

Morphology of shear-induced textures in a thermotropic liquid crystal copolyester—relationship between banded and tight textures*

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One of the attributes of thermotropic liquid crystal polymers is the ease with which they flow in the molten state. The flow processes strongly affect the resulting microstructure so that microscopy can provide a key in understanding the properties of these materials. The so-called banded and tight optical textures are two of the most commonly encountered flow-induced microstructures, occurring in mouldings and extruded fibres. This paper discusses the morphology associated with these textures as observed in sheared films of a random copolyester. Scanning electron microscopy and X-ray diffraction indicated that, despite their very different optical appearance, their morphologies are quite closely related. In both cases good molecular orientation is observed with respect to layers parallel to the shear plane within which the molecules adopt sinuous trajectories. In the banded texture the molecules follow a more ordered path within the layers and there is a higher degree of inter-layer register.

(Keywords: liquid crystal polymer; sheared films; banded texture; tight texture; chemical etching)

INTRODUCTION

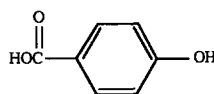
In commercial mouldings and fibres the two microstructures most commonly observed¹ are the so-called banded and tight textures as shown in *Figures 1* and *2*.

The molecular organization in the banded texture is understood in some detail as a result of optical microscopy² and transmission electron microscopy³. It has been shown that the orientation variation of the molecules in this texture is near sinusoidal about the shear direction with most of the misorientation within the shear plane. The tight texture (also called a Schlieren⁴ or Worm⁵ texture) is seen as a fine speckle pattern between crossed polarizers. Determination of the molecular organization associated with this microstructure is still an active area of research and it presents a challenge to the microscopist because the domain size approaches the resolution limit of the optical microscope. Two main approaches have been adopted in an effort to find the most appropriate techniques for studying this texture. The first is the use of a polymer of significantly lower molecular weight which has a coarser optical microstructure⁶; and the second is the use of higher resolution microscopical techniques. This latter approach is the subject of this paper, the recent advances benefiting from the ability to etch surfaces of main chain liquid crystal polymers.

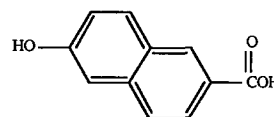
MATERIALS

The liquid crystalline polymer used in this study is a copolyester of hydroxybenzoic acid and hydroxynaph-

thoic acid in the ratio 7:3. The chemical formulae of the components are:



4-hydroxybenzoic acid



2-hydroxy-6-naphthoic acid

and it is designated here as B-N for brevity. The polymer was supplied by the Hoechst-Celanese corporation.

EXPERIMENTAL

Sheared films of the polymer, suitable for investigation by scanning electron microscopy, optical microscopy and X-ray diffraction were prepared using the technique described in detail by Donald and Windle² (*Figure 3*). Small blocks were cut from an extruded pellet, placed onto a clean glass slide and melted to form the mesophase. The polymer was then sheared using a razor blade and rapidly quenched to 5°C on an aluminium block. Varying the speed of the shear determined which optical texture was produced; rapid shear rates ($1 \times 10^{-3} \text{ s}^{-1}$) generally favouring the banded texture while slower shear rates ($5 \times 10^{-4} \text{ s}^{-1}$) led to the formation of the tight texture.

X-ray diffraction required the removal of the polymer films from the glass substrate. This was achieved by immersion of the sample in a solution of dilute sodium hydroxide for approximately 30 min after which the film could be easily peeled away from the glass. The films were then washed and examined in two orientations using transmission diffraction.

