Solvent Evaporation Induced Torsad Texture of Sheared Liquid-Crystalline Polymers

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ABSTRACT: The periodic structures formed in liquid-crystalline polymers after the cessation of shear flow can in some cases consist of a primary set of bands perpendicular to the shear direction and a secondary set of bands (called "torsads") that are slightly inclined to that direction. In this work, it is shown, for the lyotropic cholesteric polymer system (hydroxypropyl)cellulose (HPC)-acetic acid, that the torsads occur as a consequence of the hydrodynamic flow associated with evaporation of the solvent. The pitch of the cholesteric array is also found to affect the torsad spacing, but torsads are also observed in lyotropic nematic systems under similar conditions. Thermotropic cholesteric HPC did not exhibit torsads. The phenomenon is qualitatively explained by considering the hydrodynamic instabilities associated with the temperature gradient created by evaporation of solvent from the sample surface. The apparent dependence of torsad spacing on pitch is a consequence of the related changes in the materials parameters of the system.

Introduction

The formation of banded textures in fiber or thin-film samples of thermotropic and lyotropic liquid-crystalline (LC) polymers that have been subjected to shear has been widely reported in the literature.[1-9] These bands are a transient phenomenon, but they may be locked into the polymers when solvent evaporates or when solidification occurs. The bands appear between crossed polars as equidistant lines perpendicular to the direction of shear. An alternating tilt angle of the optic axis of the macromolecule of equal and opposite values, relative to the shearing direction, is considered to be the reason for band formation.[4,10-12] This periodic oscillation of the orientation of the director has been related to the elastic behavior of LC systems and attributed to contraction strains of the sheared sample induced by stress relaxation after cessation of flow.[5]

The factors affecting the formation of such a texture, however, are not well understood. Fincher used light diffraction techniques to study band formation in (hydroxypyropyl)cellulose (HPC) aqueous lyotropic solutions[13] and found that both shear rate and thickness have little effect on band spacing, whereas the concentration of the solution has an appreciable effect. Marrucci and co-workers, on the other hand, observed that the sample thickness has a strong influence on the appearance of the bands in the same system.[14] They also observed that a "threshold" deformation value exists below which no banded texture forms and that depends on the sample thickness. Horio and co-workers also studied HPC aqueous lyotropics and observed that the solution concentration plays a very important role in the formation of bands.[5] Fried and Sixou studied the cholesteric solution of HPC in acetic acid (AA) and concluded that no bands form below a certain critical thickness and that shear rate has a very strong effect on band appearance.[15] Ernst and Navard studied the aqueous solutions of HPC by small-angle light-scattering techniques and found that there is no band formation below a critical shear rate, which is independent of solution concentration but dependent on polymer molecular weight.[7] They also observed that the total shear deformation is more important than the shear rate in band formation. Marsano et al. made similar observations, reporting that there is a critical shear rate below which bands do not form and that there also is a minimal time of shear below which there is no band formation.[16]

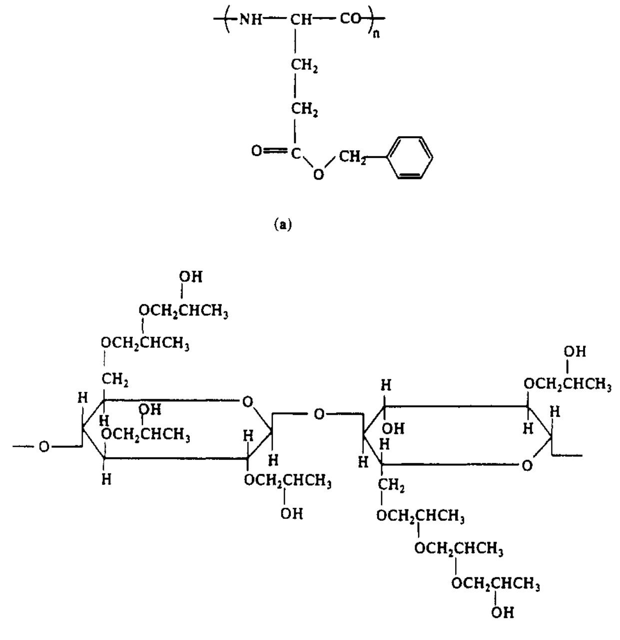

Figure 1. (a) Structure of poly(γ-benzyl L-glutamate) and (b) typical structure of a (hydroxypropyl)cellulose.

