Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Donald, A. M. , Viney, C. and Ritter, A. P.(1986) 'The parabolic focal conic texture in a lyotropic liquid-crystalline polymer', Liquid Crystals, 1: 3, 287 — 300

To link to this Article: DOI: 10.1080/02678298608086516

URL: http://dx.doi.org/10.1080/02678298608086516

LIQUID CRYSTALS, 1986, VOL. 1, NO. 3, 287–300

The parabolic focal conic texture in a lyotropic liquid-crystalline polymer

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(*Received 25 February 1986; accepted 2 April 1986*)

Hydroxypropyl cellulose (HPC) forms liquid-crystalline solutions in both water and methanol. When these solutions are sheared, the banded texture seen in many liquid-crystalline polymers is formed. Detailed optical microscopy of the bands has been carried out, showing that the bands arise from a smooth variation in the orientation of the local extinction directions, and not (as previously suggested in the literature) from sharp kinks. Over a period of time, the bands degenerate to form a new texture, which appears as a square grid pattern of extinction when specimens are viewed between crossed polars. The location of the corners of the squares depends on whether the microscope is focused near the top or bottom surface. When focus is altered to the middle of the sample, the periodicity of the pattern is halved. This texture is identified with the parabolic focal conics previously seen in small molecule smectic and cholesteric materials.

1. Introduction

The term 'focal conic' has been used to describe a variety of textures in smectic and cholesteric liquid crystals. Both of these classes of mesophase possess layered structures. In the limit where the layer thickness is fixed (i.e. infinitely resistant to deformation), the arguments of classical geometry require that the possible line defects occur as pairs of focal conics in which the vertex of one conic section is a focus of the second, and vice versa (for example, [1, 2]). Thus the observation of focal conic textures led Friedel [3] to deduce that the smectic A phase of ethyl *p*-azoxybenzoate is a layered structure.

The textures which are observed microscopically in any given sample between crossed polars depend on many factors, one of the most crucial being the nature of the alignment (for example, homogeneous or homeotropic) dictated by the constraining surfaces. The precise form of the texture can vary widely even for a single substance; for instance polygonal structures, batonnêts and fans may all be exhibited. The confocal pairs of line defects responsible for these textures usually comprise an ellipse and a hyperbola (which may degenerate to a circle and a straight line respectively).

More recently, a new focal conic texture has been observed, which consists of a regular array of interlocking parabolic line defects [4]. It is termed the parabolic focal conic (P.F.C.) texture, and has been observed in both thermotropic [4, 5] and lyotropic [6] small molecule systems under mechanical dilation. The line defects are arranged on an approximately square lattice, but the period and position of features in the observed texture vary systematically with the height at which the microscope is focused.

A schematic representation of the defects making up the P.F.C. structure, as first proposed by Rosenblatt *et al.* [4], is shown in figure 1 (*a*), under the assumption of homeotropic boundary conditions for the molecular orientation. From this diagram, it is possible to understand why variations in the height of the focal plane change the appearance of the texture. Extinction arises where the projection of the layer normal lies parallel (or perpendicular) to the transmission direction of the polarizer. For focus near the top of the sample, a square network of dark lines is seen, the corners corresponding to the meeting of four parabolae (figure 1 (*a*)). Then, as can be seen from figure 1 (*b*) (which depicts the orientation variation of the layer normal in the vicinity of a single parabola), the extinction positions will move towards the vertices of the parabolae as the plane of focus is altered towards the middle of the specimen. When the microscope is focused midway between the top and bottom surfaces of the specimen, the vertices of both the upward and downward sets of parabolae are in focus, and thus the period of the observed square mesh is halved. Finally, when the bottom plane of the sample is in focus, the original periodicity is recovered, but the corners of the squares in the observed network now fall in the positions previously marked by the centres of squares in the network pertaining to the top surface. Again this can be understood by reference to figure 1 (*a*).

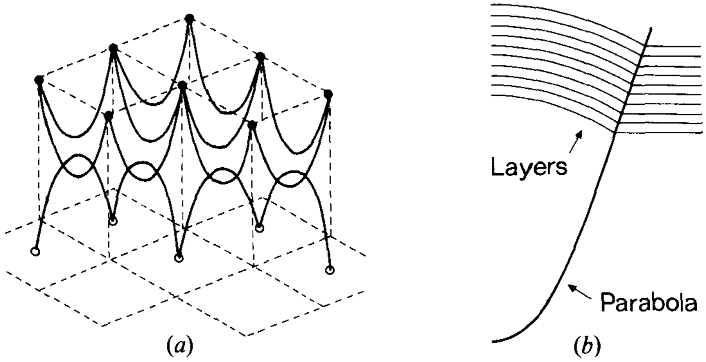

Figure 1. (*a*) Three-dimensional arrangement of parabolic line defects in a parabolic focal conic structure. Adapted from [4]. (*b*) Distortion of layers in the vicinity of a single parabolic line defect. Adapted from [4, 6].