The sheared films were examined in the scanning

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Figure 1 Banded texture in a sheared film of B-N viewed between crossed polarizers oriented as shown

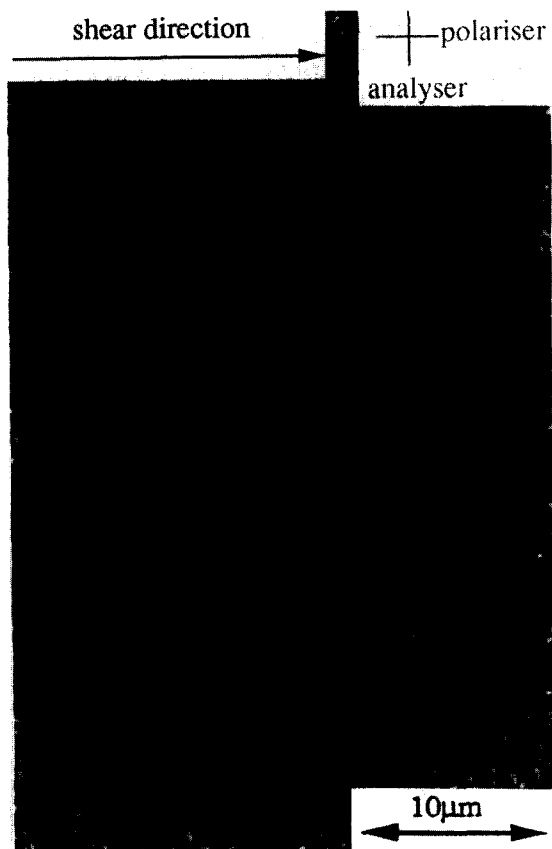


Figure 2 Tight texture in a sheared film of B-N viewed between crossed polarizers oriented as shown

electron microscope using the methods of fractography and selective chemical etching to achieve the necessary topographic contrast. The first of these techniques involves fracture in liquid nitrogen to avoid plastic flow of the film and the second is based on the method pioneered by Bassett and co-workers⁸ for polyethylene and adapted for use with main chain liquid crystal polymers in this laboratory⁹. The etch used in this work is concentrated sulphuric acid applied by immersing the polymer in the acid at room temperature while stirring.

RESULTS

X-ray diffraction

The diffraction patterns in Figures 4a and b describe the quality of alignment with the shear direction within the shear plane for the two textures. They were obtained from approximately fifty 5µm thin films stacked in identical orientation. Since the intensity is faint the diffraction patterns are illustrated schematically in Figure 5. In both cases the quality of alignment is low and of

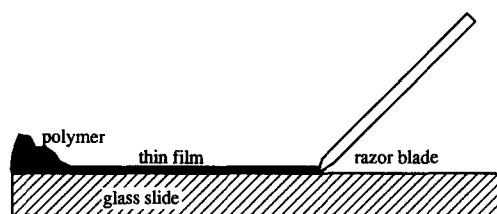


Figure 3 Illustration of the technique used for preparing thin films of B-N suitable for study by optical and scanning electron microscopy. (Adapted from reference 7)

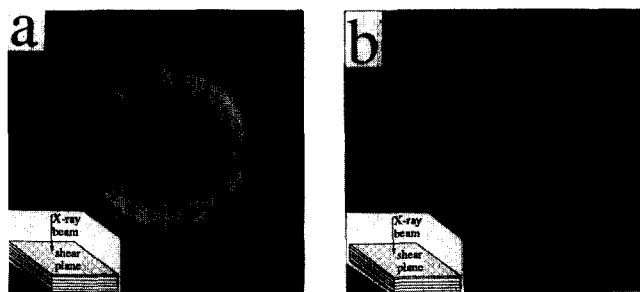


Figure 4 Transmission diffraction patterns demonstrating the degree of order with the shear direction within the shear plane for (a) the banded texture and (b) the tight texture. In each photograph the shear direction is vertical and the inset shows the orientation of the X-ray beam with respect to the stack of films