Table I
Variation of Pitch with Solvent Composition for 37 wt % HPC (Klucel L) in AA-TFA (w/w) and 20% PBLG in Dioxane-Methylene Chloride (D-MC) (v/v)

	solvent composition		
polymer	AA-TFA	D-MC	pitch, μm
HPC	80:20		9-10
HPC	72:28		16-17
HPC	63:37		45-46
HPC	0:100		>100
PBLG		100:0	20
PBLG		80:20	50
PBLG		20:80	∞

Fried and Sixou reported the occurrence of a substructure of secondary bands of alternate intensity but with a weak contrast in the case of cholesteric solutions of HPC in AA, observed only in thin samples.[15] The secondary

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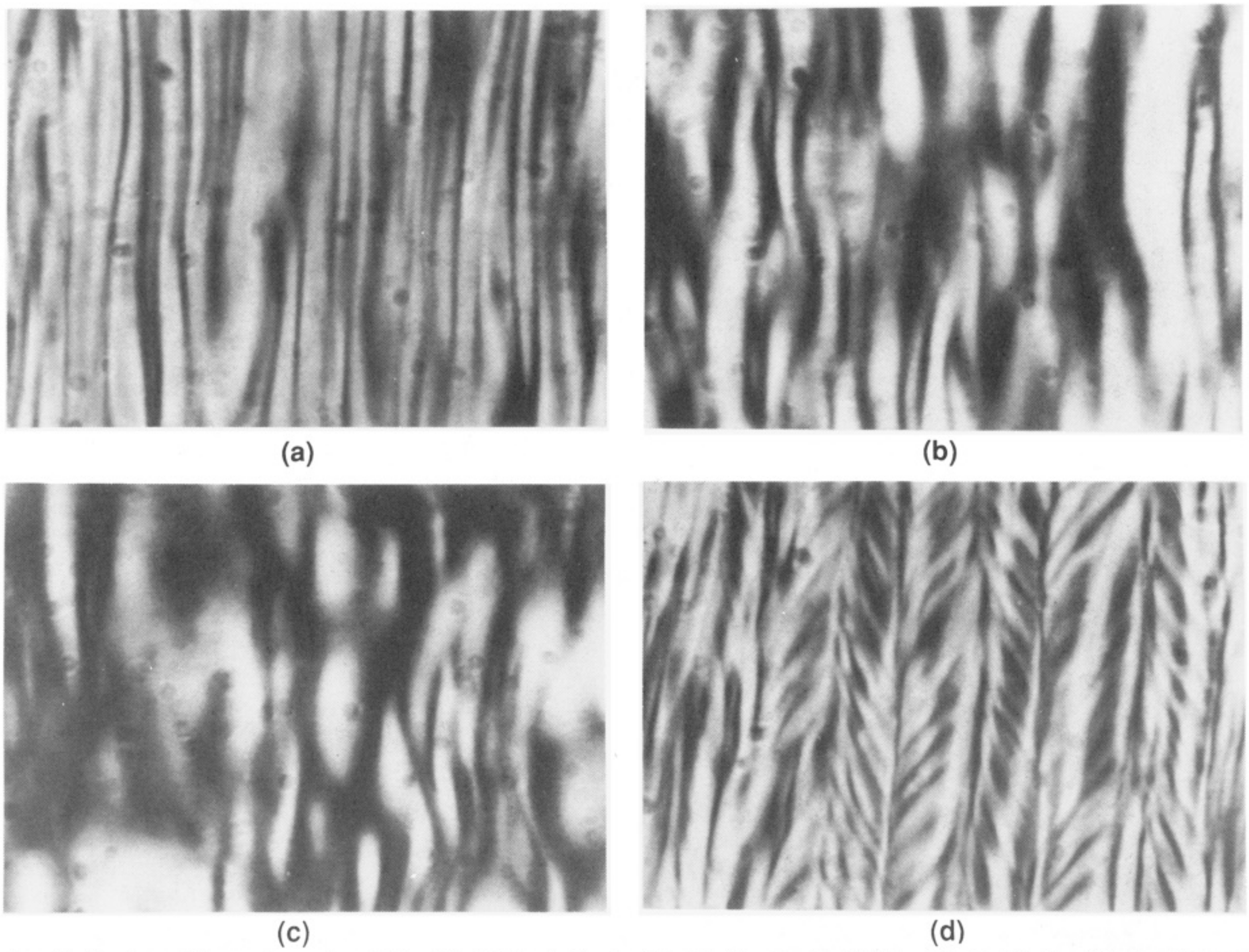


Figure 2. Texture of sheared samples of 37 wt % HPC solution in AA: (a) after 1 min; (b) after 10 min; (c) after 25 min of cessation of shear in closed samples; (d) after 7 min of opening the sample shown in c (magnification ×400).

bands are a series of stripes observed under crossed polars, forming a herringbone-like pattern between the primary bands, tilting alternately in accord with the tilt in the director. These secondary bands are referred to as "torsads". Fried and Sixou[15] observed these torsads after solvent evaporation, and it was speculated that they may be associated with the partial rewinding of the cholesteric structure, which is unwound during shear. Kiss and Porter[4] report a coarse ropelike pattern in poly(γ-benzyl L-glutamate) (PBLG) systems, which is most likely another case of torsad formation.

