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LIGHT DIFFRACTION STUDIES OF THE BANDED TEXTURE IN HYDROXYPROPYL CELLULOSE

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Abstract In most liquid crystal polymers when a thin sample is sheared the polymer exhibits a periodic pattern or texture. While this phenomena has been widely noted, a complete and satisfactory explanation is not yet in hand. We present the results of a study of the dynamics of the formation of the banded texture in liquid crystalline polymers after shear. The data were collected by the diffraction of light from the texture. This approach directly provides the key parameters to characterize the texture without the ambiguity that is often involved with microscopy. It was found that the overall nature of the modulation that gives rise to the texture appears to not vary with time except in magnitude. Both thewavelength and the coherence length of the modulation remain fixed. While both shear rate and thickness of the sample have little effect upon the texture, concentration of the polymer has a very large effect.

INTRODUCTION

The formation of banded textures after shear in polymeric liquid crystals is general to virtually all liquid crystal polymers. This texture was first studied in high strength fibers spun from nematic solution.[1,2] Because these high performance fibers derive superior strength from alignment, the resulting modulation of molecular orientation has direct bearing upon propertiesmaking it much more than simply an interesting artifact. The banded texture has since been observed in a wide variety of polymeric mesophases.[3,4,5] Recent careful investigations have rather clearly defined the banded texture itself in terms of the molecular arrangement. The coupling of the director in mesogenic materials to the flow results in unusual rheological properties in this important class of polymeric materials. Some of the earliest work showed that the first normal stress difference changed sign twice as a function of shear rate, in a liquid crystal polymer in which the banded texture is observed.[3,6] It is surprising that such a widely occurring phenomena as the banded texture has no complete or fully satisfactory explanation. Only recently have there been attempts to build a quantitative description of the final textured state. Quite often when systems exhibit some type of periodic instability (e.g. spinodal decomposition, eutectic solidification important clues are buried in the dynamical behavior near the onsetof the instability. In the case of the banded

texture of LCP's data on the dynamics of the texture formation are practically nonexistent. We present here a quantitative study of banded texture formation in hydroxypropyl cellulose. We have measured the time dependence of the development, as well as the effect of geometry (ie sample thickness), shear rate and polymer concentration.

EXPERIMENTAL

The polymer used in these experiments was Klucel C furnished by Hercules. The chemical structure of HPC is depicted in figure 1. Measurement of the inherent

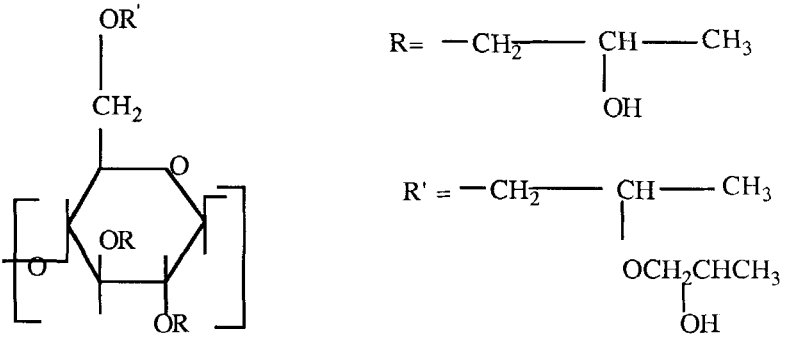

Figure 1. Schematic representation of the chemical structure of hydroxypropyl cellulose

viscosity indicated an M_w =100,000. The experiments reported here are on freshly prepared solutions of HPC in H_2O The biphasic region was determined by optical microscopy. The critical concentrations were found to be c_1 =0.415 and c_2 =0.49 as fraction by weight agreeing well with previously reported values for Klucel C[7].Using Flory's lattice theory for the formation of lyotropic mesophases[8] we would then estimate the aspect ratio to be L/d = 17.5 Å. From this one may estimate a persistence length for HPC of about 136 or 26 monomer units. Most previous workers have studied the texture formation by use of microscopy or standard rheometers.[3,7,8] There can be several problems with the use of microscopy in this problembecause of the time scales. The