In this paper, it will be shown that the P.F.C. texture can develop in solutions of hydroxypropyl cellulose (HPC) following shear. The shear originally produces the banded texture which has previously been reported for both thermotropic and lyotropic polymers [7–12]; when the transmission direction of either of the crossed polars is parallel to the shear direction, this texture consists of approximately equally-spaced extinction bands lying perpendicular to the shear direction. Detailed optical microscopy on one of the thermotropic polymers [11, 12] showed the extinction directions to vary smoothly with position, following an approximately sinusoidal path. In the present study, similar optical microscopy has been applied to the bands formed by shearing the HPC solutions. Shimamura [13] has reported similar qualitative results on the subsequent development of a square grid extinction pattern (which he refers to as 'diamonds'), but his analysis of the banded texture originally formed upon shear, and also his interpretation of the final relaxed texture, disagree with the analysis that we will present below. Thus we begin with an analysis of the banded texture in HPC before proceeding to discuss the subsequent formation of P.F.C. structures.

2. Experimental

HPC was obtained from Hercules Inc., under the commercial name of Klucel. Four different molecular weights were examined, as detailed in the table. In each case the degree of substitution was of the order of 3·7 hydroxypropyl substituents per glucose residue [14]. Most work was done on the material of lowest molecular weight (MW): Klucel E. The solutions of Klucel H (highest MW) were extremely viscous and therefore difficult to homogenize, so that results tended to be non-reproducible.

Molecular weights of Hercules HPC.

Polymer	Molecular weight
Klucel E	60 000
L	100 000
G	300 000
H	1 000 000

A range of solution concentrations was studied for each of the three lower MW polymers. All solutions were left to homogenize for at least a week; longer times were allowed for solutions of high viscosity. Experiments on the bands formed during shear were mostly carried out on aqueous solutions. Solutions in methanol showed the same qualitative results, but detailed measurements were not made. Detailed examination of the P.F.C. texture was carried out on Klucel E solutions in both water and methanol.

Thin specimens were prepared by placing a small amount of the solution on a glass slide; a coverslip was used to shear the solution within the region defined by a polyethylene spacer, $\sim 15\,\mu$m thick, which was used to control the specimen thickness. The entire 'sandwich' was then sealed with cover slip, in order to restrict the evaporation of solvent. Optical microscopy was carried out with a Carl Zeiss (Jena) polarizing microscope; observations were made with the specimen between crossed polars.

3. Results and discussion

3.1. *Bands*

The band periodicity was measured as a function of both concentration (in water) and molecular weight, for a shear rate of $\sim 20\,\mathrm{s}^{-1}$. The results are shown in figure 2, from which it can be seen that the average band spacing generally increases with increasing concentration and molecular weight.

In order to test whether the underlying molecular orientation varies smoothly with position along the shear direction (as in the serpentine trajectory found in several thermotropic copolyesters [11]), or whether it consists of a sequence of alternating sharp kinks (as in Kevlar [8]), a series of photographs was taken while systematically rotating the crossed polars. Initially, the transmission direction of the polarizer was aligned parallel to the specimen shear direction. (In the absence of any evidence to the contrary, we assume that one of the mutually perpendicular extinction directions at any point corresponds to the local in-plane component of the molecular director. This correspondence cannot necessarily be taken for granted [12].) As shown in figure 3 (Klucel L; 55 wt % in water), rotation of the crossed polars from their initial orientation results in alternate spaces between extinction bands becoming narrower, as the

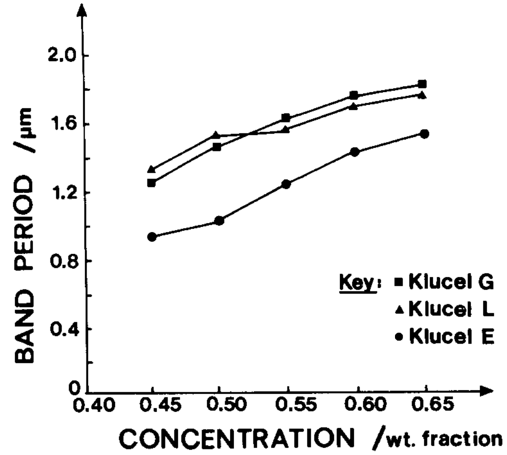

Figure 2. Effect of concentration and molecular weight on the periodicity of bands in sheared HPC/water specimens.