In this work, the formation of torsads in lyotropic LC polymer systems is thoroughly investigated with respect to both the role of evaporation of solvent and the magnitude of the cholesteric pitch. Cholesteric solutions of HPC in AA are primarily used, but other lyotropic and thermotropic cholesterics and nematics are also examined in order to put the problem in perspective.

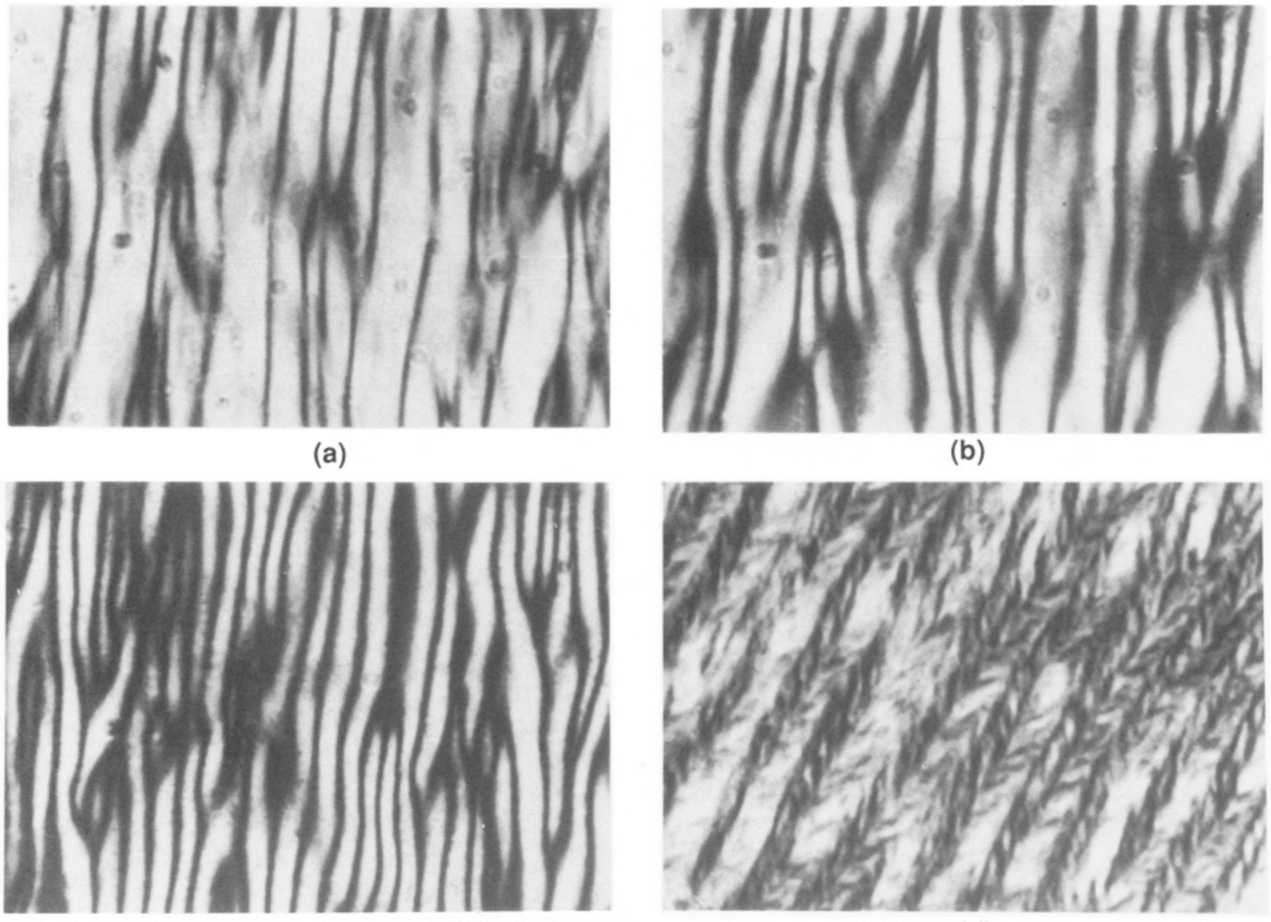
Experimental Section

The HPC used was Klucel L (95 000 weight-average molecular weight) kindly furnished by Hercules Inc. Solutions of HPC in glacial AA having a concentration of 33 wt % and above are cholesteric.[17] Solutions (37 and 44 wt %) of HPC in AA or trifluoroacetic acid (TFA) were used in this study, as well as solutions of HPC in a mixed solvent of AA and TFA. The mixed solvent preparations were made by dissolving 37 wt % HPC in weight/weight mixtures of 20:80, 28:72, and 37:63 TFA:AA. These solutions showed a large change in pitch depending on the TFA:AA ratio (Table I).

