Banded structures in oriented thermotropic polymers

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(Received 28 *April* 1982; *revised* 13 *July* 1982*)*

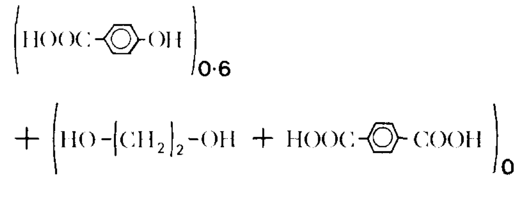
Drawn fibres and shear-oriented thin films of four thermotropic liquid crystalline polymers have been examined using polarized light optical microscopy and transmission electron microscopy. A banded structure is observed in polarized light, with the striations lying perpendicular to the fibre axis or shearing direction. This structure closely resembles those previously reported in lyotropic polymers, suggesting that the supramolecular organization implied by the banded structure is a feature characteristic of oriented liquid crystalline polymers in general.

Keywords Liquid crystalline polymer; thermotropic; supramolecular ordering; banded structures; flow-oriented

INTRODUCTION

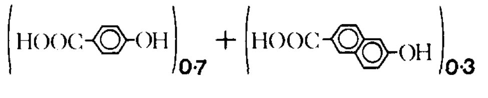
Thermotropic liquid crystal polymers are based on rigid-chain molecules. At suitably elevated temperatures, they exhibit flow with liquid crystalline characteristics; that is, there is pronounced molecular mobility and macroscopic flow without loss of the local orientation correlation of the molecules. One aspect of this behaviour is that substantial overall alignment of the molecules can be obtained with compartively modest flow rate gradients. The combination of chain alignment (with regard to an external frame) and stiff extended molecules contributes to a high axial modulus which can be exploited, for example, in fibre composites. Thermotropic polymers are to be contrasted with their lyotropic equivalents, in that the latter exhibit liquid crystalline flow properties in the presence of a suitable solvent. However the lyotropics have been the first to be commercially developed, as the Kevlar series of poly(*p*-phenylene terephthalamide) fibres.

The materials examined in this work were copolyester thermotropics built from the following residues:



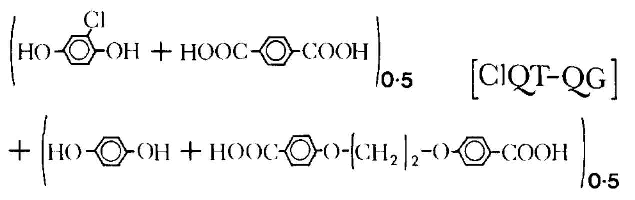
[B-ET]

[*p*-hydroxybenzoic acid] + [ethylene glycol + terephthalic acid



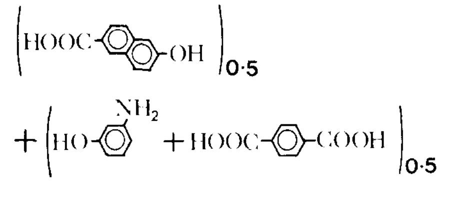
[B-N]

[*p*-hydroxybenzoic acid] + [hydroxynaphthalic acid]



[ClQT-QG]

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



[N-AT]

[hydroxynaphthalic acid] + (*m*-hydroxyaniline + terephthalic acid]

It has already been established that the [B-ET] polymer, when oriented by extrusion to $P_2 > 0.6$* (as measured by wide angle X-ray diffraction[1]) has a microstructure as seen in the polarizing optical microscope which gives no indication of the molecular orientation in terms of an overall birefringence[2]. The observations reported here arose from efforts to obtain better molecular orientation by drawing fibres and shearing films.

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* P_2 is a measure of preferred orientation in relation to one external axis (sometimes referred to as an order parameter). It is defined as $\frac{1}{2}(3\cos^2\alpha - 1)$ where α is the angle between this axis and the long axis of a molecule.

