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Optical microscopy of banded structures in oriented thermotropic polymers

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Banded structures apparent in thermotropic polymers are analysed by optical microscopy. The structures result from shear at elevated temperatures and are preserved by rapid cooling. The bands are shown to be the consequence of a periodic variation in the orientation of the principal optical vibration directions about the shear axis. It is possible that this variation may be directly related to a corresponding variation in the direction of the long axis of the molecule. The maximum divergence angle is measured for a range of copolyesters; the weakness or complete absence of the zero order reflection in the conoscopic image (optical diffraction pattern) in certain circumstances is explained in terms of a periodic alternation of phase as well as amplitude, which contributes to the image of the banded structure.

1. Introduction

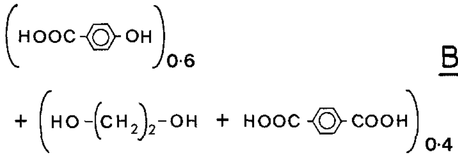
Thermotropic liquid crystalline polymers are a relatively new class of material which possess properties of potential technological importance. They show liquid crystalline order and flow properties at elevated temperatures, and it is possible to retain the characteristic microstructure by cooling rapidly to room temperature [1]. It has also been demonstrated for a range of such materials that fibres and oriented thin films show a distinctive banded structure when viewed in transmitted light between crossed polars [2]. This structure is similar to that seen: (a) in fibres of the polymer poly(p-phenylene terephthalamide) [2, 3] which is spun from a lyotropic liquid crystalline dope and marketed as Kevlar; (b) in solutions and dried films of the synthetic polypeptide, poly(γ-benzyl-L-glutamate) (PBLG) [4]; (c) in hydroxypropyl cellulose and cellulose acetate obtained both from lyotropic solutions and as melt spun fibres [5]; and (d) aligned films of small molecule nematic dye-stuffs [6, 7].

On the basis of a transmission electron microscopy (TEM) study [8], a radially symmetric pleated sheet structure has been proposed for Kevlar fibre; support for this structure was provided subsequently by optical microscopy [3], which interpreted the banded structure observed in terms of the ordering implicit in the pleated sheet model.

As indicated in a previous paper [2], the occurrence of banded type structures is thus seen to be widespread. In this paper we present the results of a detailed optical microscopy study of such structures.

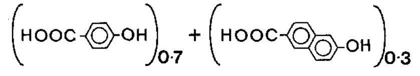
2. Experimental details

Investigations were conducted on the following copolyester materials:



B-ET

p-hydroxybenzoic acid
+ ethylene glycol
+ terephthalic acid



B-N

p-hydroxybenzoic acid
+ hydroxynaphthalic acid

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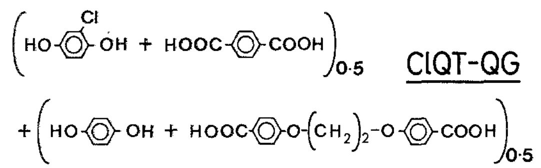
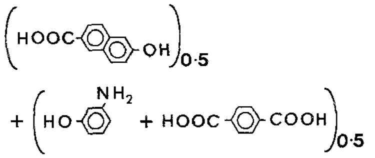


ClQT-QG

chlorohydroquinone + terephthalic acid
+ hydroquinone + bis(p-carboxyphenoxy)ethane



N-AT

hydroxynaphthalic acid
+ m-hydroxyaniline + terephthalic acid

Thin films and fibres were produced by shearing between glass slides or by drawing about 20° C above the polymer softening point, as described in [2]. Regions showing the banded structure were examined by optical microscopy in three different ways: (a) with the specimen between crossed polars, (b) with the microscope adjusted to give Zernicke phase contrast [9], and (c) with a Bertrand lens incorporated into the optical path so that the optical diffraction pattern is brought into focus at the eyepiece (conoscopic imaging). Whereas the qualitative results which will be discussed below are valid for all the specimens studied, the detailed measurements and all micrographs will refer to oriented films of the (B-ET) polymer: this material gives banding with the largest, and thus most easily resolved, periodicity. Furthermore, because the scale of the optical diffraction pattern is correspondingly small, the pattern can be studied up to comparatively large distances from the zero order.

