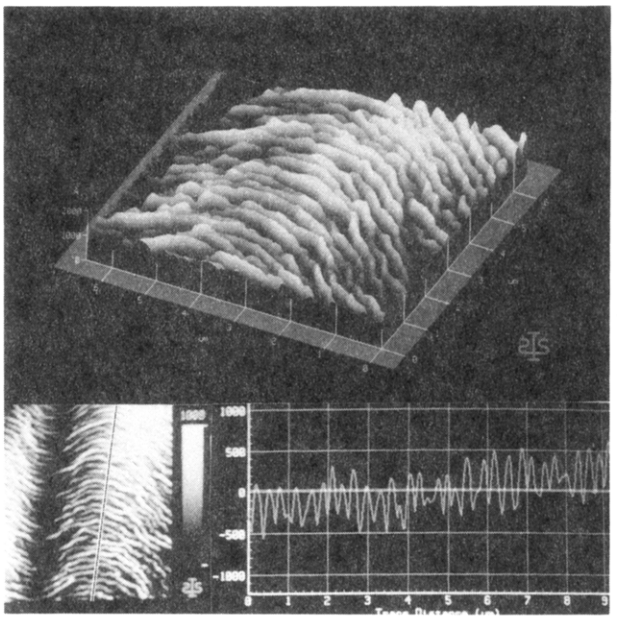

Figure 3. AFM image of the sheared surface of a HPC film. The top figure (a) shows a dimensional image of the fibrils in a shear band. The bottom figure (b) shows height profile analysis across the fibrils.

The topographical image contrast seen in the LVHRSEM micrographs is mainly due to two factors, contrast at edges and contrast observed due to the collection efficiency of the detector which is dependent on the position of the detector relative to the sample. The detector is located on the left-hand side above the sample; therefore, the section of the fibrils facing the detector appears brighter than the section facing away from the detector. The edges of the fibrils appear brighter than the rest (as seen in Figure 1b) due to a larger number of secondary electrons (SE) escaping from the edges. The SE yield also increases with increasing local tilt in the sample due to the increase of the percentage of the interaction volume (volume defined by the path length of the primary electrons in the sample) within the SE escape depth (depth inside the specimen from where SE electrons can escape, ≈50–100 Å). Therefore, the periodic variation in the brightness of the image of the fibrils along the shear direction clearly demonstrates that there is an associated periodic variation in the z component of the sample surface. This further implies that the sinusoidal variation in the molecular orientation is not in the plane of shear (defined as the plane of the substrate on which the film was cast) but in a plane which makes an angle θ ($\neq 0°$) with the shear plane.

Atomic Force Microscopy. AFM was used to examine the film surface and to measure its surface topography. Figure 3a (top) shows the three-dimensional structure of the surface showing a shear band with a periodicity of 6.5 μm. This is comparable to the bandwidth observed in the LVHRSEM images. Height profile analysis (Figure 3b, bottom) along the shear band characterized the topography of the fibrils and measured an average peak-to-valley height of ≈120 nm and an average width of ≈285 nm for the fibrils.

Although the SEM images provide a qualitative measurement of the out-of-plane component of the molecular director, for a more quantitative measurement the height profile analysis obtained from AFM