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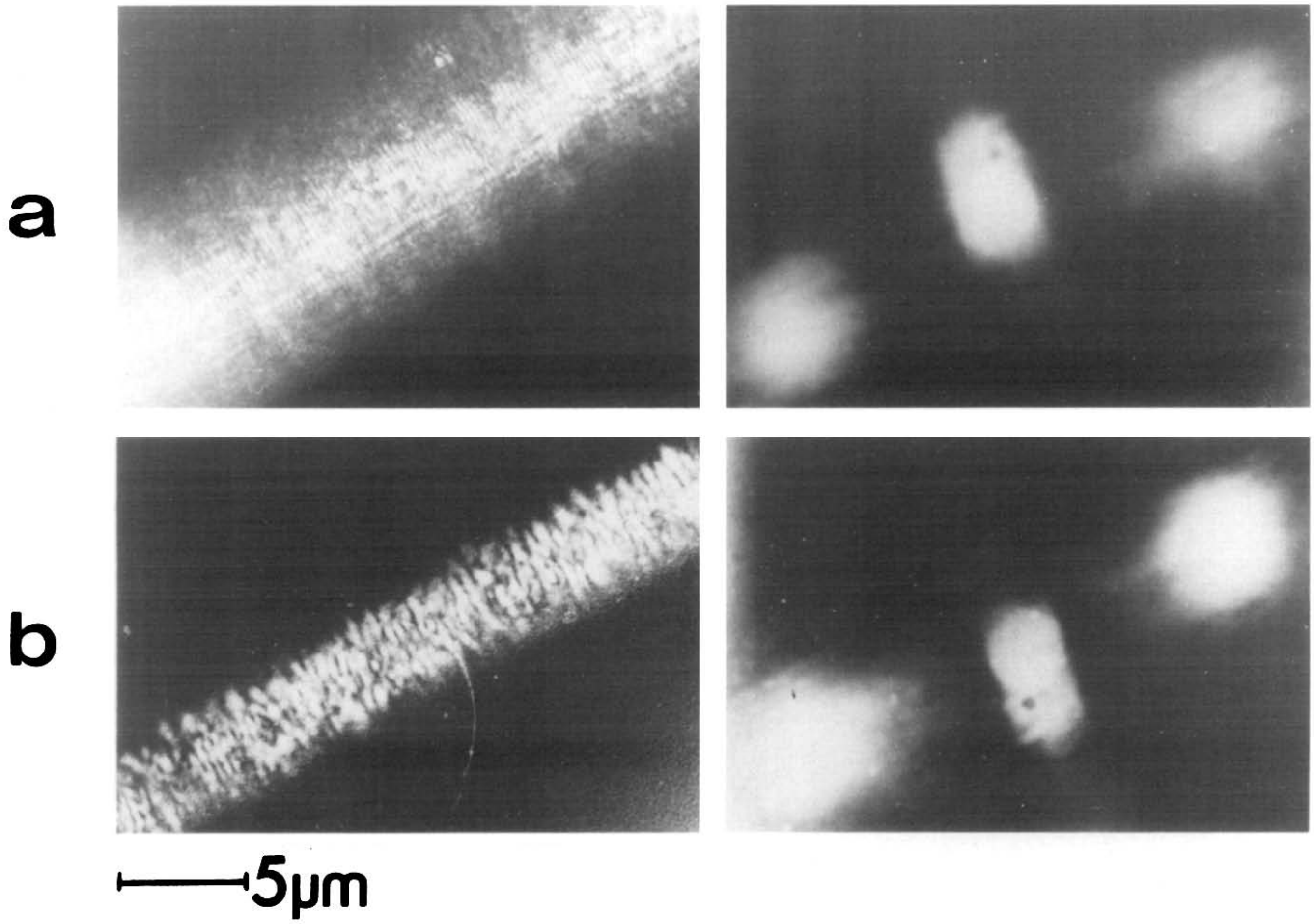

Figure 1 Optical micrograph and corresponding optical diffraction pattern for fibres of (a) [B–ET] and (b) [B–N]

OBSERVATIONS

Fibres were drawn from the polymers [B–ET] and [B–N] at 250°C and 320°C respectively, i.e. above the polymer softening points. Over some regions of the fibre length a banded structure, consisting of a series of bands normal to the fibre axis, was apparent when the crossed polarizer and analyser were aligned with this axis. This structure was also studied by means of its optical diffraction pattern (which is its Fourier Transform and is also known as the conoscopic image) by the insertion of a Bertrand lens into the optical path. *Figure 1* (*a–b*) shows the microstructure and optical diffraction pattern for each of the two polymer fibres.