3. Results

With either the polarizer or crossed analyser parallel to the direction of shear (the "orthogonal" position), specimens display a structure consisting of a series of fairly regular dark bands running normal to the shear direction. Fig. 1a shows the banding in a thin oriented film of (B-ET). If the crossed polars are rotated away from this position, pairs of adjacent dark bands move closer together, until they merge and disappear. On further rotation of the polars, the bands reappear, but are displaced by a "half period" with respect to the position at which they were last clearly visible. This behaviour is shown in Figs. 1b to f for (B-ET). Rotating the crossed polars in the opposite sense from the orthogonal position causes those pairs of bands which previously moved together to move apart. When a specimen is maintained in the orthogonal position and a sensitive tint (full wavelength) plate is introduced in the 45° position between the crossed polars, the regions between the dark bands appear alternately blue and yellow. This is shown in Fig. 2, where a yellow filter has been used to achieve contrast on black and white film; the blue areas in the specimen appear dark.

The image obtained under phase contrast conditions in unpolarized light (Fig. 3) displays banding which is identical in periodicity and position to that seen with the specimen in the orthogonal position between crossed polars.

Optical diffraction patterns obtained with the specimen in the orthogonal position between crossed polars, as in Fig. 4a, show first order maxima, but the zero order, surprisingly, is relatively weak. If, however, the specimen is rotated away from the orthogonal position (Fig. 4b) the zero order rapidly becomes visible, and dominates the diffraction pattern after a rotation of only a few degrees.

4. Discussion

4.1. Direct imaging of a specimen between crossed polars

The alternating regions of addition and subtraction obtained with the sensitive tint plate on the one hand, and the behaviour of the bands when the crossed polars are rotated from the orthogonal position on the other, indicate a periodic variation in the orientation of the in-plane components of the principal axes of the optical indicatrix. The axes are often referred to as optic axes, but this leads to confusion with axes normal to circular sections of the indicatrix, and so we shall refer to them as "extinction" axes, since that is their characteristic when aligned parallel to the crossed polars.

The effect is most simply interpreted if the periodicity in the orientation of the extinction axes is assumed to be caused by a periodic variation in the direction of the molecular long axis. It must be emphasized that this simple picture must be treated with circumspection, since optical textures and molecular alignment need not be directly related. However, electron diffraction evidence presented in the following paper [10]