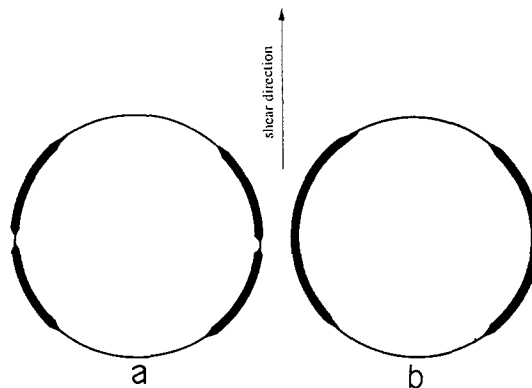


Figure 5 Schematic illustration of the diffraction patterns shown in Figure 4

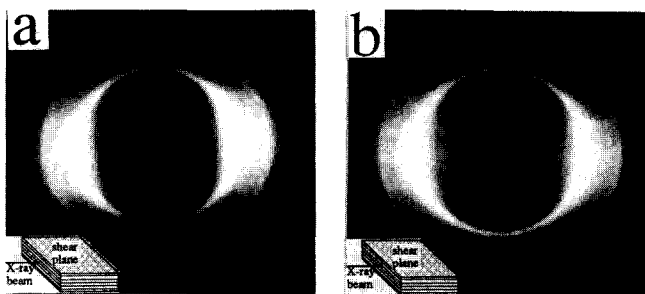


Figure 6 Transmission diffraction patterns demonstrating the degree of order with respect to the plane of shear for (a) the banded texture and (b) the tight texture. Again the inset shows the orientation of the X-ray beam with respect to the stack of films, and the shear direction is vertical on the diffraction pattern

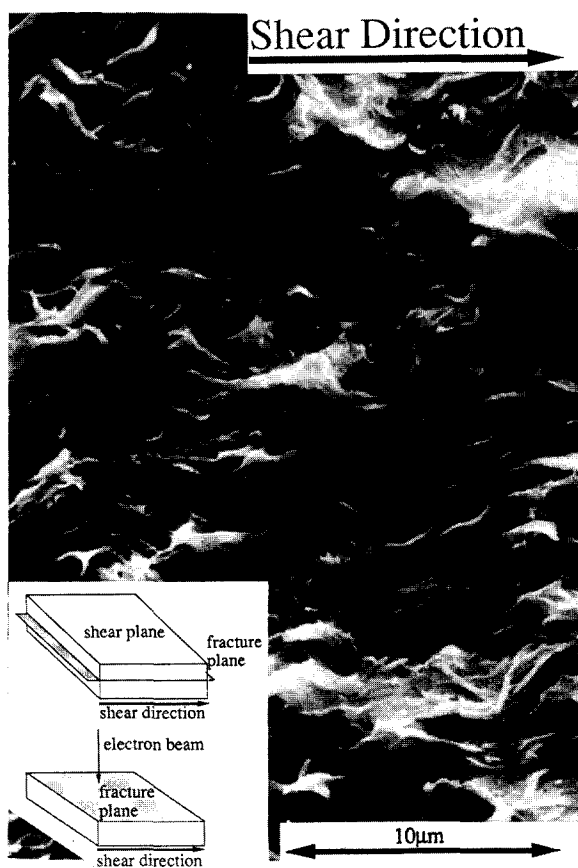


Figure 7 Scanning electron micrograph of a sheared film of B-N exhibiting the optical tight texture which has been fractured in liquid nitrogen. The inset shows that the fracture plane is parallel to that of the shear and is viewed orthogonally to the electron beam. A lamellar morphology is observed, the edges of which are sinuous

similar magnitude. A faint *four point* pattern may be observed in the case of the banded texture which is consistent with the almost regular sinusoidal trajectory of the molecules. This is not observed in the pattern from the tight texture. The diffraction patterns in *Figures 6a* and *b* illustrate the quality of alignment with respect to the plane of shear for the two textures. It is of a much higher order than the alignment *within* the planes parallel to the shear plane, but again is similar for both the banded and tight texture samples.

