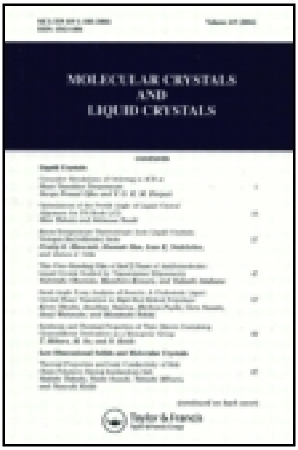

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Effect of Processing Variables on Banded Textures in Hydroxypropyl Cellulose Solutions

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Version of record first published: 24 Sep 2006.

To cite this article: W. S. Putnam & C. Viney (1991): Effect of Processing Variables on Banded Textures in Hydroxypropyl Cellulose Solutions, Molecular Crystals and Liquid Crystals, 199:1, 189-195

To link to this article: http://dx.doi.org/10.1080/00268949108030929

Mol. Cryst. Liq. Cryst., 1991, Vol. 199, pp. 189–195
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Printed in the United States of America

Effect of Processing Variables on Banded Textures in Hydroxypropyl Cellulose Solutions

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(Received July 26, 1990)

Our research focused on banded textures in three lyotropic systems of hydroxypropyl cellulose (HPC): HPC-water, HPC-methanol, and HPC-acetone. Banded textures were induced by shearing solutions with a motorized parallel plate apparatus. The evolution of the banded texture was investigated by transmitted polarized light microscopy. Measurements of band spacing were used to develop a quantitative basis for comparing relaxation rates. Our study showed that the molecular orientation introduced by shear is preserved longest by using thermodynamically poor solvents and working with high concentrations. Alternatively, if the solvent is thermodynamically good, increasing dilution promotes slower relaxation rates.

Keywords: Banded textures, band spacing, hydroxypropyl cellulose, Klucel, lyotropic, relaxation, shear

INTRODUCTION

Banded textures are exhibited by sheared thermotropic and lyotropic polymers when observed microscopically between crossed polars.[1,2] The bands arise when aligned microstructures relax to topologies in which the local molecular orientation varies periodically relative to the shear direction.[3] Efforts to optimize the mechanical properties of sheared liquid crystalline polymer fibers and films require an understanding of the conditions under which bands are formed.

This work is a systematic study of the evolution of banded textures in lyotropic HPC solutions. Our research focused on the effect of various processing parameters: shear rate, concentration, and solvent type. The shear rates used in this study were higher than those quoted by previous investigators[4–6] and therefore better approximate actual fiber-drawing and film-forming processes.

Banded textures were formed by shearing the polymer solutions with a motorized stage, which allows for controlled and reproducible shear. Polarized light microscopy was employed to observe the evolution of the banded texture after shear. We characterized this evolution qualitatively in terms of the time elapsed between