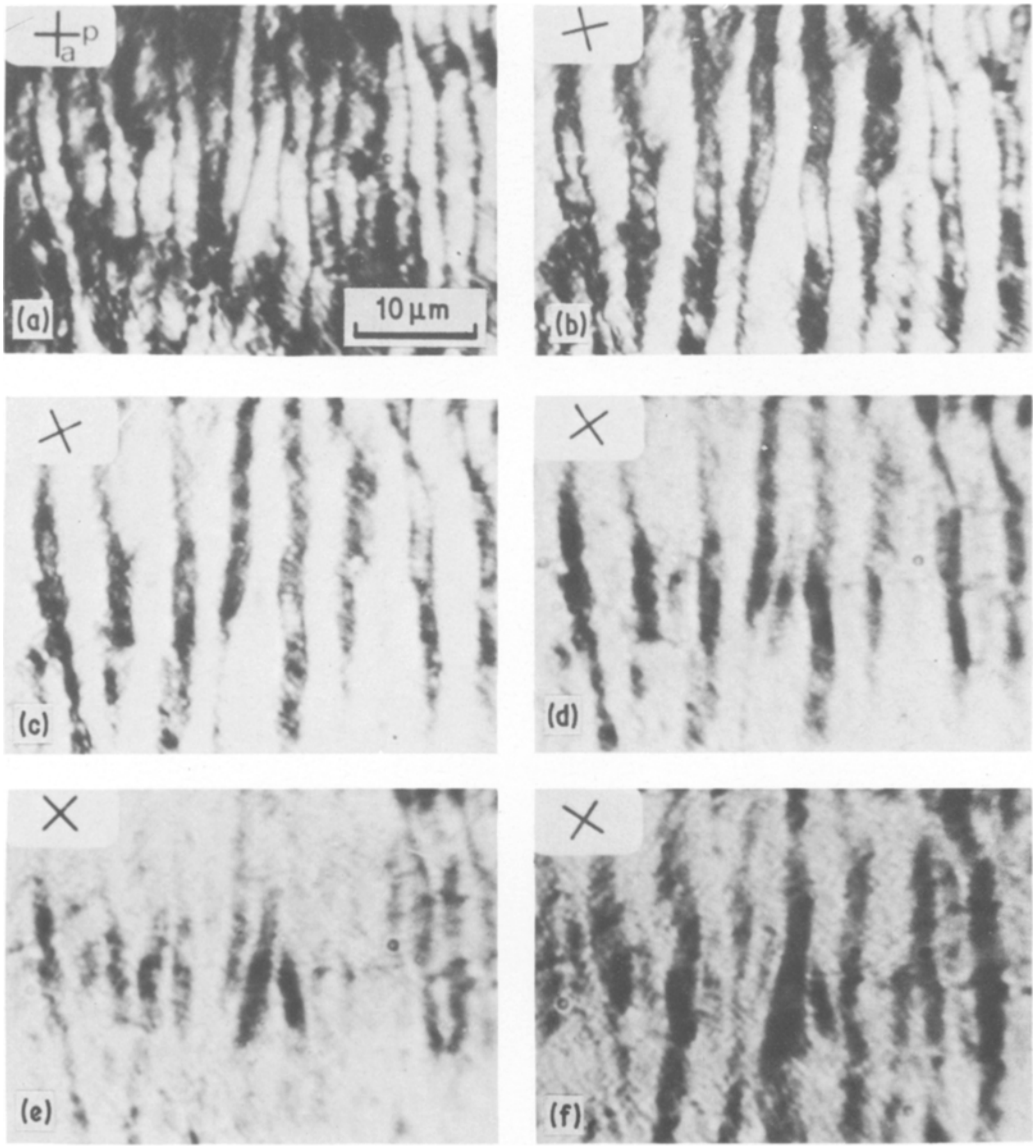


Figure 1 Thin oriented film of (B-ET) between crossed polars; (a) specimen in orthogonal position, (b to f) anticlockwise rotation of crossed polars away from this position by 15°, 25°, 35°, 45° and 55°, respectively. p = polarizer, a = analyser. The shear direction is horizontal.

indicates that in the case of banded structures the simple model is indeed correct.

The periodic variation in the orientation of these axes relative to the shear direction along the specimen can be represented by a divergence function $f(x)$, sketched in Fig. 5. The origin is chosen such that $f(x) = 0$ corresponds to a particular position where one extinction axis is aligned with the shear direction. The effect of rotating from the orthogonal position on the appearance of the bands, as shown in Fig. 1, can now be understood by reference to Fig. 5. Extinction bands, initially at positions G, will move together in pairs, completely merging when the polars have been rotated from the orthogonal position by an angle $|\Omega|$. Determination of this limiting divergence angle, Ω, depends on assessment of the point at which pairs of bands merge and finally disappear altogether. A series of values for Ω for the different materials examined is listed in Table I.

Examination of the specimen using the sensitive

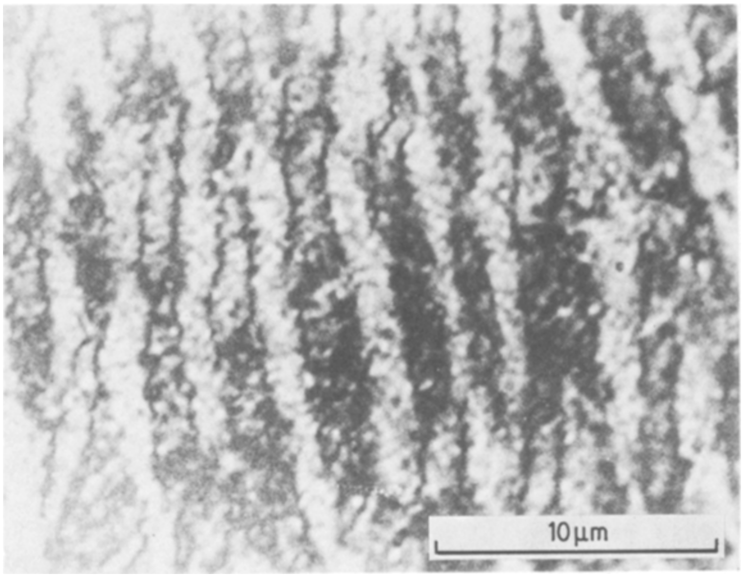


Figure 2 Thin oriented film of (B-ET) between crossed polars in the orthogonal position; a sensitive tint plate in the 45° position has also been introduced, together with a yellow filter so that the blue areas appear dark.

tint plate provides a quicker (although less precise) method of measuring the maximum divergence angle. The specimen shear axis is rotated away from the principal axis of the sensitive tint plate until either maximum addition or subtraction is observed in each of the bands. (The polars are held at 45° to the sensitive tint plate). Values of Ω obtained using this approach agreed with those in Table I to within 5%.