Samples of all four polymers were sheared between glass slides at temperatures a few tens of degrees above their softening points (i.e. at 250°C, 310°C, 310°C and 310°C for polymers [B–ET], [B–N], [ClQT–QG] and [N–AT] respectively) and then quenched on a copper block. It has been shown[3] for copolyesters that rapid cooling enables microstructures of the higher-temperature phases to be successfully quenched in. Micrographs and optical diffraction patterns for the four polymers are shown in *Figure 2* (*a–d*). In all cases, banded structures are apparent when either the analyser or crossed polarizer is parallel with the direction of shear. In general, the banding is equivalent to that seen in the fibres, although of a somewhat larger period.

Shearing of a sample between a glass slide and a rock-salt crystal enabled films to be obtained which, on dissolution of the salt, were suitable for transmission electron microscopy (*TEM*) *Figure 3* shows bright field and dark field electron micrographs of the same area, in this case of [B–N]; the dark field picture is imaged in one extremity of the main equatorial diffraction arc. The appearance of the banded structure in dark field alone indicates that is is associated with periodic changes in molecular orientation and not thickness variations.

DISCUSSION

The structures in *Figures 1* and *2* show that the four thermotropic liquid crystalline polymers all exhibit the same type of banded structure when flow-oriented as thin films and fibres. These microstructures are strikingly similar to those seen in Kevlar fibres by *TEM*[4,5] and polarized light microscopy[6]. In contrast to the thermotropic polymers, Kevlar is highly crystalline, although it is prepared from a lyotropic solution. A *TEM* study of sections microtomed from Kevlar fibres parallel to the axis[5] permitted a detailed analysis of the three-dimensional distribution of unit cell orientations. On the basis of this analysis a radially symmetric pleated sheet structure was proposed for the fibre. The alternating bands of bright and dark contrast observed in certain dark field images closely resembles the dark field micrograph of *Figure 3.* The later optical microscopy study[6] showed banded type structures which were related to the optical diffraction pattern of the image. The