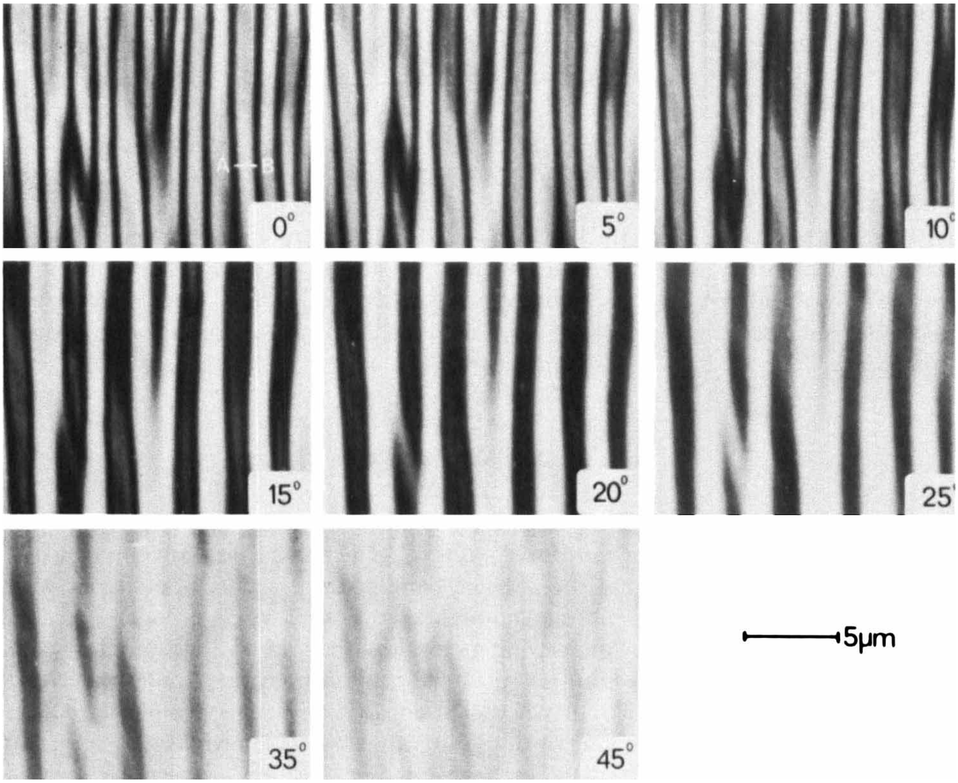

Figure 3. Banded texture in sheared Klucel L (55 wt % in water). The sequence of micrographs shows the effect of rotating the crossed polars. Initially, the polarizer transmission direction was parallel to the specimen shear direction (left to right); the anticlockwise angle through which the crossed polars have been rotated from this orientation is marked on each micrograph. The segment AB is relevant to the solid line in figure 4.

bands move closer together in pairs. The narrow spaces between the dark bands go into extinction when the crossed polars have been rotated by ~20°. This angle corresponds to the *maximum* divergence angle between the prior shear direction and the local optical director. The solid line in figure 4 shows the variation in divergence angle as a function of position measured along the shear direction, for a small region of the specimen shown in figure 3. The serpentine form of the curve is also typical of other regions.

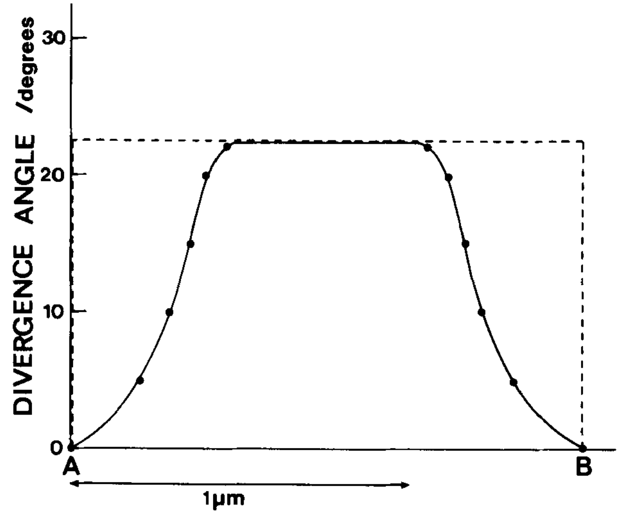

Figure 4. Solid line: measured variation in director divergence angle as a function of position along the shear direction, for the segment of specimen labelled AB in figure 3. Broken line: expected variation in director divergence angle in a specimen having a sharply kinked director trajectory.

Unquestionably, the in-plane director trajectory varies smoothly with position along the shear direction. Were the trajectory to consist of straight sections joined by sharp kinks, the observed behaviour of the extinction bands would be quite different from that recorded in figure 3. One would expect the extinction bands to disappear, rather than move, as the crossed polars are rotated from their initial orientation where one of them was parallel to the shear direction. Alternate spaces between the positions previously occupied by bands would become progressively darker, extinguishing completely once the polars have been rotated by an amount equal to the (constant) divergence angle. The variation in divergence angle with position along the shear direction would follow the broken line in figure 4.

This conclusion of a smooth trajectory in aqueous HPC is to be contrasted with that reached by Shimamura [13] and also by Nishio *et al.* [15], who asserted that the trajectory is sharply kinked, though they did not report the necessary quantitative optical microscopy. Horio *et al.* [16] also claim a zig-zag trajectory in their detailed work, but they do not define clearly which regions of their specimens are in extinction for particular orientations of the crossed polars. Nishio and Takahashi [17] also favour a sharply kinked structure for *thermotropic* HPC, again from cursory optical microscopy, although some of their scanning electron micrographs, as they discuss, do appear to show a smoother variation. Navard [18] has recently presented evidence supporting a smooth trajectory in sheared HPC/water, but without the detailed analysis as given here.

Figure 4 suggests that, for a 55 wt % solution of HPC in water, the in-plane molecular orientation rotates by 20° over a distance of 0·5 μm, i.e. a rotation of 1° requires (very approximately) 0·025 μm. This value can be compared with approximate values for other liquid crystalline polymers:

(*a*) 1° per 0·03 μm in a thermotropic copolyester based on poly(ethylene terephthalate) and *p*-hydroxybenzoic acid (Tennessee Eastman X7G, also known as B-ET) (from [9]).

(*b*) 1° per 0·01 μm in a thermotropic copolyester based on hydroxybenzoic and hydroxynaphthoic acids (B-N) (from [9, 15]).

(*c*) 1° per 0·13 μm for lyotropic poly(γ-benzyl-L-glutamate) (PBLG) in methylene chloride [19].