The results in *Figures 4–6* thus indicate that there is an intriguing similarity between the two textures despite their very different optical appearance, and that the perfection with which the molecules are aligned with the

shear plane in both textures is much greater than their alignment within this plane. This result is consistent with that of a layered morphology in which there is comparatively poor orientational order within the layers.

Scanning electron microscopy

Figure 7 shows a sheared film exhibiting the tight texture which has been fractured on a plane parallel to that of the shear. A lamellar morphology is observed with the edges of the lamellae appearing to weave sinuously through the structure. From previous work it is known that the material fractures preferentially along the molecular chains^{10,11} so the fractured edges of the lamellae may be taken as being representative of the path of the molecules. *Figure 8* shows another view of the tight texture again on a plane parallel to that of the shear, however, in this case the film has been heavily etched (40 min etching time) but not fractured. The morphology closely resembles that of the fracture surface in the previous micrograph. Again lamellae with sinuous edges are apparent indicating that the etch reveals the direction of the molecular chain axes. These results, consistent with those obtained by X-ray diffraction suggest that the molecules are arranged into layers within which they adopt sinuous trajectories. The lamellar morphology arises when the crack or etchant attacks along the chains for some distance and then transfers to another layer. The edges of the layers are shown clearly in *Figure 9* in



Figure 8 Scanning electron micrograph of a sheared film of B-N exhibiting the optical tight texture viewed in the same orientation as in *Figure 7*. In this case the film has been deeply etched (40 min) in concentrated sulphuric acid but not fractured. The morphology closely resembles that observed in *Figure 7*. (Micrograph courtesy of T. J. Lemmon)

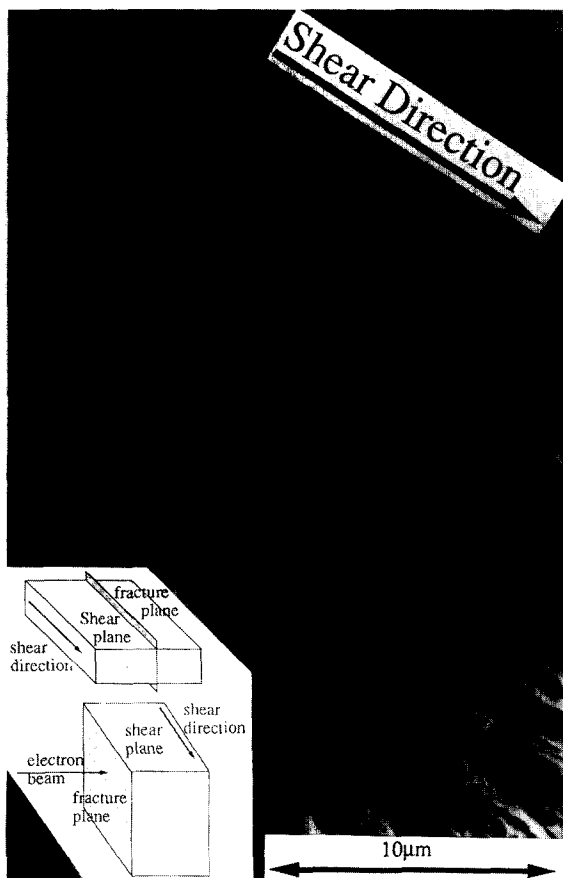


Figure 9 Scanning electron micrograph of a sheared film of B-N exhibiting the optical banded texture which has been fractured in liquid nitrogen. The inset shows that the fracture plane is orthogonal to that of the shear. The edges of the layers are clearly revealed

which a film with the banded texture is viewed on a fracture plane perpendicular to that of the shear.

Figure 10 shows the morphology in both the banded and tight textures as revealed by a much lighter etch (10 min etching time). Once again the edges of the lamellae through which the etch has penetrated show up as sharply defined sinuous lines (dark or bright contrast depending on the local topology). In both cases we can find no evidence for molecular trajectory patterns associated with disclinations, at least in any classical sense¹². The lamellae also show a fine cross texture which are generally oriented normal to their sinuous edges. It is possible that these are non-periodic layer crystallites¹³ which have been clearly revealed by scanning electron microscopy in a low molecular weight polymer¹⁴ and also by transmission electron microscopy of this polymer where they have been demonstrated to be generally normal to the local molecular trajectory⁷. The cross texture observed here is certainly of the right dimensions and spacing.