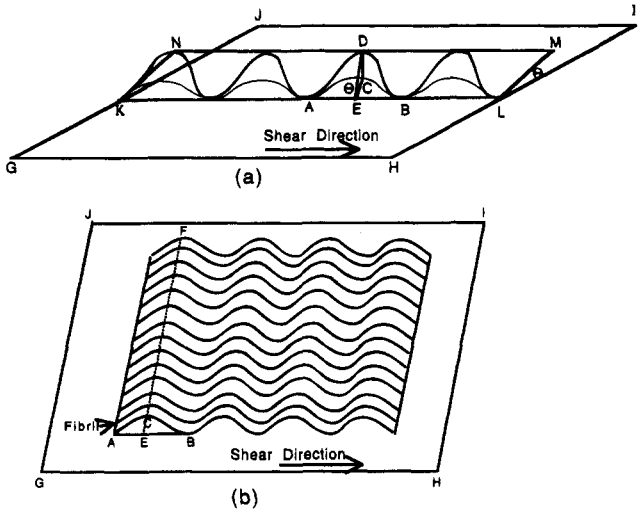

Figure 4. (a) Schematic showing the angle θ between the shear plane (GHIJ) and the plane of the fibril (KLMN). (b) Schematic of the fibrillar texture viewed normal to the shear plane (GHIJ).

images was used. A schematic of the fibrillar texture is shown in Figure 4. In Figure 4a, the trajectory of a fibril is shown by a thick sinusoidal line and its projection on the shear plane by a thin line. When viewed normal to the shear plane, as in the case of the LVHRSEM images taken with zero tilt of the sample, in actuality we observe the projection of the fibrils on the shear plane (Figure 4b). The out-of-plane component of the fibrillar trajectory (when the fibrillar trajectory deviates from lying on the plane of shear) can be estimated by measuring θ (Figure 4a). Here θ is the angle between the plane of shear (GHIJ) and the plane (KLMN) defined by the fibrillar trajectory and the shear axis. The curved segment ADB represents a section of the sinusoidal trajectory, and its projection on the shear plane is represented by the curved segment ACB such that the peak of the trajectory D has its projection on the shear plane at C. θ is equal to $\angle$DEC and $\sin(\theta) =$ DC/DE. DC here represents the z component of the peak. In the case where the fibrils are lying on the plane of shear, DC = 0 and $\theta = 0$. DE can be measured directly from the AFM images. DC was estimated from the height profile analysis along two line scans, one through A, parallel to DE, and another through DE. The first scan gave the height of A (which is the same as that of C as both the points lie on the shear plane), and the second scan gave the height of D. The difference between these two heights gave a measure of DC. These scans were sampled over different areas, and θ was estimated to be $\approx$4−10° from a measured DC value of $\approx$1000 Å and a DE value $\approx$ 1.2−1.4 μm.

The out-of-plane component reported here is probably caused by the contractional strain induced by stress relaxation following cessation of shearing. The extent of this contraction is expected to be dependent on the film drying conditions (i.e., rate of evaporation of solvent) and the film thickness. The contractional strain has also been considered responsible for the out-of-plane components observed in films of HPC prepared from shearing the thermotropic melt of HPC[4] and from the shear-induced crystallization of HPC from an aqueous lyotropic solution.[3] There is, however, a slight difference in the associated morphologies. We observed a gradual distribution of the contraction over the fibrils, whereas, in refs 3 and 4, the contraction is accommodated by a "pleated" morphology. In refs 3 and 4 it was found that compared to thicker films, thin films of HPC show a less pronounced out-of-plane component due to larger interaction between the sheared film and the substrate, leading to less contraction during stress relaxation. Similar effects of reduction in the out-of-plane component were also observed for cases where the sheared films were rapidly dried, thereby not allowing for large relaxation.

Conclusions. LVHRSEM and AFM studies both indicate that a sinusoidal fibrillar morphology is associated with the banded texture observed in HPC. The AFM studies clearly demonstrate that the fibrillar trajectory deviates from lying on the plane of shear, and for shear bands with 6-μm wavelength, this deviation was found to be $\approx$4−10°. The use of AFM to map the surface topology allowed us to obtain quantitative measurements which were not available from conventional characterization tools such as optical microscopy. Although there have been other observations of the out-of-plane component,[3,4,6] there has been no quantitative estimate of the angle of the deviation prior to this work. The origins of the out-of-plane component are probably similar to those observed in earlier reported cases where contraction of the sample accompanying evaporation of solvent was viewed to be responsible for the fibrillar trajectory's deviation from the plane of shear.

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