direct observation of the texturein motion can not be at all satisfactory and even quite misleadingas we have found in this laboratory. The timescale necessary forthe exposure of a micrograph can be roughly estimated using a characteristic number for the wavelength of the texture ($\lambda = 1.0\ \mu m$) and a velocityappropriate to the shear rate (v = 1 cm/sec). With these numbersone can then estimate that the exposure time must be much less than $\tau \cong 10^{-4}$ sec. In addition the required data is contained in a few averages of the greatwealth of information provided by microscopy. This is becausedonly a few numbers needed to characterize the texture, the wavelength and two coherence lengths. Diffraction measures these quantities directly averaging over a significant volume of the sample. Furthermore, diffraction is unaffected by the relative motion of the texture. These reasons make a clear argument that study of the banding by light scattering would be a direct route to the desired information.The shearing cell consisted of two glass plates with a polymer spacer between them. The top plate was held in contact with the spacer and bottom plate via three nylon screws. The spacing between the plates was varied from 25 to 100 μm. The variation in thickness was less than 5 μm Movement of the top glass plate was achieved by a computer controlled stepping motor driving a precision lead screw. Easily obtained velocities varied from 5 cm/sec to .1 cm/sec. This permitted the use of a large range of shear rates with 30 sec $^{-1} < \gamma < 3x10^2$ sec $^{-1}$ The shear cell was mounted upon the center of a rotary table equipped with arm having a 50 μm slit from which the light was collected and focused on a photodiode. Since the angular resolution of the system ($\delta\theta < .05^{o}$) was better than any of the observed features, the data represents the intrinsic line widths. An example of the obtained diffraction profile after shear is shown in figure 2 appear to have slightly different intensities due to collecting data by scanning in angle resulting in the two peaks being scanned at different times.

RESULTS

One prime objective of the experiments was to establish which parameters control the characteristics of the texture. Figure 3 shows data for several different sample thicknesses while varying the plate velocity for constant shear rate. Note that the peak position is essentially independent of the sample thickness. The scattered intensity appeared to be strongly dependent upon the sample thickness indicating a much higher grating efficiency for thinner samples. A second important result is demonstrated by the