The lightly etched micrographs not only reveal the similarities between the microstructures of the banded and tight textures in sheared samples, but they also clearly reveal their essential differences. Although each is based on layers within which the molecules follow sinuous trajectories, in the banded texture the sinuosity is much more regular and there is much greater register between the separate layers. A schematic diagram which illustrates the two morphologies is given in *Figure 11*.

Demonstration of the equivalence between a tight texture and a poorly ordered banded texture

Eight thin banded texture samples were assembled with various degrees of misorientation about a preferred axis. Observation of this poorly ordered layered structure in the polarizing microscope showed a microstructure similar to that in samples sheared under conditions which produce a tight texture (*Figure 12*). As the crossed polars were rotated in relation to the sample, the contrast within individual domains changed through the expected dark-light-dark sequence every 90° but there was no change in the transmitted intensity averaged over the whole field of view. This is exactly the observation made by Windle *et al.*¹⁰ in their detailed optical investigation of the tight texture.

SUMMARY

Scanning electron microscopy and X-ray diffraction both indicate that there are several microstructural features common to sheared films whether they exhibit either a banded or a tight texture. In both cases there is good molecular orientation with respect to the layers parallel to the shear plane and a sinuous molecular trajectory within the layers. The orientation variations are thus achieved without the need for line disclinations. The difference between the two textures is that in the banded texture the variations tend to be sinusoidal and there is

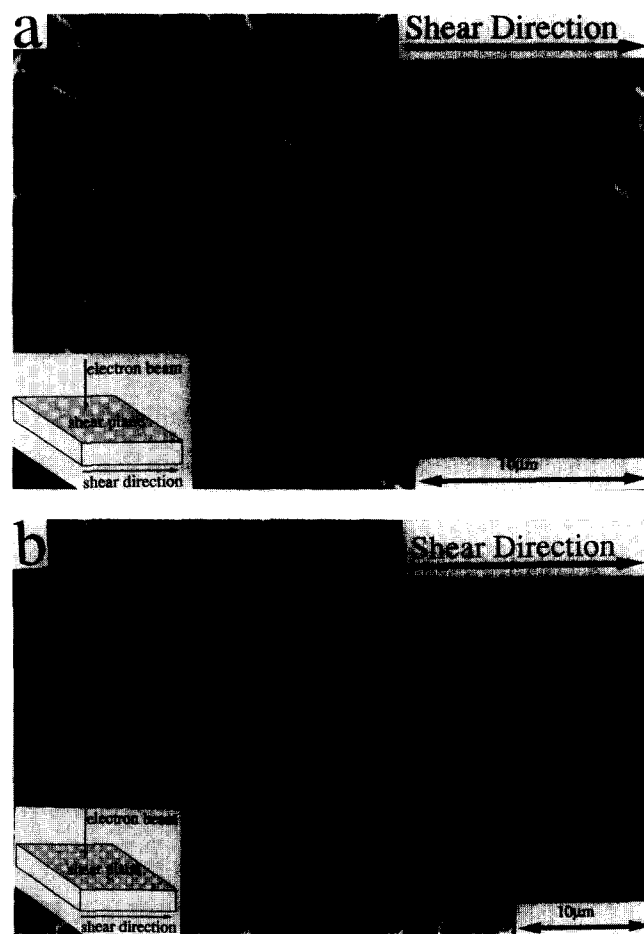


Figure 10 Scanning electron micrograph of sheared films of B-N which have been etched for 10 min in concentrated sulphuric acid. The film in (a) exhibits the banded texture in the light microscope and that in (b) the tight texture. In both cases sinuous layer edges are observed on which is superimposed a fine cross texture of platelets

