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A preliminary morphological evidence for the existence of back-flow effect associated with the formation of band texture after cessation of shear for a polymeric liquid crystal

Jiandong Ding, Jun Feng, Yuliang Yang

Department of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

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Summary

The band texture of the hydroxypropylcellulose (HPC) film is observed after cessation of shear by optical microscopy and scanning electron microscopy (SEM). The sinusoidal supramolecular structure associated with the band texture of HPC is verified by polarized optical microscopy, so the band texture corresponds to the spatial periodicity of local director or molecular orientation. On the other hand, however, the pleated morphology, a depth periodicity, is confirmed by SEM and the pleat period is consistent with the band period. What is more, even without polarizer and analyser, the bands can still be found in an optical microscope with the same periodicity as those under cross polars, and these bands might be attributed to a density periodicity. Both the depth and density periodicities result from the mass flow after cessation of shear and must be coupled to the orientation periodicity resulting from director rotation. As a consequence, we propose that the back-flow effect is striking in the formation of band textures and should be taken into consideration in order to give a plausible and explicit mechanism of band formation.

Introduction

The band formation is a phenomenon common to all main chain polymeric liquid crystals (PLCs). The alternating dark and bright bands perpendicular to the preshearing direction was observed in a polarizing microscope first by Elliott and Ambrose (1) and then by many other people (2-33). Besides of interest in the light of the fundamental research, the band texture affects the mechanical properties of PLC materials (22) and has, therefore, attracted much attention of scientists and engineers.

The mechanism leading to the formation of the band texture has, therefore, been am important question. Marrucci (34) suggested that the bands arise from the coherent tumbling of neighboring domains and introduced Frank elasticity into this problem. Fincher (35) proposed the idea that a large value for the splay elastic constant in PLCs favors a rapid lateral relaxation. Picken *et al.* (36) recently presented a model along similar lines. Gleeson *et al.* (37) suggested that both molecular and texture elasticity influence the band formation. On the other hand, Chan and Rey (38, 39) distinguish themselves as putting forward the coupling between the director rotation and the back-flow effect as a mechanism for the selection of the wavelength of the perturbations. Unfortunately, they only consider a one-dimensional evolution of the texture. Although the theoretical efforts mentioned above can explain part of experimental results, the formation mechanism of band textures is still an open question at the present time, due to the approximation and incompleteness of the theoretical approaches. It is even not very clear that which physical factors trigger the band formation. In our opinion, the formation mechanism of band texture can not be revealed at least until the liquid crystalline (LC) elasticity and the back-flow effect are both considered in more than one dimensions. The LC elasticity is obvious. On the other hand, the experimental evidence is scarce for the striking back-flow or hydrodynamics effect in the band formation.

It is well known that the band textures are a polarizing optical effect resulting from the periodicity of molecular orientation. Some people indicated that out-of-plane component was also present (24, 25). The authors would like to term the phenomenon of the wavy film surface as the depth periodicity, another kind of spatial periodicities in contrast to the orientation periodicity. In this paper, the spatial periodicity for the wavy surface is confirmed along with that for the orientation. Furthermore, the density periodicity is assumed according to direct observation of hydroxypropylcellulose (HPC) film in an optical microscope. To our knowledge, the band textures observed in an optical microscope without polars have not been reported in literature. Both depth and density periodicities result, obviously, from the mass flow after cessation of shear. Hence, this paper affords a preliminary, although indirect, morphological evidence for the existence of striking back-flow effect in the band formation.

Experiment

HPC was supplied by TCI (MW 60, 000). The lyotropic liquid crystal was prepared by mixing HPC and water at room temperature followed by centrifugation to remove air bubbles. The solution (50 wt %) was sheared between two glass slides in a simple self-built shear apparatus. The film depth is about 40 μm and the shear rate is about 1000 s^{-1}. Immediately after shearing, the wet film was fast dried by a strong electric cold-wind-maker lasting for 20 s. The dried film was observed in a Leitz polarizing optical microscope (POM). The source is the white light with orthoscopic incidence. The optical micrographs were captured by a CCD camera with 512×512 pixels and 256 relative intensity levels. The specimen was also observed in a Hitachi S-520 scanning electron microscope (SEM) after spurting Au on the film surface.

Results and Discussion

Band textures of HPC film are shown by polarizing micrographs (Figure 1). According to our previous studies (33), if the optical director is periodically sinusoidal, not only the contrast ratio, but also the position and number of the extinction bands change with α, the relative angle between the preshearing direction and the polarizer. Especially when α is between zero and the maximum divergence angle of the local director to the preshearing direction, the paired bands may occur. It is the case in Figure 1(b), and we can estimate that the maximum divergence angle for our specimen is near 30° (Figure 1(c)). So, the orientation periodicity is associated with the band texture and the corresponding supramolecular structure in our sample is sinusoidal.