Solutions of poly(γ-benzyl L-glutamate) in chloroform, 1,4-dioxane, and the mixed solvents 1,4-dioxane and methylene chloride were also prepared for comparison purposes. PBLG samples of 85 000 and 248 000 molecular weights were supplied by Sigma Chemical Co. A 30% solution (w/v) of PBLG of 85 000 molecular weight in chloroform gave a nematic phase.[18] Solutions (20 wt %) of PBLG of 248 000 molecular weight were made in mixed solvents of dioxane and methylene chloride (v/v) in the proportions 100:0, 80:20, and 20:80.[19] The pitch values for these solutions are given in Table I. Poly(γ-benzyl D-glutamate) (PBDG) from Sigma Chemical Co. of approximately the same molecular weight as PBLG was used to make nematic solutions by mixing equal weights of PBLG and PBDG and then making 20 wt % solutions in dioxane.[20] The chemical structures of HPC and PBLG are given in Figure 1. For HPC, this structure is only representative—the structure and distribution of substituents is not necessarily exactly as shown.

For the measurements of pitch, solutions were sealed in 0.4-mm × 8-mm × 60-mm rectangular capillaries obtained from Vitro Dynamics. Sealed samples were annealed for at least 30 days to assure equilibrium. The pitch was measured from the fingerprint texture[21] observed under crossed polars on a Nikon microscope. Photomicrographs were taken by using a Nikon Microflex Model EFM semiautomatic attachment.

Samples for shearing studies were prepared by placing a few drops of solution between two glass slides separated by Mylar spacers (typically 50.8 μm) to control the film thickness. For applying shear at any given rate and to any given level of total deformation, a cell was constructed similar in design to that described by Marrucci et al.[14] The bottom glass slide was held fixed, while the top slide was allowed to move at a predetermined speed with the help of a dc motor. From the number of pulses per second and the total number of pulses at any given time applied to the motor, the rate of shear and the total deformation at that time could be calculated.



(a) (b) (c) (d)

Figure 3. Textures of sheared samples of 37 wt % HPC solution in AA after cessation of shear, opened and kept at 0 °C for (a) 2 min, (b) 10 min, (c) 20 min, and (d) 10 min after the temperature was allowed to warm to room temperature. In d, the sample has been rotated to achieve better contrast, and the bands are in reality perpendicular to the shear direction as in all other samples (magnification ×400).