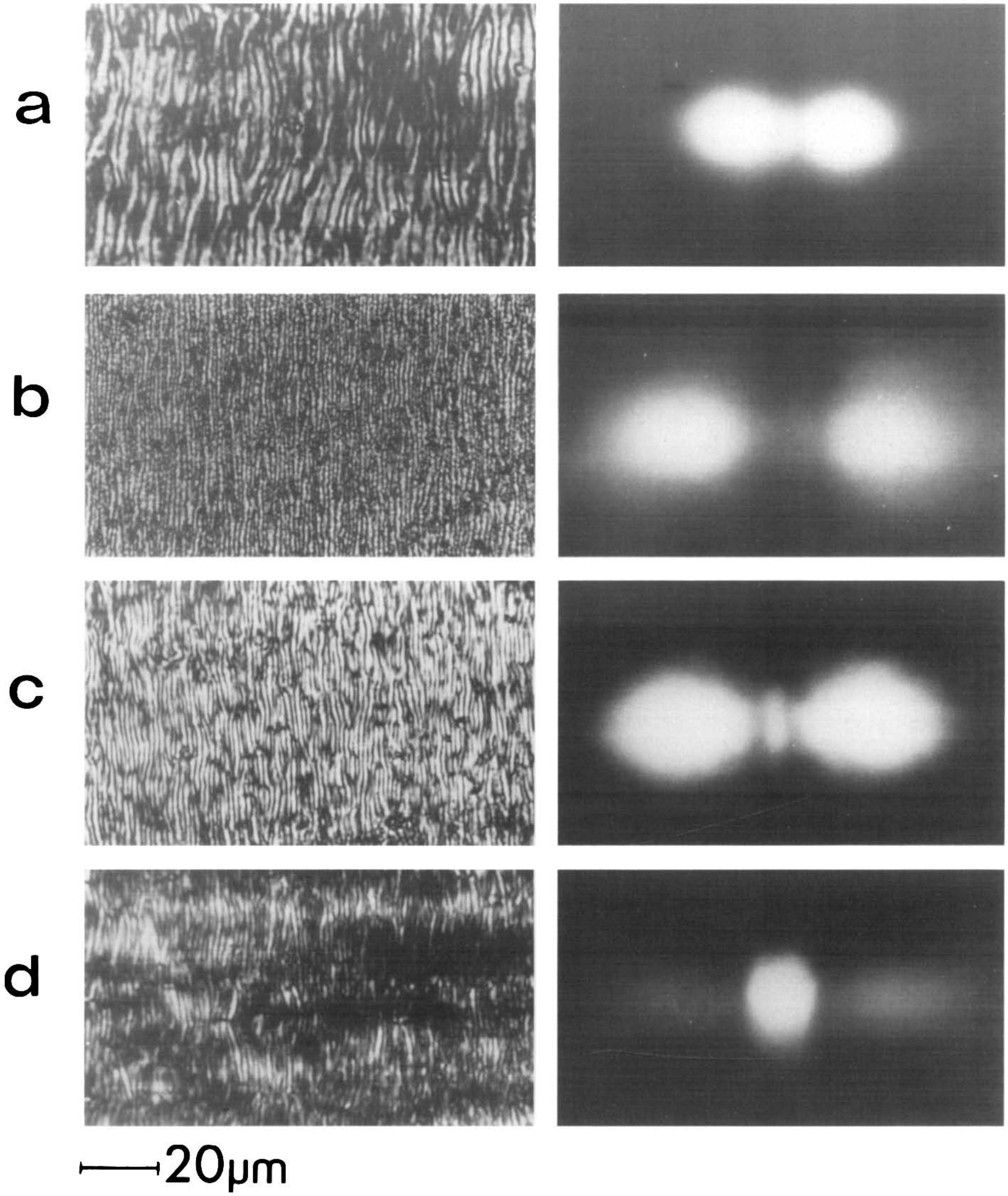

Figure 2 Optical micrograph and corresponding optical diffraction pattern for films of (a) [B—ET], (b) [B—N], (c) [ClQT—QG] and (d) [N—AT]. The shear axis is horizontal in each case

occurrence of the banded structure was attributed to the ordering implicit in the pleated sheet model proposed by Dobb *et al.*, and in essence provided support for the model. An optical micrograph of Kevlar 49 and its diffraction pattern, taken under identical conditions to those of *Figures 1* and *2*, is shown in *Figure 4* for comparison. It underlines the similarity between the microstructures of Kevlar, (crystalline but prepared from a lyotropic solution) and the thermotropic polymers of this study.

A recent rheo-optical study[7] of poly(γ-benzyl-L-glutamate) (PBLG), a synthetic polypeptide which is cholesteric in appropriate solvents, but whose helix can be 'unwound' during shear to yield a nematic lyotropic