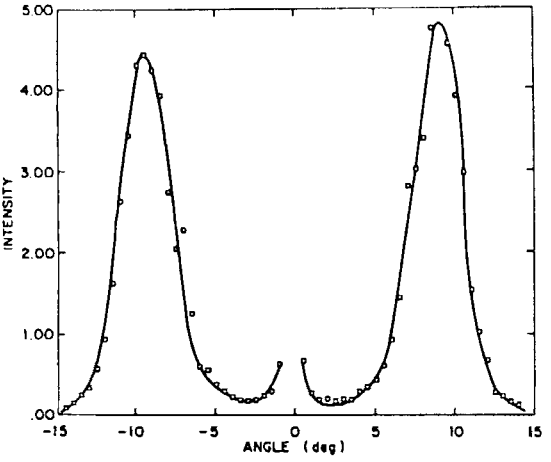

FIGURE 2 Representative diffraction profile obtained from texture

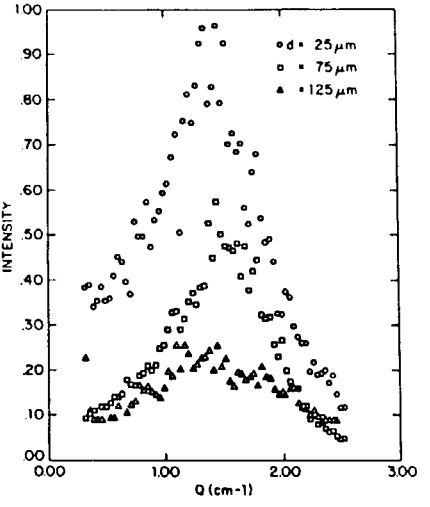

Figure 3 Diffraction peak obtained at a series of shear rates

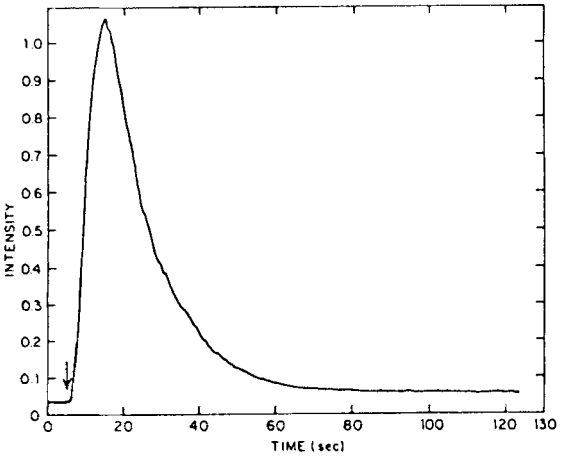

FIGURE 6 These data show the time dependence of the texture development. The arrow indicates the time at which shearing of the sample stopped. Note that prior to the cessation of shear the texture is completely absent.

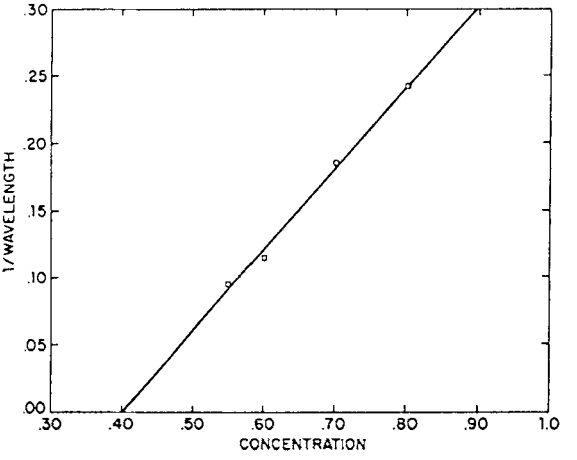

FIGURE 7 Plot of the inverse of the texture wavelength verus the concentration in weight percent of the polymer. Note that the line extrapolates to to zero at the concentration for which the mesophase first begins to form.

data of figure 4 showing the obtained diffraction profile for various velocities of the glass plate. The data are reported in terms of the relevant variable, shear rate showing clearly that for the range of shears in this experiment the spacing of the bands is independent of the shear rate. Figure 5 shows data collected for different concentrations of the polymer from which it is obvious that the diffraction peak is strongly dependent upon the concentration. Although the peak positon varies with concentration the ratio of peak width to peak position, ($\delta q / q_{peak}$) does seem to remain roughly constant. This implies that the coherence length of the pattern is constant if measured in the wavelength of the pattern itself. Although not shown by these data it was noted that the peak width in the transverse direction was narrower by roughly a factor of two The data of these experiments also contain important information on the time dependence of the texture formation. A key question has been if the banding sometimes occurs during shear or if the effect is always a result of relaxation.[9] The data of figure 6 demonstrates that without a doubt that the banding is the result of relaxation. The data of this figure show the time dependence of the light scattered at the angle of the diffraction maximum. The time t=0 denotes the point at which shearing ceased. Note that for the time interval prior to the cessation of shear that there is not any indication of the periodic texture. This experiment provides extremely clear evidence since one does not need to have direct visual observation of the texture which is extremely complicated during shear. Even after the cessation of shear the intensity does not begin to build immediately, but rather only after an induction period does the intensity grow rapidly. Within the experimental limits of the apparatus ($30 < \dot{\gamma} < 3x10^2\ sec^{-1}$), we could not locate any critical shear rates that the texture did not develop to at least some degree. We attempted to obtain data relating the diffraction efficiency or the amplitude of the texture with the shear rate, however the data did not show any clear trends. This is still under investigation. Figure 6 shows the reciprocal of the wavelength of the texture plotted versus the polymer concentration. As can be seen there is a linear relation extrapolating to zero at the concentration of c=.41 by weight. The critical concentration for the beginning of the formation of the mesophase is c^* =.42. The lowest concentration that data was collected was at c=.52 in order to be above the biphasic concentration range.