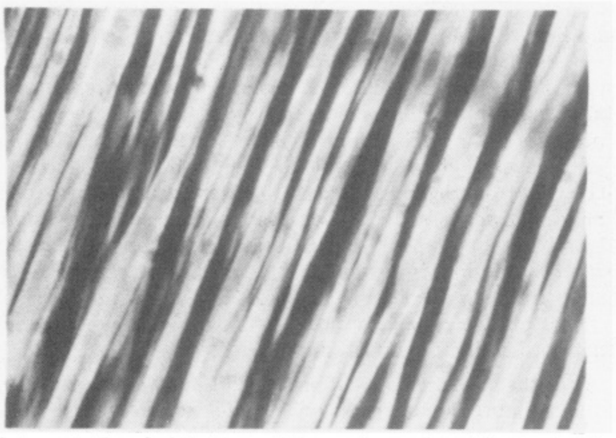


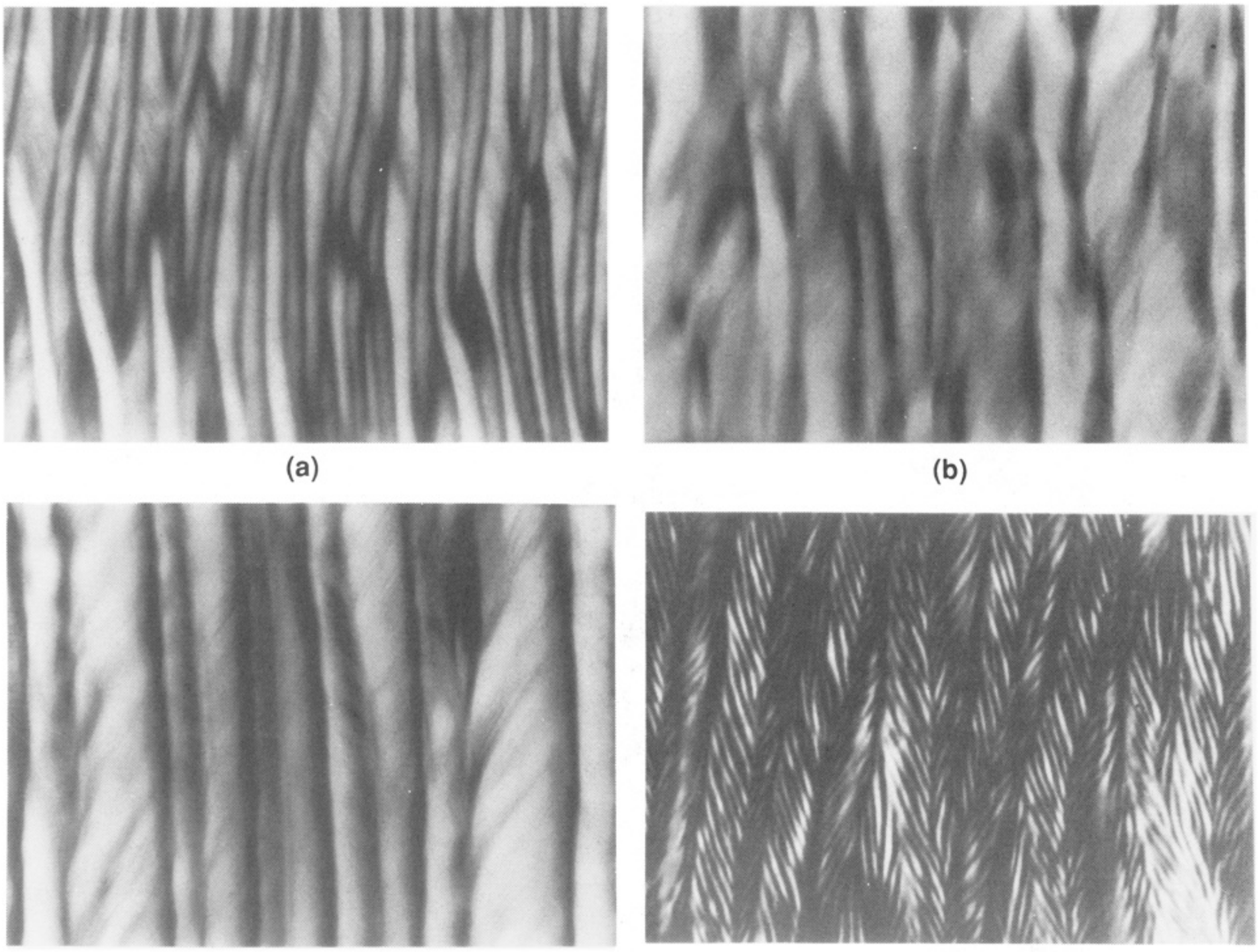
Figure 4. Banded texture of sheared sample of thermotropic HPC at 257 °C after cessation of shear (magnification ×400).

To study the effects of solvent evaporation on these banded samples, the shearing process was conducted at similar rates and total deformation, but the top slide was completely removed from the sample at the end of (and as a part of) the shearing motion. Alternately (as in the studies reported in Figure 2), the sample was sheared and the top slide physically removed from the sample by carefully lifting it at prescribed times. This procedure did not significantly perturb the primary bands. In order to prevent or slow the evaporation, samples could then be placed on a thermoelectric cold stage (Bailey Instruments). For studying the banded texture of HPC in thermotropic experiments, a Mettler FP82 hot stage was used.

Results

In the shear cell experiments with HPC (37 wt % solution in AA), it was observed that at high shear rates the bands were very closely packed while at low rates the bands were separated by large spaces. For example, when the rate of shear deformation was 31 s^{-1}, the bands were more closely packed than when the rate was 7.9 s^{-1}. We had earlier observed that, during extrusion of fibers from this solution using the commercial spinning apparatus obtained from Bradford University, U.K., one obtained a very high density of bands in fibers even at the lowest shear rates (spinning under gravitational force). It was also observed that, at higher levels of applied shear deformation, the time required for the onset of band formation from the time of cessation of stress was higher. Three rates of shear deformation were used: 102, 13.2, and 8.9 s^{-1}.