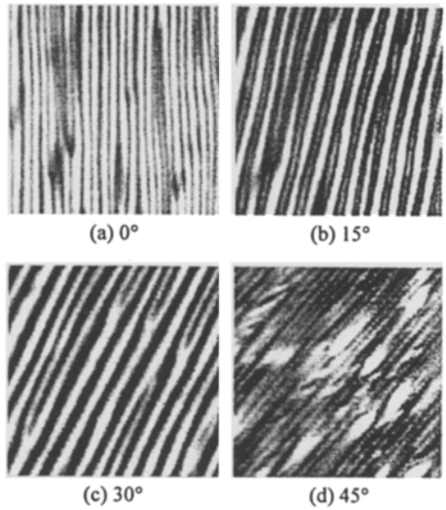

Figure 1. Polarizing optical micrographs of the sheared HPC film. (a) specimen in orthogonal position under cross polars; (b) to (d) rotation of the specimen with the noted angles. The bands are perpendicular to the preshearing direction. The band widths in (a) and (c) are about 2 μm and 4 μm, respectively.

Figure 2. SEM micrograph of the sheared HPC film. The pleat period is about 4 μm.

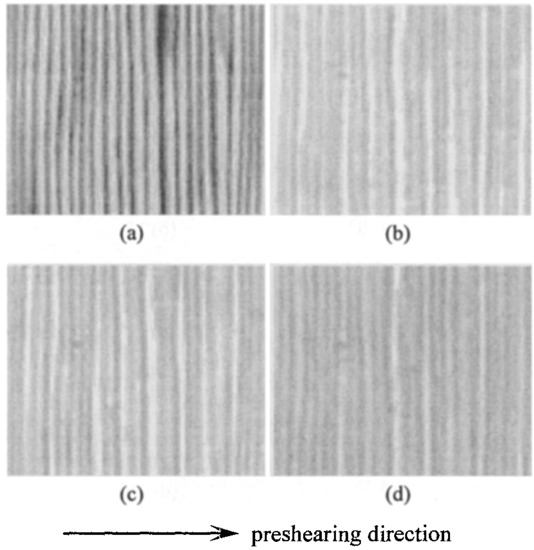

Figure 3. Optical micrographs of the sheared HPC film. (a) with cross polars in the orthogonal position; (b) merely with analyser; (c) merely with polarizer; (d) without polarizer and analyser. The period for every two bands is about 4 μm.

Our electron micrographs show, on the other hand, that the band texture is not merely an optical effect. The pleated morphology can be seen clearly from Figure 2. The detector is located on the left-hand side above sample, so the left faces of the pleats are bright while the right faces are black. Such a morphology was first reported by Nishio *et al.* (24). However, they failed to notice that the pleat period obtained from SEM is almost equal to the band period obtained from POM. This point can be seen by comparison between Figures 1 and 2 in the present paper. (Note: The band width in orthogonal position by POM is only half of the band period, if the supramolecular structure is sinusoidal.) That means the adjustment of the molecular orientations is coupled with the movement of the mass centers of molecules and implies that the velocity field in the formation process of the band texture has the same period as the director field. So, the back-flow effect might be important in the formation of the periodic bands.

Such an idea is further confirmed by optical micrographs (Figure 3). The interesting phenomenon is that even without polars, the specimen can still take on band textures with relatively low contrast ratio. These bands never change with the rotation of the specimen, and the band width is only half of the band periods by POM and SEM. To our knowledge, no one has ever reported the band textures of PLCs observed in an optical microscope without polarizer and analyser. The texture in Figure 3(d) can not be explained completely by the pleats in Figure 2, considering the mismatch between the band width and the pleat width. Hence, the authors tentatively attribute the band texture without polars to the periodic change of the density. Comparison between Figures 3(a) and 3(d) shows that the black bands without polars correspond roughly to the extinction bands under cross polars in orthogonal position. Therefore, a relative large density is formed in the position where the local molecules are orientated parallel with the preshearing direction. We imagine that the periodic spatial change of density has something to do with that of the local order parameter. Of course, the density periodicity is also a result of mass flow after cessation of shear.

Conclusions

The band texture of HPC is found not merely a polarizing optical phenomenon. The pleated morphology is confirmed along the third dimension normal to the film plane for our specimen. Therefore, together with the orientation periodicity, the surface elastic wave can be found. Even the periodicity of order parameter and hence of density might, in some case, be included in the band texture. The period of the velocity and the period of the density might be the same as or half of that of optical director or molecular orientation.

In our opinion, the pleated morphology and the bands observed without polars may not always accompany the conventional band textures. Some conclusions such as the density periodicity is still premature in the present paper and extensive investigations are desired. But anyway, the spatial periodicity with respect to the band texture is not limited within the orientation change and the back-flow effect plays an important role in band formation. Up to now, the formation mechanism of the band texture is still a challenging question, although some efforts have been made helpfully (34-39). Several factors such as the Frank elastic effect, the back-flow effect and the evolution of local order parameter might be taken into consideration in order to give a plausible and explicit explanation to the band texture. Some theoretical treatment about the LC dynamics after cessation of shear is in progress by us after considering both Frank elasticity and back-flow effect in two dimensions. The preliminary theoretical result seems meaningful and will be published later (40).

Acknowledgments

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