Measurement of the positions of the extinction bands as the polars are rotated permits the exact form of the divergence function, $f(x)$, to be determined. Fig. 6 shows two such plots from different parts of a sample of B-ET, with measurements taken every 2° of crossed polar rotation. The function is essentially sinusoidal, and within the terms of the simplest model would indicate that the molecules follow a serpentine path about the shear axis. This interpretation contrasts with the pleated sheet model proposed for Kevlar, in which the molecules zig-zag in sharply defined pleats about the fibre axis. Also, in the case of

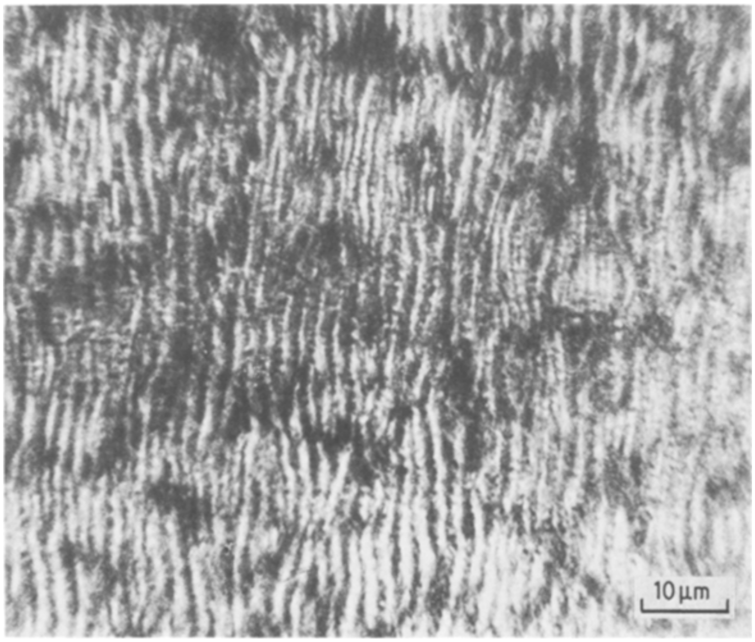


Figure 3 Phase contrast image of thin oriented film of (B-ET).

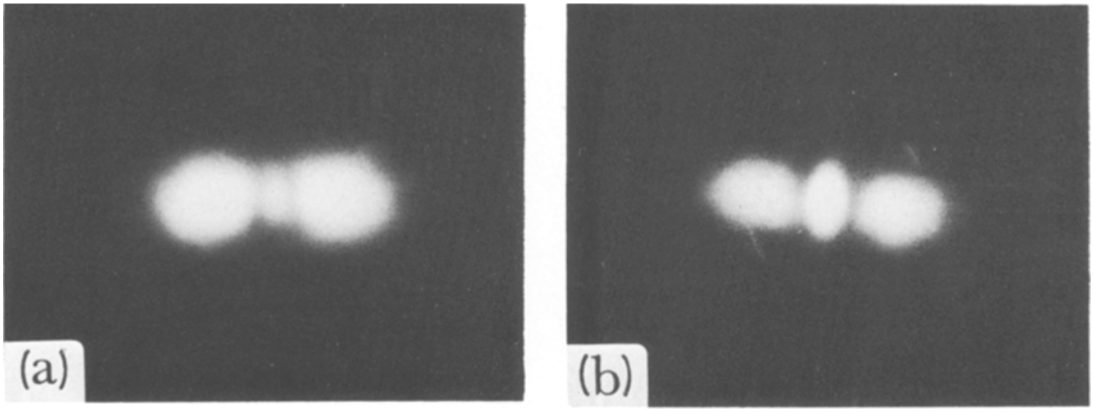


Figure 4 Conoscopic image of thin oriented film of (B-ET) viewed between crossed polars; (a) orthogonal position, (b) crossed polars rotated 10° away from this position. The sharp arcs are an artefact due to light being reflected from the microscope substage assembly.

Kevlar the maximum divergence angle is much less, of the order of ± 5° [8].

4.2. Conoscopic imaging

Further evidence that the banded microstructure is indicative of a near-sinusoidal variation in the direction of the extinction axis about the shear direction is provided by an analysis of the conoscopic image, which is, in essence, the intensity distribution in the back focal plane of the objective lens. It therefore represents the optical diffraction pattern of the microstructure, in which the phase information is preserved.