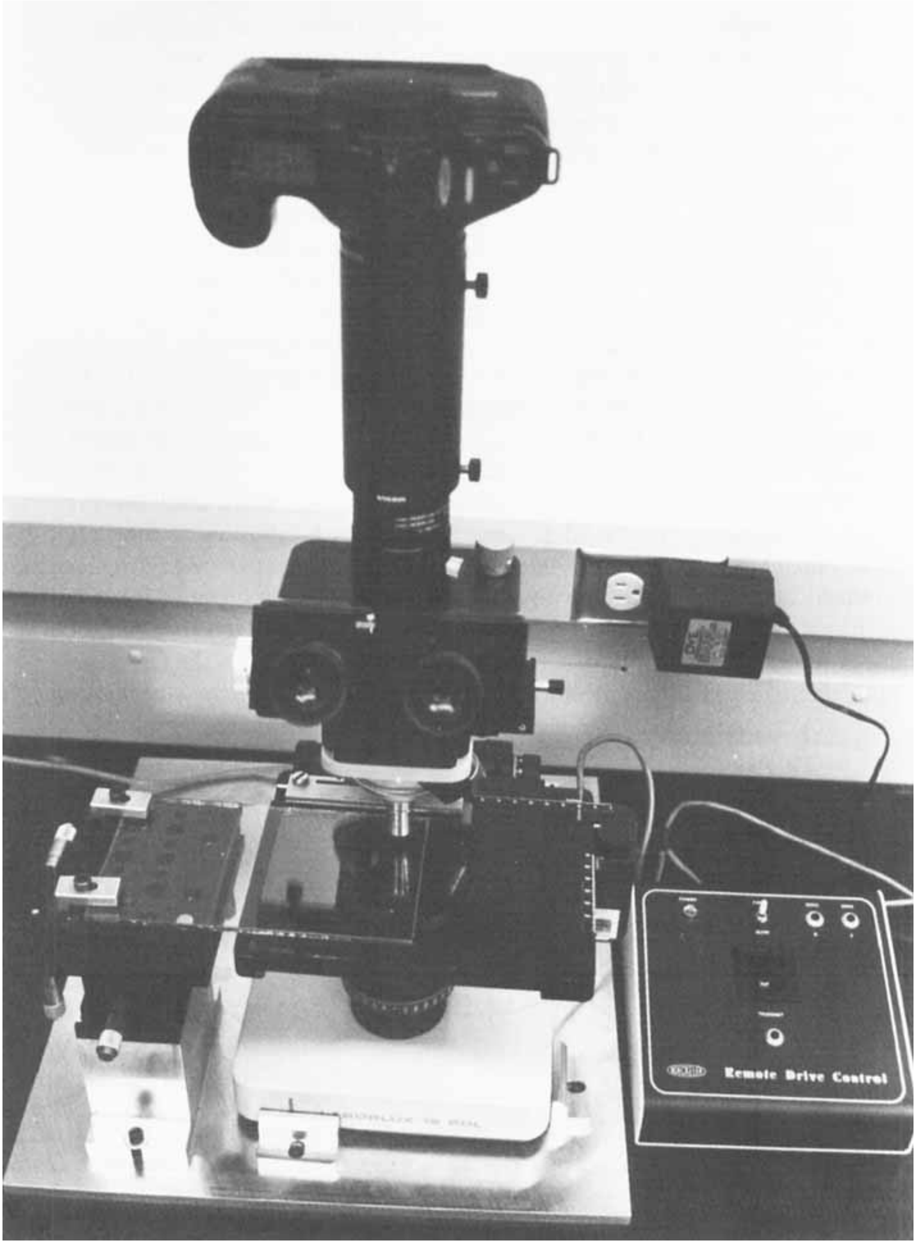

FIGURE 1 Motorized shearing stage fitted to transmitted polarized light microscope.

systems. A concentration of 45 wt.% corresponds to the biphasic region for the water and methanol systems and to the isotropic region for the acetone system. The Klucel E-water results are consistent with the work of Ernst and Navard,[4] who reported that a shear rate exceeding 100 sec^{-1} was insufficient to induce bands in isotropic or biphasic solutions. It is possible that higher shear rates would induce bands in the biphasic solutions, since a banded texture was previously reported[10] for a biphasic solution of nitrocellulose at a shear rate of 10^4 $\sec^{-1}$.

The 53 and 61 wt.% solutions were anisotropic for all three systems. Banded textures did form in these solutions. The time-scale of band formation after shear varied from seconds in the water and methanol solutions to minutes in the acetone solutions.

To determine the effect of processing conditions on band relaxation, it was necessary to develop a criterion for defining the relaxation time. The first criterion that we considered was the time when the banded texture had completely disappeared. Applying this criterion was difficult because relaxation is a gradual process; the microstructure retains evidence of periodicity for some time after the initially straight bands have degenerated into wavy lines. We attempted to determine this time by using a Bertrand lens to detect periodicity in the objective back focal plane, but this approach proved impractical due to the short time-scale of the relaxation process in water and methanol solutions.

The criterion that we selected was based on a quantitative analysis of the band periodicity. A plot of the average band spacing as a function of time after shear revealed the existence of a minimum (Figure 2). The error bars in Figure 2 represent a standard deviation. To determine the position of the minimum for a particular experiment, the data points close to the minimum were fitted to a parabola using a computer graphics program, Cricket Graph Version 1.3.2.

The time to reach the minimum indicates a rate of microstructural change. We

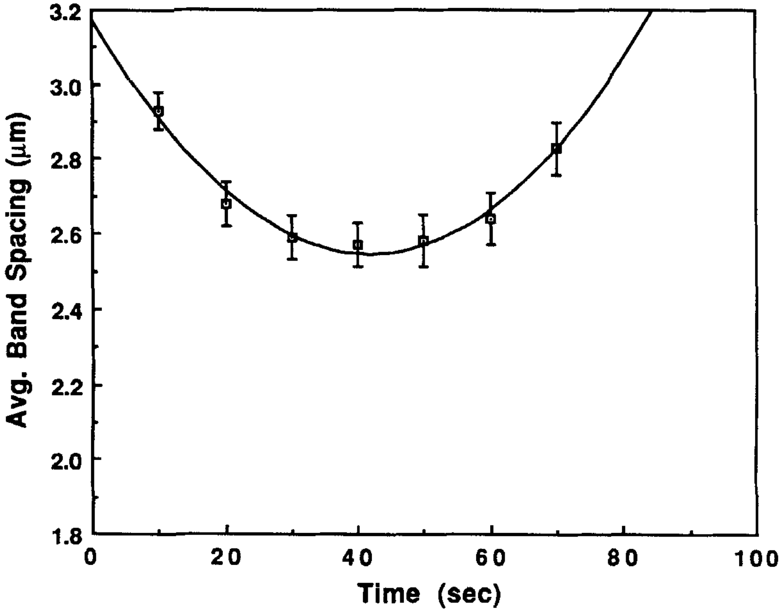

FIGURE 2 Plot showing the time-dependence of the average band spacing in 61 wt.% Klucel E-water solution. Shear rate = 1810 $\sec^{-1}$. Thickness = 50 µm. The error bars represent a standard deviation.

were concerned about whether this time indicated band formation or relaxation. By studying a series of photographs of the evolving banded texture, we noted that the bands appeared to break up *after* the average band spacing had reached a minimum. We also found that the time to reach an arbitrary increase in band spacing (e.g. 10%) above the minimum followed the same trends as the time to reach the minimum band spacing. This check lends support to our method of measuring band relaxation times and therefore relative microstructural relaxation rates in terms of the time to reach the minimum average band spacing.