When a thin film of 37 wt % HPC solution in AA was sheared, the banded texture appeared almost instantaneously after cessation of shear. When the solvent was allowed to evaporate, the torsads appeared after about 3 min. When the solvent was not allowed to evaporate, however, by keeping the sample closed, no torsads were seen even after 25 min, during which time considerable relaxation of the bands occurred. When the sample was opened at that point and the solvent evaporated, the torsads formed even on weak bands in about 3 min. Figure 2 shows the results of these experiments. In Figure 2d, the primary bands appear to be sharper and more regular than in Figure 2a–c, at least in the central part of the



(a) (b)

(c) (d)

Figure 5. Textures of sheared samples of HPC in the mixed solvent TFA–AA after cessation of shear, the solvent composition (w/w) being (a) 100:0, (b) 37:63, (c) 28:72, and (d) 20:80, respectively (magnification ×400).

photograph. This is because the region of the sample identified in Figure 2d was selected because of its extremely good orientation and organization. Examining a larger area of the sample, however, makes it apparent that there is no real difference in the primary bands before and after evaporation.

Experiments performed with a thin film of 44 wt % HPC solution gave essentially the same results, demonstrating that, all other parameters being the same, the dependence of torsad formation on solvent evaporation is independent of concentration. It should be noted at this point that 37 and 44 wt % HPC solutions in AA have similar values of pitch (between 3 and 5 μm).

When a similar sample of 37 wt % HPC solution in AA was sheared and instantaneously cooled at 0 °C, thereby not following any significant evaporation of AA, the banded texture appeared immediately but no torsads were observed. Even after 30 min, during which time complete relaxation of the bands occurred, no torsads were formed. However, when a sample was sheared, cooled at 0 °C for 20 min, and then allowed to return to room temperature, the torsads appeared in about 2–3 min (Figure 3). Experiments with 44 wt % HPC solution gave identical results, proving conclusively that the formation of the torsad secondary substructure is indeed dependent on the evaporation of solvent from the system and independent of concentration of HPC. When there is no solvent evaporation, there is no torsad formation. In fact, when a cholesteric HPC melt at 257 °C was sheared, although the banded texture appeared immediately, no torsads were observed under any conditions (Figure 4).

In the next series of experiments, the dependence of torsad formation and spacing on the cholesteric pitch was studied. As shown in Table I, HPC exhibits a wide range of pitch in solution of the mixed solvent TFA and AA. Figure 5 shows the torsads formed in sheared samples of HPC in solutions of different compositions of TFA and AA when the solvents were allowed to evaporate after the cessation of shear. Torsad formation was more prominent in the case of solutions exhibiting shorter pitch values. At long pitch, not only was the torsad formation less prominent, but the torsads were also more closely packed. One additional observation made was that, at shorter pitch, the torsads were much more homogeneous in distribution throughout the sample (Figure 5d).

The effect of pitch on torsads was also studied for PBLG in the mixed solvent dioxane–methylene chloride, which shows a wide variation of pitch with solvent. Table I shows the change in pitch of a 20% concentrated solution of PBLG in dioxane–methylene chloride mixture with composition.[19] In this system, the torsads were also more homogeneously distributed, more prominent, and more widely spaced at shorter pitch (Figure 6).

It is important to note that torsad formation can even be observed in nematic samples. The nematic PBLG solution in 20:80 v/v composition of dioxane–methylene chloride showed the same type of secondary substructures in the form of dark slanted lines in between bands (Figure 6c). The torsads in this case are similar in appearance to those observed in very long pitch cholesterics, e.g., HPC