It has been shown, in this study and previously for B-N [20], that the band spacing depends on viscosity (i.e. on molecular weight, concentration and temperature). However, from the work on B-N, it would seem that this does not necessarily imply a corresponding significant variation in the rate at which the extinction axes rotate as a function of position measured along the shear direction. For B-N it was shown [20] that, while the band spacing decreases markedly with decreasing temperature until it ultimately falls below the resolution limit of the light microscope, there is a concomitant reduction in the maximum divergence angle from the shear axis. Thus the curvature of the in-plane component of the molecular director, as introduced by shear, appears to be approximately constant for this polymer. It is therefore tempting to relate this behaviour to the inherent flexibility/rigidity of the molecule, but further work is necessary before this suggestion can be substantiated.

The formation of bands may not occur immediately after shear, as has previously been noted by Kiss and Porter [7] for PBLG solutions in *m*-cresol. Also, the bands subsequently relax. Figure 5 shows a typical series of photographs illustrating the time-dependence for Klucel E (55 wt % in water). As shown by Kiss and Porter, the rate at which the bands evolve and subsequently disappear depends on solution viscosity and on prior shear rate: all processes occur faster for a faster prior shear rate. Similar observations have been made on a thermotropic random copolyester by Graziano and Mackley [9], and Nishio *et al.* [15] have shown that band perfection in aqueous HPC solutions is improved by a faster shear rate.

3.2. *P.F.C. Textures*

After a period of time (which depends on the solution concentration and the polymer molecular weight), a rectangular grid pattern of dark lines appears when the specimens are viewed microscopically between crossed polars, the transmission direction of one polar being parallel to the prior shear direction. Figure 6 (*a*)–(*d*) shows the appearance of this grid in Klucel E (60 wt % in water) for the microscope focused at various levels in the specimen. Such patterns were also observed in solutions of polymer having each of the other three molecular weights listed in the table, at similar concentrations. Figure 7 (*a*)–(*c*) shows a similar set of photomicrographs for a solution (50 wt % polymer) in methanol, taken 4 days after the specimen was originally sheared.

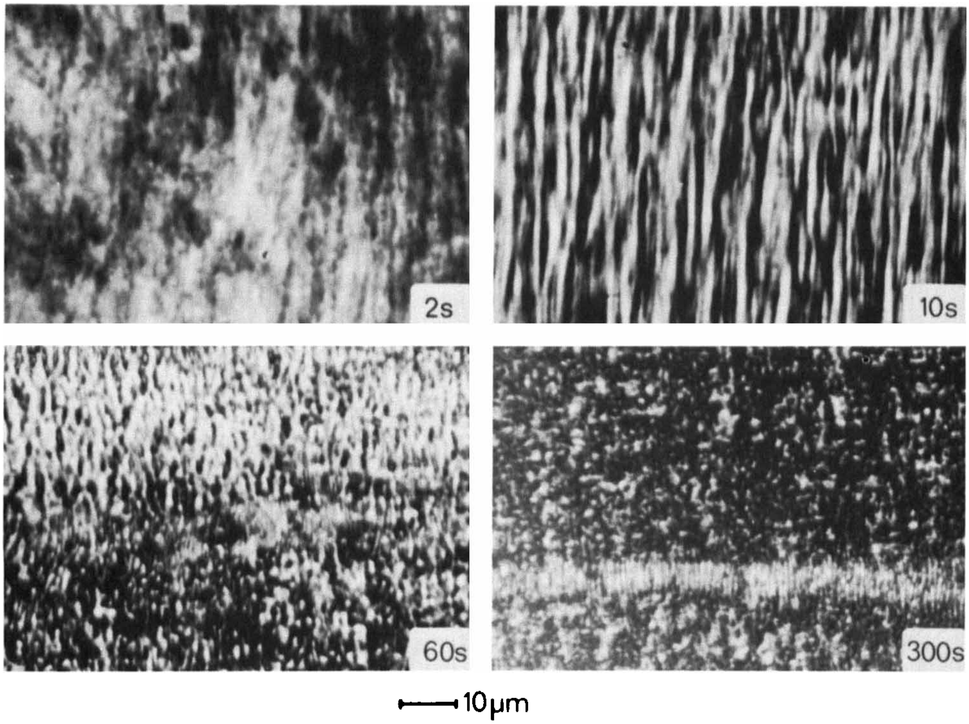

Figure 5. Time dependence of the formation and relaxation of banded textures in Klucel E (55 wt % in water), at room temperature. The elapsed time in seconds, since cessation of shear, is marked on each micrograph. Crossed polars; polarizer transmission direction parallel to the specimen shear direction (left to right).

In all cases, these patterns only formed after the prior application of shear, and the perfection of the patterns improved over a period of several days or longer. A similar texture has also been observed to develop occasionally from banded textures in the thermotropic random copolyester consisting of 40 mol % poly(ethylene terephthalate)/60 mol % *p*-hydroxybenzoic acid (Tennessee Eastman X7G, or B-ET). The grid pattern, an example of which is shown in figure 8, only appears to form in specimens sheared at ~300°C and subsequently held in the temperature range 280°C–300°C for at least an hour.

When the crossed polars were rotated, successive squares became alternately lighter and darker, as typified by those shown in figure 9 (*a*)–(*c*). For a large enough rotation of the polars, only dark lines parallel to the prior shear direction remained visible in the texture (figure 9 (*d*)–(*f*)). For the microscope focused at a given depth in the specimen, the position of these lines was the same as that previously observed with the transmission direction of one polar parallel to the shear direction (figure 7 (*a*)–(*c*)). Thus figure 9 (*e*), showing the texture for the central plane of the specimen in focus, has twice as many dark lines as either figure 9 (*d*) or (*f*) (which show the texture for focus on the top and bottom surfaces of the specimen respectively).