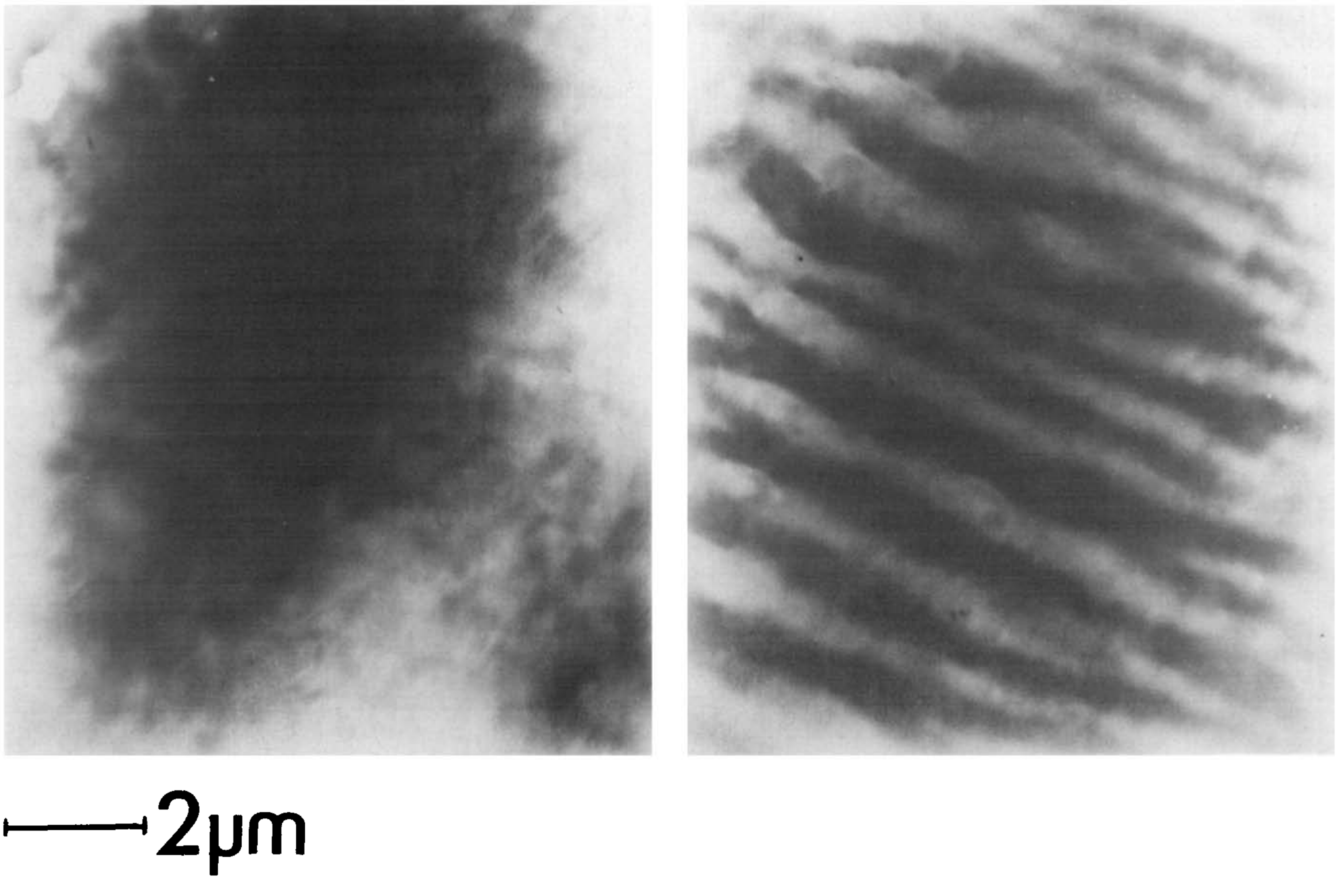

Figure 3 Bright and dark field *TEM* images of [B—N]. The dark field image is formed using one extremity of the equatorial arc