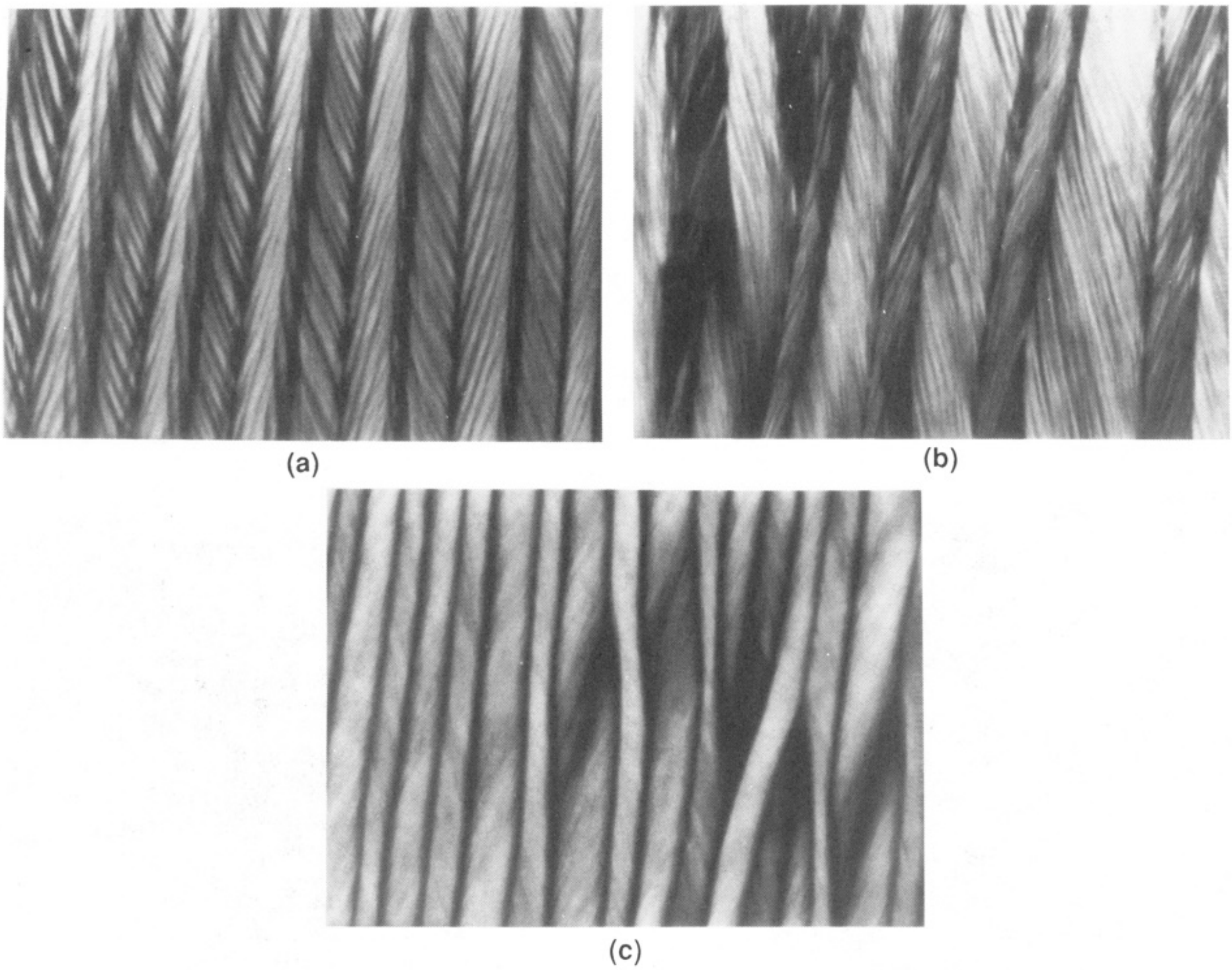


Figure 6. Textures of sheared samples of PBLG in the mixed solvent dioxane–methylene chloride after cessation of shear, the solvent composition (v/v) being (a) 100:0, (b) 80:20, and (c) 20:80, respectively (magnification ×400).

solution in TFA.

Attempts were made to observe torsads in other nematic systems. HPC (85 000 molecular weight) gives a nematic solution at 30% concentration in chloroform[18] and equimolar (racemic) mixtures of PBLG and PBDG are also obviously nematic.[20] In the first case, no prominent substructures (neither bands nor torsads) could be observed under identical experimental conditions. This is probably because of the very low viscosity of this solution, resulting in rapid flow and relaxation immediately after shear. In the racemic mixtures of PBLG and PBDG, widely spaced torsads were observed although not as prominent as in some other cases (Figure 7).

Discussion and Conclusions

It appears that (at least) *two* factors are involved in the formation of torsads in LC polymers. The primary factor is, clearly, the formation of this secondary structure due to solvent evaporation, since torsads are seen both in cholesteric and nematic LC polymer solutions and not in thermotropic polymers. A secondary factor is the pitch of the cholesteric array prior to the onset of evaporation.

It would appear reasonable to explain torsads as arising primarily from the hydrodynamic instability associated with a temperature gradient in the liquid. It is well-known that convection cells form when a layer of fluid is subjected to a temperature gradient. The most carefully studied case is that of a horizontal layer of fluid heated from below, in which convection cells were originally observed by Benard[22] and later explained by Rayleigh[23] and Pearson[24] in terms of buoyancy and surface tension effects, respectively. Nield[25] considered the combination of both effects and observed that these two factors causing instability reinforce each other: the convection cells formed by surface tension are approximately the same size as those produced by buoyancy.

In the case of torsad formation, it is reasonable to assume that evaporation of solvent from the surface of the polymer solutions results in a decrease in surface temperature, which in turn leads to the generation of a temperature gradient across the sample. Thus, buoyancy and surface tension effects arise. At some critical value determined by the Rayleigh number representing buoyancy forces, and the Marangoni number representing surface tension forces, hydrodynamic instabilities arise.[25] Thus, convection cells are formed. The direction normal to the bands in the sample must be the easy axis for cellular motion. The pitch of the sample is, of course, related to the values of the anisotropic elastic constants,[26] and therefore, some apparent dependence of torsad size on pitch is experimentally observed.