The perfection of these arrays was extremely variable. Although large areas of a typical specimen exhibited a structure closely related to the square grid described, only some regions showed an ideal pattern of orthogonally intersecting families of straight

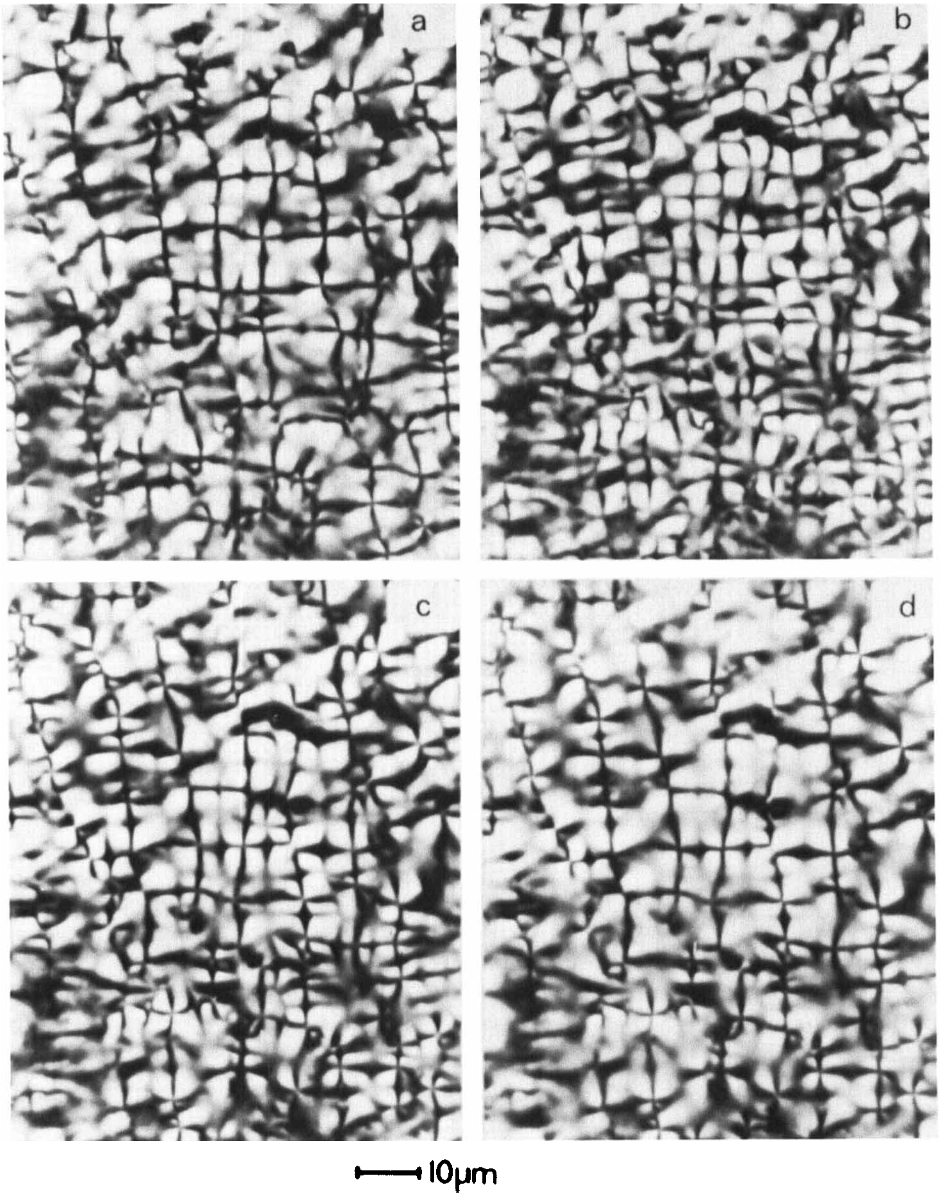

Figure 6. Rectangular grid-like extinction pattern in Klucel E (60 wt % in water), 1 day after shearing. The sequence of micrographs shows how the pattern changes as a function of the height at which the microscope is focused: (*a*) focus at top of specimen; (*b*) focus slightly above middle; (*c*) focus slightly below middle; (*d*) focus at bottom of specimen. Crossed polars; polarizer transmission direction parallel to the specimen shear direction (left to right).