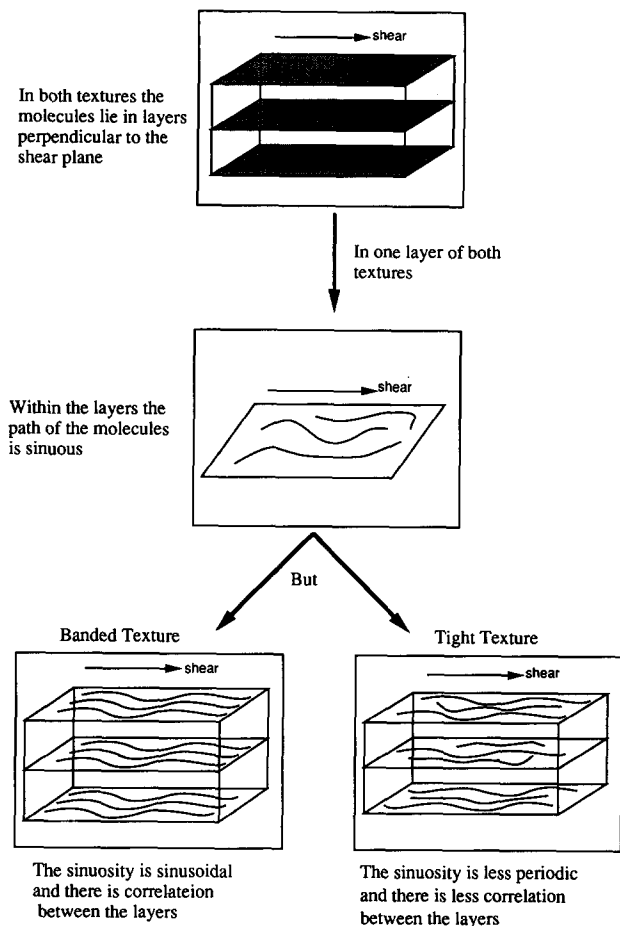


Figure 11 Schematic diagram illustrating the similarities and differences between the banded and tight textures

a high degree of register of the molecules between each of the layers. In the tight texture there is evidence for less in-layer order and there is little, if any, specific positional register between the layers.

The banded texture and the tight texture thus share common microstructural features, with the banded texture appearing to be an especially well correlated variant of the tight texture.

In the etched sheared films it has also been possible to image non-periodic layer crystallites in the scanning electron microscope which, for this polymer, have been previously observed only by transmission electron microscopy.

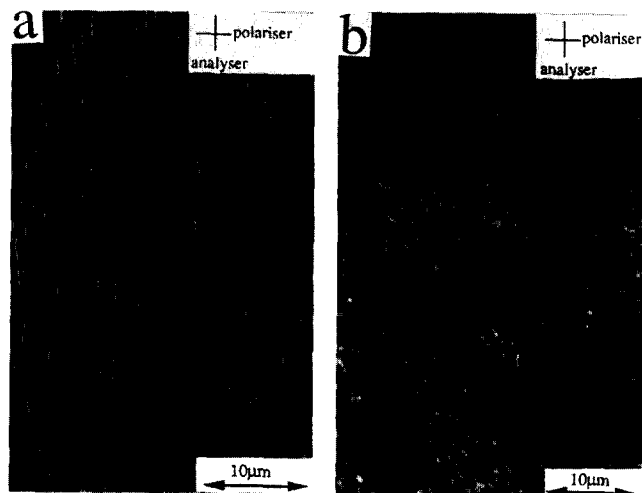


Figure 12 Optical micrographs illustrating that a tight texture is equivalent to a poorly correlated banded texture. (a) Banded texture in a single thin film (about $3\ \mu\text{m}$ thick) of B-N. (b) Stack made of eight such films stacked on top of each other with random angular displacements about the shear direction

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