A report of convective instabilities produced by a thermal gradient in a nematic lyotropic liquid crystal consisting of potassium laurate, decanol, and water was recently presented, indicating that the phenomenon may be quite different from the classical Rayleigh–Benard instability,[27] but the details have not as yet been published.

It should be noted that the subject of periodic structures occurring after shear alignment is quite closely related to the numerous studies of similar structures induced by

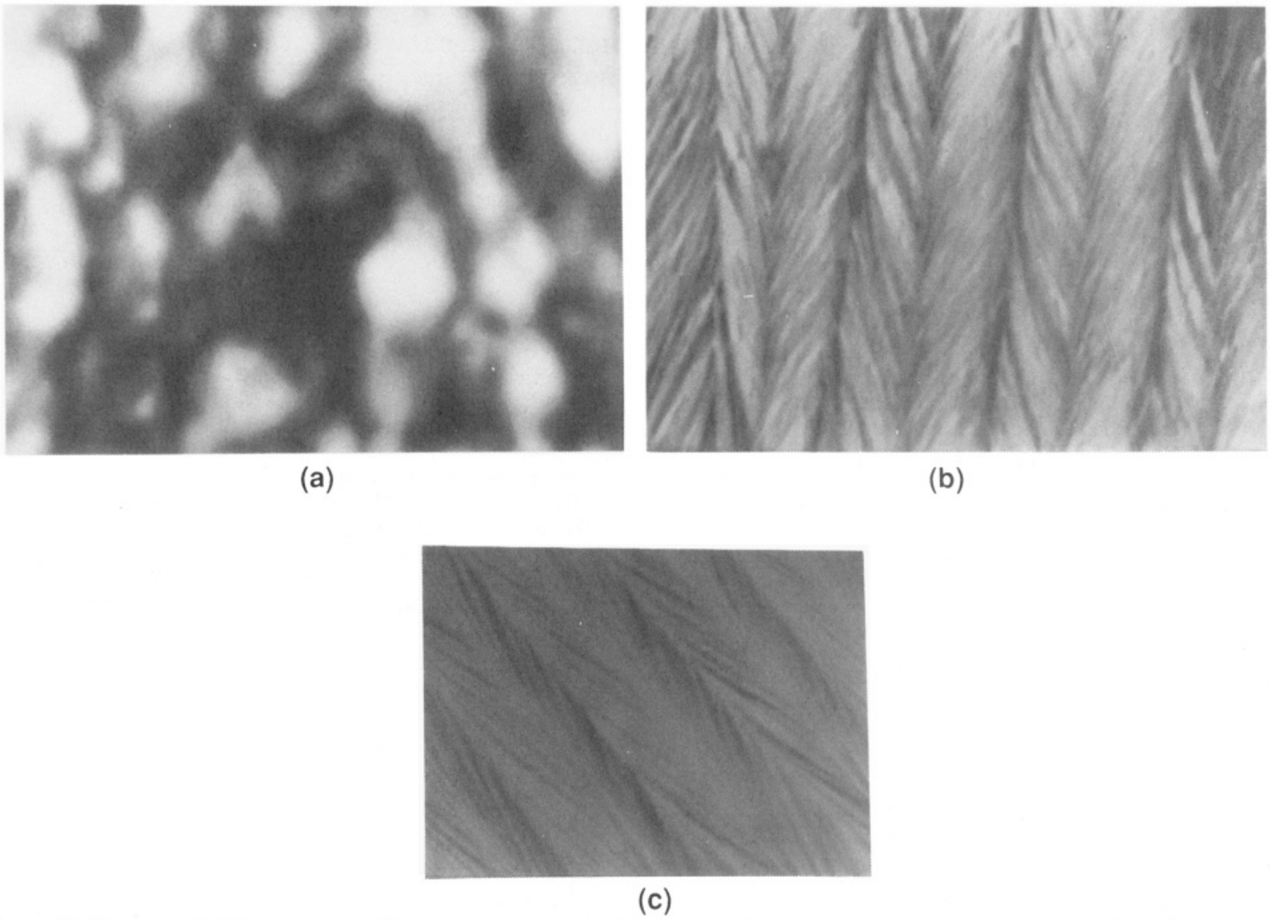

(a) (b) (c)

Figure 7. Textures of 20% concentrated racemic mixtures of PBLG and PBDG in dioxane: (a) nematic texture before shearing; (b and c) texture of sheared samples after cessation of shear (magnification ×400).

magnetic reorientation.[28-38] In low molecular weight cholesteric lyotropics, we have even observed a secondary structure between the bands, which clearly is directly related to the pitch.[36] A physical mechanism for these phenomena was first formulated by Guyon et al.[28] and has been elaborated by a number of authors. Modifications of these models would probably be applicable to the shear induced structures observed in polymers.

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