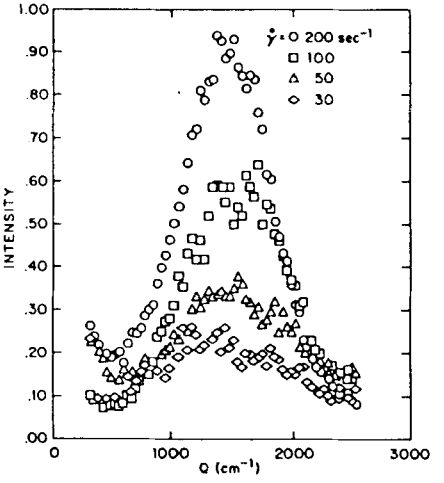

FIGURE 4 Diffraction profile obtained for a series of sample thicknesses

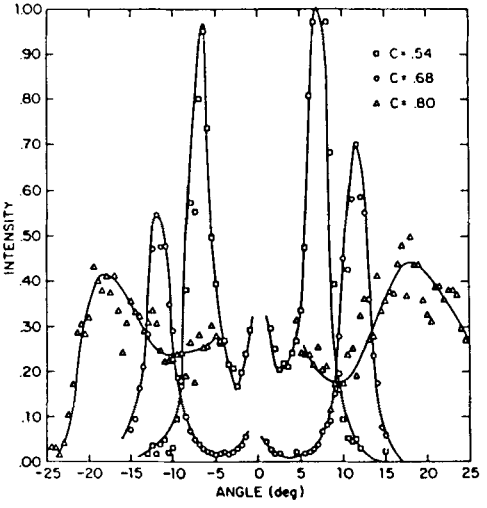

Figure 5 These data show the large changes in the texture diffraction when the concentration of the mesophase is varied

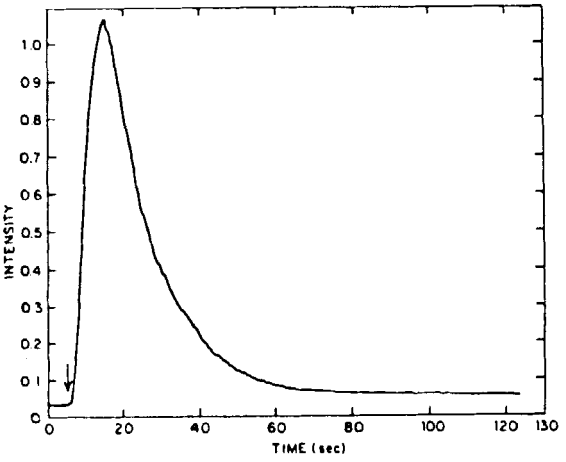

FIGURE 6 These data show the time dependence of the texture development. The arrow indicates the time at which shearing of the sample stopped. Note that prior to the cessation of shear the texture is completely absent.

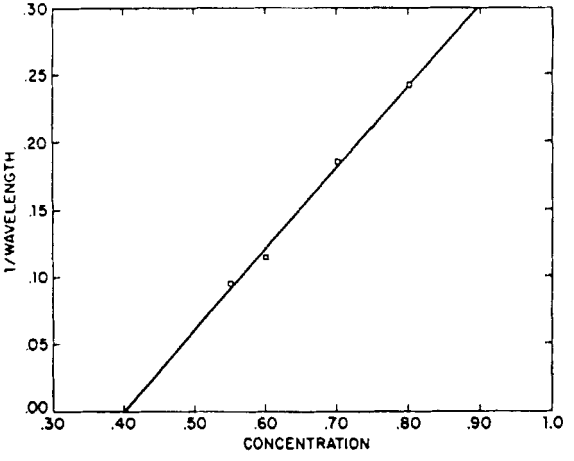

FIGURE 7 Plot of the inverse of the texture wavelength verus the concentration in weight percent of the polymer. Note that the line extrapolates to to zero at the concentration for which the mesophase first begins to form.