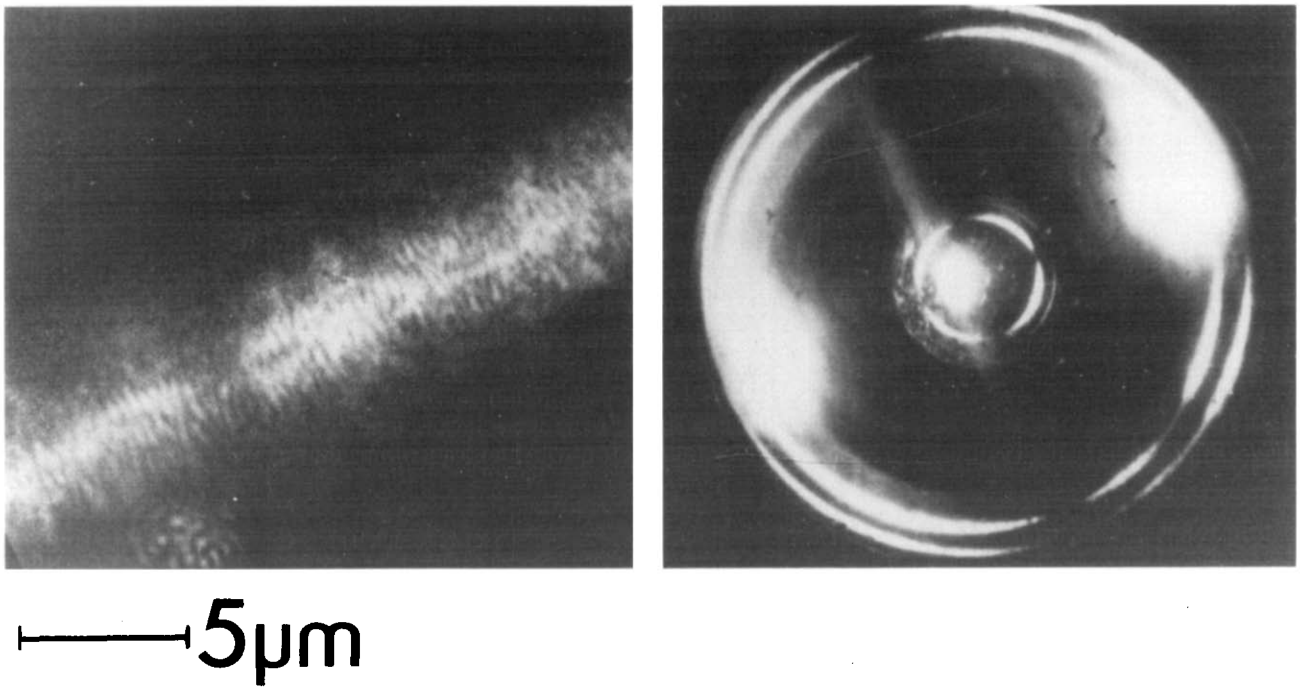

Figure 4 Optical micrograph and resultant optical diffraction pattern for Kevlar 49 (the rings on the optical diffraction pattern are an artifact)

solution, has also shown a similar microstructure. In this case the banded structure appears either during the actual shearing process for relatively high shear rates and concentrated solutions, or, for less concentrated solutions, as a relaxation phenomenon upon cessation of shear. The banded structure was also apparent in dried thin films of PBLG which had been sheared onto a glass slide, i.e. films formed by a process analogous to that used here for film preparation of the thermotropic polymers.

Banded structures have also been observed by Atkins, Fulton and Miles[8] in hydroxypropyl cellulose and cellulose acetate prepared from lyotropic solutions. The structures were seen both in stretched films and in cast films, although in the latter case the possible role of surface tension forces during drying was noted. The authors also demonstrate the existence of similar structures in a melt-spun fibre of hydroxy propyl cellulose.

The supra molecular ordering implied by the occurrence of the banded structure may be significant in determining the optimum elastic modulus, as has been discussed in relation to the 'crimped' structure in rat tail tendons[9]. It is also perhaps significant that the structure is not apparent in the highest modulus variant of Kevlar, PRD 49[5], which is assumed to have received a significant heat treatment following fibre formation.

SUMMARY

Although the detailed analysis of the supra molecular organization within these thermotropic liquid crystalline polymers is still in progress, it is clear that the banded structure observed is remarkably similar to that reported in lyotropic polymer systems. It is therefore apparent that such structures are a general feature of liquid crystalline polymers which have been oriented by flow. However it is not yet clear whether their formation is induced directly by flow, or whether they represent some stage of a relaxation process[7,10].

ACKNOWLEDGEMENTS

The authors wish to thank Dr E. D. T. Atkins, Dr M. R. Mackley and Miss D. Graziano for helpful discussions, and Dr G. A. Chinner for photographing the optical diffraction pattern of Kevlar. ICI (Plastics and Petrochemicals) Ltd. and Eastman-Kodak Ltd. kindly provided samples. We also thank SERC for the provision of funds and Professor R. W. K. Honeycombe for facilities.

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