Referring back to the conoscopic image of Fig. 4a, two first order diffraction maxima are seen, which are derived from the periodic banding. If the conoscopic image were merely a different presentation of the periodic information so apparent in the microstructure, such as might be obtained by subsequent transformation on an optical bench, then it would be but of passing interest. In this case, however, it is particularly noteworthy in that the zero order ("straight through beam") is very weak, and in some samples virtually non-existent, when the specimen is viewed in the orthogonal position. A similar effect has been noted in Kevlar fibres [3], although it was not fully explained.

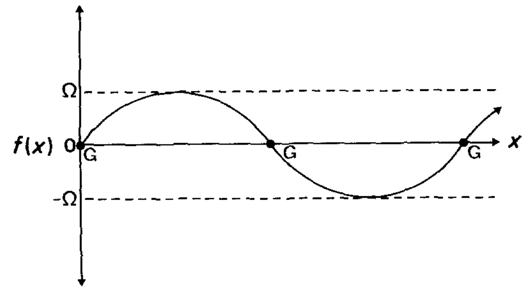


Figure 5 Variation of divergence function with distance along the shear axis. The divergence function is defined as the variation in the angle between the local extinction direction and the shear axis.

In order to understand the reason for the missing zero order, it is necessary to examine the relationship between: (a) the amplitude at a point in the image plane, and (b) the relative orientations of the polarizer/analyser pair and the extinction axes at the corresponding point in the specimen.

Consider an anisotropic material, with two permitted local vibration directions OV_1 and OV_2 (Fig. 7), with corresponding refractive indices μ_{max} and μ_{min}. When plane polarized light is incident on this material, it will be resolved into components along OV_1 and OV_2, with complex amplitudes:

$$A_1 = (A_0 \exp i\omega t) \cos \theta \qquad \text{along } OV_1, \tag{1a}$$

and

$$A_2 = (A_0 \exp i\omega t) \cos (\theta + 3\pi/2)$$

$$= (A_0 \exp i\omega t) \sin \theta \qquad \text{along } OV_2, \tag{1b}$$

where θ is defined in Fig. 7.

TABLE I Maximum angle, Ω, observed between shear axis and extinction direction

Polymer	Maximum angle, Ω
B-ET	37.5°
B-N	27.5°
C1QT-QG	20.0°
N-AT	32.5°

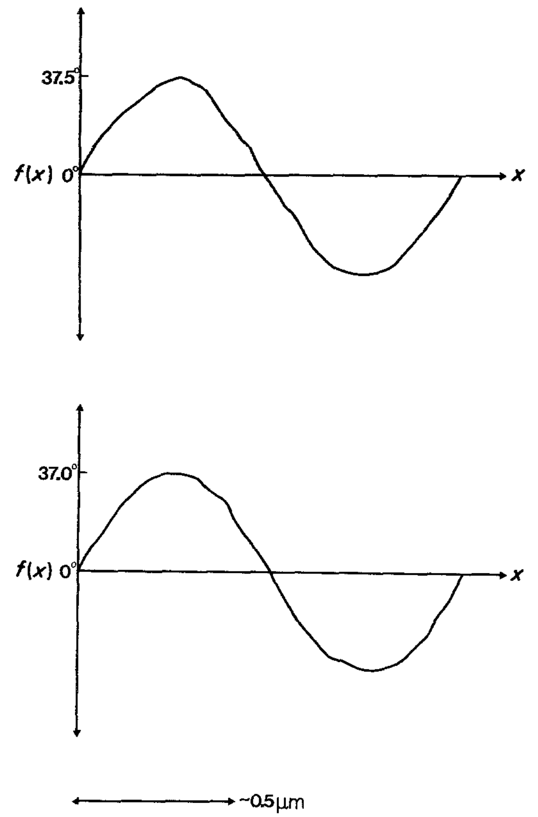


Figure 6 Two plots of the divergence function $f(x)$ prepared from different parts of a sample of B-ET. Experimental readings were taken at 2° intervals of crossed polar rotation.