Using this method, we compared the relaxation behavior observed under different processing conditions. Table I gives values of relaxation times for banded textures induced in Klucel E-water, Klucel E-methanol, and Klucel E-acetone solutions. The relative relaxation rates were found to be a function of solvent, concentration, and shear rate.

The relaxation behavior will be interpreted in terms of how thermodynamically good the solvent is and how this affects chain conformation and entanglement. HPC dissolves most readily in polar solvents, indicating that they are thermodynamically good solvents for the polymer. We determined the relative polarity of water, methanol, and acetone by comparing their solubility parameters: 23.4, 14.5, and 9.9 $(\mathrm{cal/cm^3})^{1/2}$, respectively.[11] Thus, we expect that water is a thermodynamically good solvent for HPC, while methanol and acetone are relatively poor solvents.

As Table I shows, relaxation occurs much more slowly in the Klucel E-acetone system than it does in the Klucel E-water or the Klucel E-methanol solutions. Bands take minutes to relax in the acetone solutions and tens of seconds to relax in the water and methanol solutions. Since acetone is a relatively poor solvent, the

TABLE I

Effect of processing variables on relaxation times

System	Conc. (wt.%)	Shear Rate ($\mathrm{sec^{-1}}$)	Thickness (μm)	Relaxation Time
Klucel E-water	53	490	50	55 sec
	61	490	50	43
	61	1810	50	42
Klucel E-methanol	53	490	50	9 sec
	61	490	50	15
	61	1810	50	17
Klucel E-acetone	53	490	Bands not fully developed	
	61	490	50	22 min
	61	1810	50	9

molecules tend to have a random coil conformation. These molecules entangle readily, reducing the opportunity for relative motion of the polymer chains, which in turn retards the relaxation process.

In the Klucel E-water system, band relaxation occurred more slowly in the 53 wt.% solution than in the 61 wt.% solution. The more rapid relaxation at the higher concentration suggests that relative motion of the chains is easier. In water, a thermodynamically good solvent for HPC, the polymer chains have an extended conformation, which favors the chains assembling with a degree of alignment. Since higher concentrations favor greater extension of the polymer chains, the degree of alignment tends to increase as the polymer concentration increases. An interdependence of concentration, chain extension, and cooperative alignment in the nematic phase has been previously suggested for semiflexible lyotropic and thermotropic polymers.[12] Molecules in a highly oriented, extended state are less likely to entangle. Therefore, we expect that microstructural rearrangements will occur more rapidly at higher concentrations.

The opposite trend is observed in the Klucel E-methanol solutions. Since methanol is a thermodynamically less good solvent for HPC than water, the polymer chains have a less extended conformation than those in an aqueous solution. A less extended conformation favors chain entanglements. These entanglements reduce the relative motion of the chains, retarding the relaxation process. As the concentration of the polymer increases, the number of chain entanglements increases. Slower relaxation is therefore expected at higher concentrations.

Whether or not the solvent is thermodynamically good is not the only factor governing band relaxation in HPC solutions. We expect that the elastic constants for the three distortion modes, particularly bend distortion, should also affect the relaxation. A theory for rigid rod molecules[13] gives a relationship between the elastic constants and the solution concentration. While this theory is not directly applicable to HPC, which is a semiflexible molecule, we anticipate a similar qualitative dependence of the elastic constants on solution concentration.

A shear rate dependence was observed in the Klucel E-acetone solutions, as shown in Table I. As the shear rate increased, the band relaxation time decreased. This trend has been reported in the literature for aqueous Klucel E solution[4] and solutions of poly-γ-benzyl-L-glutamate in m-cresol.[14]

CONCLUSIONS

The rate at which the global molecular orientation relaxes in sheared liquid crystalline polymers depends on solvent type, concentration, and shear rate. The dependence on solvent type is especially sensitive. Relaxation rates can be compared effectively by identifying the minimum that occurs in plots of the time dependence of the average band spacing. Our results for a semiflexible polymer suggest that relaxation of the global molecular orientation can be retarded by choosing thermodynamically poor solvents. Slow relaxation rates in these solvents can be further promoted by using higher concentrations. In cases where the solvent is thermodynamically good, slower relaxation rates can be obtained by increasing dilution.

Acknowledgment

We gratefully acknowledge Aqualon Company for the donation of Klucel E. Support for this work was received from the College of Engineering (Univ. of Washington), ACS-PRF (No. 21300-G7), and the IBM Corporation.

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