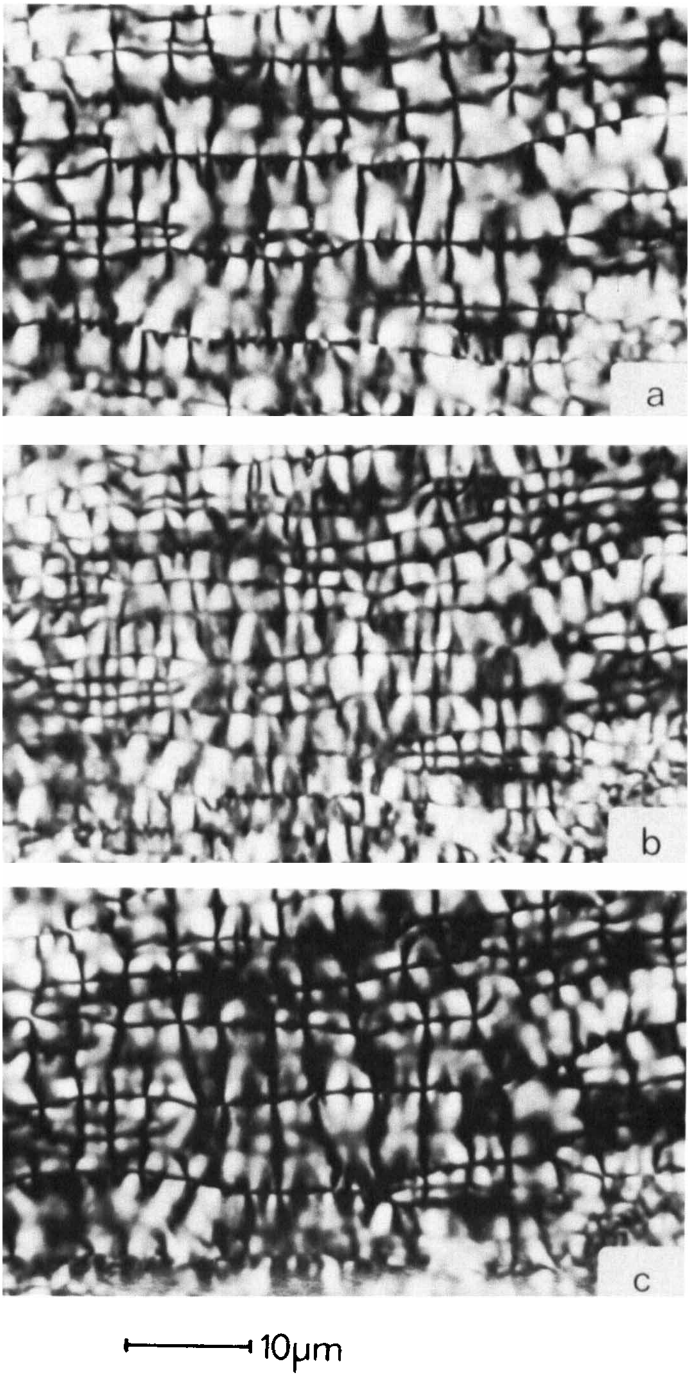

Figure 7. Texture similar to that shown in Figure 6, observed in a 50 wt % solution of Klucel E in methanol. The specimen was photographed 4 days after shearing. (*a*) focus at top of specimen; (*b*) focus at middle; (*c*) focus at bottom of specimen. Crossed polars; polarizer transmission direction parallel to the specimen shear direction (left to right).

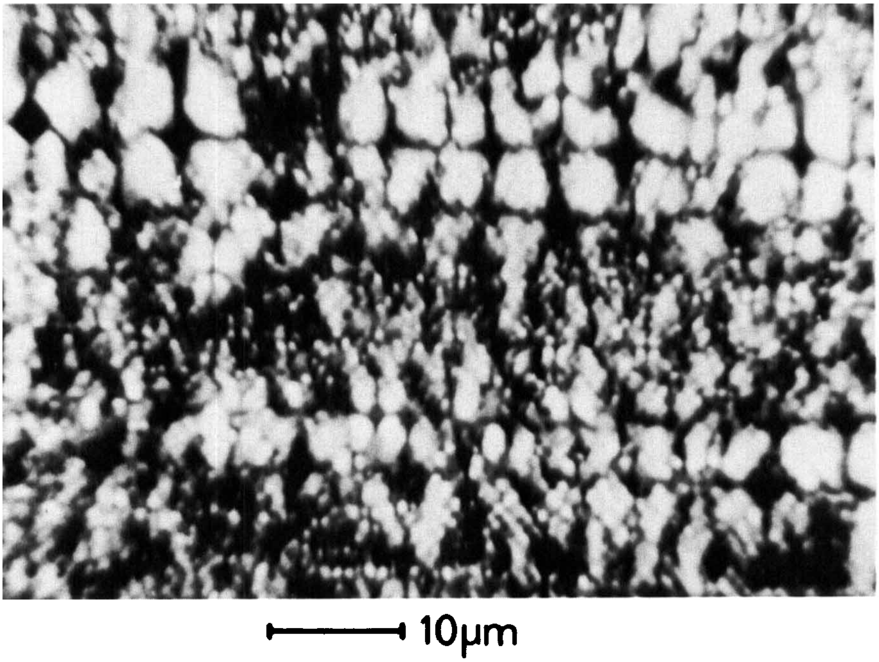

Figure 8. Rectangular grid-like texture in a thin sample of the thermotropic copolyester X7G. The specimen was sheared between glass slides at 300°C, annealed at 280°C for an hour, and quenched to room temperature on a cold metal block. Crossed polars; polarizer transmission direction parallel to the specimen shear direction (left to right).

parallel lines (figure 10). One final observation was that, over a period of days to weeks, the pronounced effect that a change in focus has on the texture was lost. Superficially, the pattern remained unchanged—a square net of dark lines still being visible if the polarizer or crossed analyser was parallel to the prior shear direction—but this pattern was observed independently of the plane of focus. This may be a consequence of a slow loss of solvent. Candau *et al.* [21] have also observed similar patterns which do not exhibit a plane of focus effect.