DISCUSSION

The plot of the selected wavevector verus the polymer concentration shown in figure 7 demonstrates that the effect is connected to the formation of the mesophase. These data in conjunction with the fact that the banding can be observed at wavelengths more than an order of magnitude greater than the contour length of the polymer itself proves that the banding cannot be the result of any type of single chain buckling as has been previously suggested.[9] The importance of this is of establishing that the banded texture is a phenomena of liquid crystal physics and not the result of the dynamics of a single chain. Many aspects of these observations are similar to those of Roche et al.[10] One of the similarities is that the diffracted beam is of the opposite polarization of the incident beam. This can be easily understood by modifing the theory for the description of their observations. We simply consider the sample to be a thin layer with an anisotropic dielectric constant. If the incident beam is polarized along the y-axis then after propagating through the sample the electric field can be written as

$$E = E_o \left\{ \hat{j}\left[e^{ik\varepsilon_{||}} \cos^2\theta + e^{ik\varepsilon_{\perp}} \sin^2\theta \right] + \hat{i}\left[\frac{1}{2} \sin 2\theta \left(e^{ik\varepsilon_{||}} - e^{ik\varepsilon_{\perp}} \right) \right] \right\} \quad (1)$$

Then considering the sample in the limit of a thin grating where the principal axis of the dielectric tensor are sinusoidally modulated, the observed electric field can be written as

$$\frac{E_{obs}}{E_o} = \frac{\delta}{2} \int_{-\infty}^{\infty} \sin[2\theta(y)]\, e^{iky\sin\phi} \quad (2)$$

where δ is the phase lag $\delta = e^{ik\varepsilon_{||}} - e^{ik\varepsilon_{\perp}}$ and ϕ is the scattering angle satisfying the Bragg condition.

$$k\, l \sin\phi = m\, 2\pi \qquad m = \text{integer}$$

The resulting intensities are given as

$$\frac{E_{obs}}{E_o} = J_{2m+1}(2\theta_o) \tag{3}$$

where $J_m(x)$ is the mth Bessel function and q_0 is the amplitude of the modulation of the principal directions of the index of refraction..

The data presented here clearly establish that the banded texture arises as the result of relaxation from a shear induced configuration or texture of the director. Fortunately these experiments do provide someimportant clues as to the nature of the directorconfiguration during shear. As discussed the data of figure 6 clearly shows that the director is unmodulated during shear. We also monitored the transmitted beam through crossed polarizers and sample as a function of time. Although before shear the intensity was considerable reflecting the birefringent nature of the mesophase, upon the initiation of shear the beam intensity dropped several orders of magnitude to essentially complete extinction. After shear the intensity would slowly grow in roughly the same way as the diffraction peaks at early times. The complete extinction of transmitted light through crossed polarizers during shear implies that the projection of the director in the plane of the sample is highlyaligned along the shear direction. Note that the extinction does not imply that the director is completely aligned because the measurment is insensitive to any component out of the plane of shear. Therefore,while the experiments make it clear that the banded texture is a result of the modulation of the director in the plane of the sample, we do not know if the stressedinitial state that the system is relaxing from is simply highly alignedalong the shear direction in the plane of the sample or whether the stressed state also involves a director component out ofthe sample plane.

Let us consider the second possibility first. Donald et. al.[11] also show evidence that the final texture is a modulation of the director in the plane and suggest that there may be a component out of the plane. This observation is very important in consideration of the development of the banded texture leading one to two significant conclusions. Since the modulated state (the banded texture) is clearly of a higher energy than a uniform planar state, the configuration during shear must be of an even higher energy state, but consistent with the observation that the projection of the director onto

the plane is highly aligned. The only possibiliity is a uniform (not periodic along the shear direction) distortion out of the plane of shear.