Upon leaving the specimen a phase lag of δ will have been introduced into the component travelling along OV_1 relative to that travelling along OV_2. Hence the two components of the emergent light are:

$$A_1' = A_0 \cos\theta \exp i(\omega t - \delta) \tag{2a}$$

$$A_2' = A_0 \sin\theta \exp i\omega t. \tag{2b}$$

The total amplitude transmitted by the analyser is therefore given by:

$$\begin{aligned} A_R &= A_1' \cos(2\pi - \phi) + A_2' \cos(\pi/2 - \phi) \\ &= A_1' \cos\phi + A_2' \sin\phi \end{aligned} \tag{3}$$

where ϕ is defined in Fig. 7. For the case of crossed polars $\theta = \pi/2 + \phi$ and therefore A_R can be rewritten as

$$\begin{aligned} A_R &= A_0 \cos(\phi + \pi/2) \cos\phi \exp i(\omega t - \delta) \\ &\quad + A_0 \sin(\phi + \pi/2) \sin\phi \exp i\omega t \\ &= A_0/2 \sin 2\phi \, [\exp i\omega t - \exp i(\omega t - \delta)] \end{aligned} \tag{4}$$

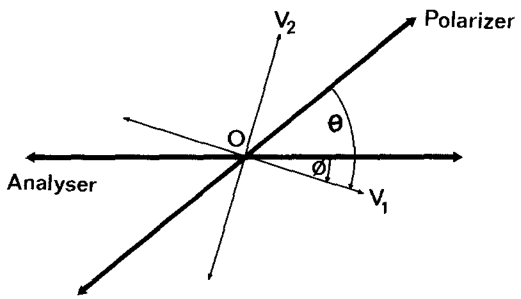


Figure 7 Defining the angles and directions necessary for the derivation of Equation 4. All angles are consistently measured in a clockwise sense.

One consequence of Equation 4 is that whenever the crossed polars are rotated through the extinction position (i.e. as ϕ changes sign through zero), the sign of the complex amplitude passes through zero, changing from positive to negative (or vice versa).

The consequence of the periodicity in the orientation of the extinction axes about the shear axis now becomes clear. In Fig. 5 this variation is represented by the periodic function $f(x)$; in turn this means that ϕ is not a constant but is also a function of position. With the polars in the orthogonal position $\phi(x) = f(x)$, and thus, because of the symmetrical nature of the function, summation of the complex amplitude over several periods will be zero. The maximum number of periods involved in the summation of amplitudes will depend on the coherency of the illumination, and has not been determined. However, as no steps were taken to reduce the coherency artificially (e.g. as described on page 274 of [11]), it seems reasonable that the illumination was effectively coherent over the complete field of view at the magnifications used.

If the periodic function $\phi(x)$ is odd about $x = 0$, then by definition all cosine components of its Fourier transform will be zero. If, in addition, $\phi(x)$ is at the same time even about $x = T/4$, where T is the period of $\phi(x)$, all even sine terms (including the zero order) will also be zero. One is left, therefore, with a series of sine terms involving odd harmonics only. In the limiting case in which the function is sinusoidal (cf. Fig. 6) the absence of all orders higher than first is to be expected.

If the crossed polars are rotated from the orthogonal position by an angle ψ, then $\phi(x) = f(x) + \psi$. The addition of the "d.c." component manifests itself in the conoscopic image as a prominent zero order, seen because $\phi(x)$ is no longer odd about $x = 0$. From this approach it is therefore clear why, upon rotating the polars a few degrees from the orthogonal position, the banded microstructure changes but little, whereas the zero order beam begins to dominate the conoscopic image.

4.3. The specimen in phase contrast

If the Zernicke method of phase contrast is used, the image intensity reflects the uniformity of the optical thickness in the object [9]. An in-plane variation in the orientation of the extinction axes, as assumed above, should have no effect on the optical thickness, giving rise to a featureless phase contrast image. The periodicity apparent in Fig. 3, which is similar to that seen when the specimen is in the orthogonal position between crossed polars, is therefore a strong indication that there is some out-of-plane component to the structure, with a periodicity directly related to that in the specimen plane.

5. Conclusions

1. Banded structures are common to a wide range of liquid crystalline systems.

2. A periodic variation in the directions of the extinction axes about the shear axis explains the behaviour of the bands between crossed polars.

3. The absence of a zero order in the conoscopic image formed with the specimen in the orthogonal position is also directly attributable to the symmetry inherent in the divergence function $f(x)$.

4. This function, $f(x)$, is approximately sinusoidal.

5. The variation in the directions of the extinction axes about the shear axis is not totally confined to the specimen plane.

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