Asher and Pershan [6] have summarized the features associated with the P.F.C. structure that was originally proposed by Rosenblatt *et al.* [4]. These are:

(*a*) When focus is near the top of the sample, an array of black lines is seen, with their intersections corresponding to the points where one set of parabolae join (see figure 1 (*a*)).

(*b*) When focus is near the bottom, a similar array of lines is seen where the second set of parabolae join. This array of lines is identical to that seen at the top, but it is displaced so that the intersections lie beneath the centres of the squares in the top grid.

(*c*) For focus near the central plane in the specimen, the array seen has half the periodicity of either the top or bottom arrays.

(*d*) As the focus is varied from the top to the middle of the sample, the locus of sharpest focus in the texture moves systematically from that which includes

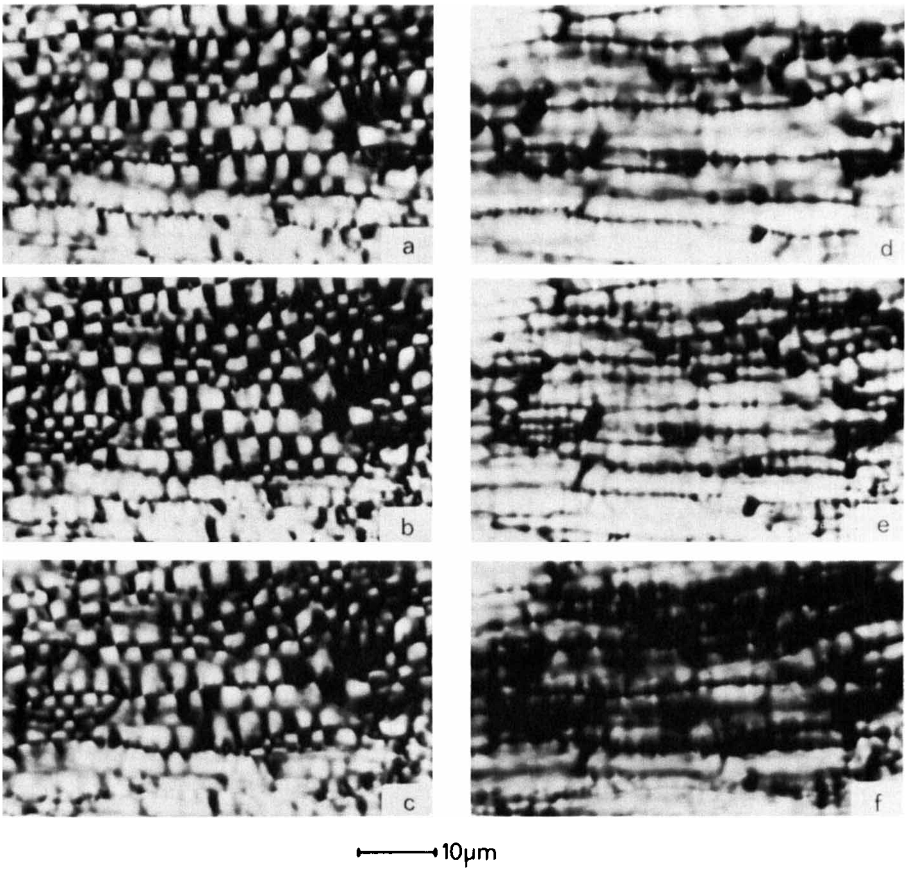

Figure 9. The same specimen and field of view as that shown in figure 7, with the crossed polars rotated anticlockwise through 20° (*a*)–(*c*) and 45° (*d*)–(*f*). Micrographs (*a*) and (*d*) are for the microscope focused at the top of the specimen; micrographs (*b*) and (*e*) for focus as the middle, and micrographs (*c*) and (*f*) are for focus at the bottom of the specimen.

points where parabolae join at the top surface, to that which includes the points where the two sets of intersecting parabolae cross. A further change of focus then brings the lower set of parabolae into sharp view, until, finally, the points where parabolae join at the bottom surface are in focus.

This characteristic behaviour of the P.F.C. texture with variation in focus is exactly the same as that seen in figures 6 and 7. Thus it is apparent that lyotropic HPC exhibits the P.F.C. texture. This explanation is different from that proposed by Shimamura [13], who discusses formation of the grid-like array in terms of crystal-like nucleation and growth. However, the P.F.C. texture is essentially associated with a layered structure: in smectics [4, 6], in cholesterics [2] (although Bouligand at that time proposed a somewhat different model to explain his observations), and in the lamellar phases associated both with surfactants [22, 23] and with block copolymer systems [21]. It therefore seems that there is no need to assume that the HPC solutions are anything other than cholesteric—a characteristic demonstrated by Werbowyj and Gray [24]—and crystallinity need not be invoked.