Recent studies have shown that in polymeric liquid crystals the splay elastic coefficient may be much larger than either twist or bend.[12]These similarities suggest that one may think of the process in analogy with these other experiments on polymeric nematics which also resulted in periodic textures. The observed periodic textures formed by poly(benzamide) in a magnetic field[13] bear a striking resemblence to the banded texture. The textures found in PBA also behave under a polarized microscope in an identical fashion to the banded texture. The basic difference is that the magnetic field textures are on a much longer length scale. The wavelength is about 100 μm rather than 1-10 μm With such strong similarities one should suspect that dynamics of formation of the two textures might have much in common. This and other previous work has shown that in the case of large anisotropy the nematic liquid may find that non-uniform (i.e. periodic) modes may sometimes provide a faster route for the relaxation of a stress.[12,13,14,15,16] Even though the periodic texture is not of as low energy as a uniform state the backflow terms may reduce the effective viscosity enough that the response is much faster. In such a case a periodic texture may relax to the uniform texture on a much longer time scale. The banding itself would then result from a periodic fluctuation of the splay deformation towards a twist deformation resulting in a faster relaxation rate than the uniform mode.

It is certainly true as state that the state immediately after shear mustbe of a higher energy than the modulated texture which is the result ofthe relaxation process. However, it is not true that the only way toallow for this energy is by assuming an out of plane deformation of the director. The viscoelastic nature of the polymer allows for the accumulation of significant stress during shear with the release afterwardsby fluid flow. If we consider this as a possibility then the observed texture would then have an analogy to previously observed results for small molecule cholesterics.[17] These workers reportedthe buckling of a sheared cholesteric as observed by the diffraction of light from a thin sample. In this case the release of the accumulated stresses would resultin a similar texture. One would then have to explain how the effectcan also be observed in nematic polymers.

CONCLUSIONS

We have demonstrated that the banded texture is closely connected with liquid crystal phenomena while the wavelength of the texture varies inversely with $c-c^*$ Not only is there little or no effect upon the texture wavelength with sample thickness, but also the shear rate appears to be irrelevant in this regard. The data suggest that the texture results from the relaxation of either a splay like deformation or the viscoelastic stresses both of which are generated by the shear of the sample.

REFERENCES

1) M.G. Dobb, D.J. Johnson, and B.P. Saville, J. Polym. Sci. Polym. Phys. Ed.,15,2201, (1977).
2) G. Kiss and R.S. Porter,J. Polym. Sci. Polym. Phys. Ed. ,18,361 , (1980).
3) S.C. Simmens and J.W.S. Hearle, J. Polym. Sci. Polym. Phys. Ed.,18,871,(1980).
4) G. Kiss and R.S. Porter,J. Polym. Sci. Symp.,65,193,(1978).
5) A.M. Donald, C. Viney, and A.H. Windle, Polymer,24,155 ,(1983).
6) A.E. Zachariades and J.A. Logan,Polym. Eng. Sci. ,23,797, (1983).
7) F. Fellers, J. Polym. Sci. Polym. Phys. Ed,22,45 , (1980).
8) P.J. Flory, Proc. Roy. Soc. London Ser. A.,234,73, (1956).
9) A.E. Zachariades, P. Navard, J.A. Logan, Mol. Cryst. Liq. Cryst. ,110,93,(1984).
10) E. Roche, M. Wolfe, A. Suna and P. Avakian ,J. Macromol. Sci. Phys.,B24, 141,(1985).
11) A. M. Donald and A.H. Windle, Jour. Mater. Sci.,19,2085 ,(1984).
12) F. Lonberg and R.E. Meyer, Phys. Rev. Lett.,55,718 , (1985).
13) C.R. Fincher Jr., Macromolecules,19, 2431,(1986).
14) Y.W. Hui, M.R. Kuzma, M. San Miguel and M.M. Labes, J. Chem. Phys., 83, 288 , (1985).
15) F. Lonberg, S. Fraden, A.J. Hurd and R.E. Meyer, Phys. Rev. Lett., 52,1903 , (1984).
16) D.J. Graziano and M.R. Mackley, Mol. Cryst. Liq. Cryst.,106,73 , (1984).
17) N. Scaramuzza,R. Barberi,F. Simoni,F. Xu,G. Barbero, and R. Bartolino.,Phys. Rev.,A32,1134,(1985).