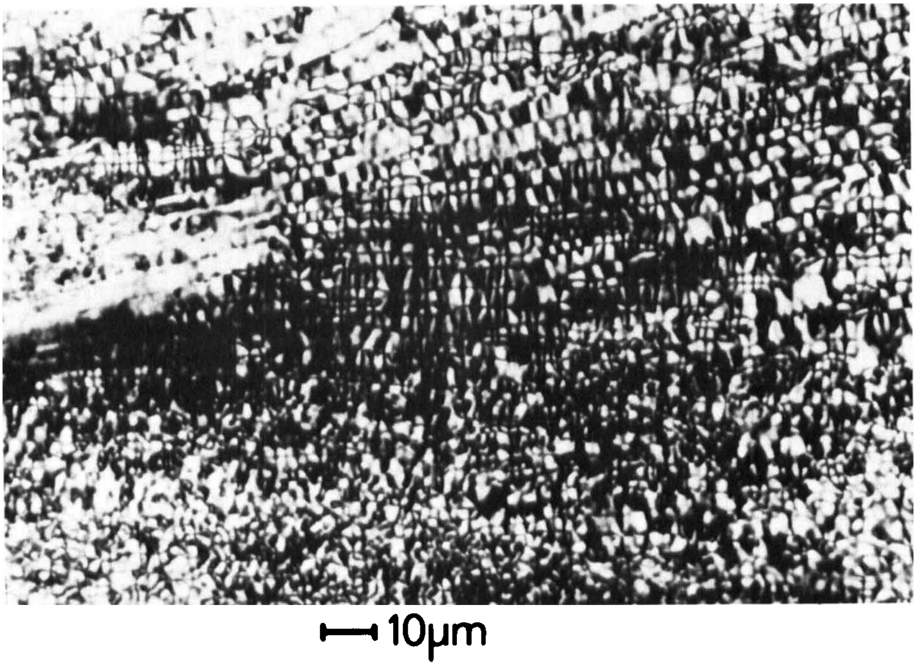

Figure 10. A low magnification micrograph (large field of view) of the specimen shown in figures 7 and 9. The microscope was focused at the central plane of the specimen. Crossed polars; polarizer transmission direction parallel to the specimen shear direction (left to right).

In one respect, the observations presented here differ from those of Asher and Pershan [6]. These authors found that, upon rotation of the crossed polars, the top and bottom arrays rotated in the same direction as the polars, but the middle (half-period) array rotated in the opposite sense. In the HPC solutions, only one set of lines in the array rotate—those normal to the prior shear direction—and it is not apparent that the middle array behaves any differently from the top and bottom ones. Furthermore, the dominant feature observed on rotating the crossed polars is the changing contrast between neighbouring 'boxes', rather than rotation of lines. It seems that the prior shear, necessary to cause the P.F.C. texture to form in these solutions, removes the degeneracy of the perpendicular directions of the grid. Thus the P.F.C. texture observed here must correspond to a distorted variant of the model proposed by Rosenblatt *et al.* [4].

This raises questions of why the prior shear is necessary, and of how the development of these structures relates to the conditions which previous workers have observed as necessary for their formation. Usually, a mechanical dilation [4, 6] or shear [25] acting upon already well-oriented structures (i.e. where the molecules adjacent to the specimen surfaces are already aligned normal to those surfaces) is required to produce the P.F.C. arrays. For the case of lyotropic lamellar phases containing amphiphilic compounds and water, it has been suggested [23] that the dilation could be a simple consequence of variations in the local thickness of water layers, occurring when dislocations move to relieve local strain energy. The P.F.C.

structure in this latter case was seen to develop as a relaxation ('annealing') phenomenon, and was intimately associated with the formation of 'oily streaks' and dislocation arrays. It is therefore evident that the mechanical stress need not necessarily be applied externally as a prerequisite for P.F.C. formation.

In the present situation, it is not obvious what is playing the rôle of an internal dilation, or precisely how the P.F.C. formation is related to the original serpentine structure. Only a very tentative suggestion can be made here. Initially, when the HPC solutions are sheared, it is probable that the inherent cholesteric organization is destroyed, the local helix being 'unwound' to give a simple nematic. If this were not so, it would be difficult to reconcile the proposed serpentine structure with the helical organization inherent to a cholesteric. However, the P.F.C. texture is associated with a layered structure, as are focal conics in general, so that it must be assumed that the cholesteric ordering is eventually regenerated in the HPC solutions. To achieve this, significant local molecular reorganization and orientation must occur, and this may produce local dilations. This might be difficult to envisage if the structure were confined to two dimensions. However, in the case of thermotropic copolyesters at least, the director in specimens showing a banded texture does possess a small out-of-plane component [12]. If this also holds for bands in HPC, then, as the molecules adopt the layer-like structure of the cholesteric, local compression and dilation may occur. Further work is clearly necessary to substantiate (or refute) this picture of the evolution of P.F.C. structures.

4. Conclusions

(1) When liquid crystalline solutions of HPC in water or methanol are sheared, the banded texture is formed.

(2) Detailed polarized light microscopy shows that the bands correspond to the orientation of the local extinction axes varying smoothly as a function of position along the shear direction.

(3) The band period increases with increasing polymer concentration and molecular weight.

(4) Over a period of time the bands degenerate, and a more or less regular square grid pattern of extinction is observed.

(5) As the height at which the microscope is focused moves downwards from the top surface, the positions of sharpest focus in the texture move from the corners of the squares towards the midpoint of each side. When the microscope is focused on the central plane of the sample, two intersecting (but aligned) square grid patterns are seen, such that the overall pattern periodicity is halved. Further lowering of the microscope focus causes the first set of squares to disappear. With focusing near the bottom surface, the original grid periodicity is recovered, but with a displacement of half a period along each of the sides, so that each corner now lies below the centre of a square in the original pattern.

(6) This behaviour is characteristic of the parabolic focal conic texture previously reported in the literature for small molecule smectics and cholesterics.

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