

# A new banded texture in sheared thermotropic liquid crystalline polymers

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Liquid crystalline polymers (LCP) often show after a shearing procedure a so-called banded texture as reported in the literature. The appearance of the banded texture is mainly influenced by the chemical structure of the LCP, the shear rate and the thickness of the layer. In addition to the well known banded texture a particular tractor texture (or herring-bone texture) can be obtained. By subsequent annealing of the sheared specimens at elevated temperatures the banded texture can be changed, especially in dependence on the thickness of the sheared layer. In some cases the banded texture remains unchanged, whereas in other cases it is transformed into a domain structure or into spherulites.

## 1. Introduction

The appearance of banded structures in liquid crystalline polymers (LCP) was first observed in high strength fibres produced by solution spinning [1, 2]. Fibres spun from such lyotropic polymers (e.g. from poly(p-phenylene terephthalamide); Kevlar) are commercially produced and marketed [3, 4].

Banded structures were also observed in thermotropic liquid crystalline polymers. This characteristic texture could not be found in low molecular weight liquid crystals. The bands result from the periodicity in the segmental orientation of the chain molecules about the shear axis [4]. Investigations of the time dependence of the texture formation in polarized light prove that the director is oriented into the shear direction during shearing [5]. The banded structure is formed as a result of the relaxation processes taking place after shearing; it is created if the shear rate is high enough [6]. Scanning electron microscopical studies show that the banded texture exhibits fibrillar zigzag structures [7].

Annealing of thin sheared films containing the banded structure leads to a texture change: the banded texture is replaced by domains elongated in the flow direction [8]. For liquid crystalline poly(esters) it has been found that the band periodicity is increased visibly by annealing.

In this paper two chemically different LCPs are investigated by optical microscopy. With the first sample a new banded texture is observed which is named "tractor texture". The second sample exhibits a change of morphology from a banded texture to a spherulitic structure as a result of annealing.

## 2. Experimental procedures

Thermotropic copoly(esters) LC 10 108 (X7G) from Tennessee Eastman Kodak and EPE 240 from Mitsubishi Chemical Industries were used. The specimens in the form of pellets or chips were sheared between

two glass plates at different temperatures above the melting point and subsequently quenched to room temperature.

The optical investigations were carried out with a Leitz microscope ORTHOLUX II POL-MK under crossed polarizers using white light. The specimens were annealed in a Mettler heating system FP 52 and observed at the chosen temperature.

The thickness of the samples after shearing could not be measured exactly but could be estimated from the optical transparency. Samples with a thickness of more than 5  $\mu\text{m}$  appeared opaque. From the intensity of the transmitted light the average thickness of the sheared specimens was estimated to less than 1  $\mu\text{m}$ . In the following sections the expression "thin" was used if the transmitted light intensity was high and the thickness of the specimen at the area under observation was considerably thinner than 1  $\mu\text{m}$ .

## 3. Results and discussion

Sheared specimens of both investigated materials have a high molecular orientation and show a so-called banded structure. The optical behaviour of the samples during rotation under crossed polarizers is similar to that which has been reported in the literature [9]. This behaviour results from the fact that the molecular orientation is changed periodically in a sinusoidal manner about the shear axis. The well-known doubling of the band thickness as a result of the rotation of the specimen can be clearly recognized from Fig. 1.

The optical behaviour of the two samples — especially after annealing — differs in fact so that the results will be discussed in separate sections.

### 3.1. EPE 240 (Mitsubishi)

Parts of the specimens which were sheared at 300°C and subsequently quenched down to room temperature exhibit a high molecular orientation and a banded

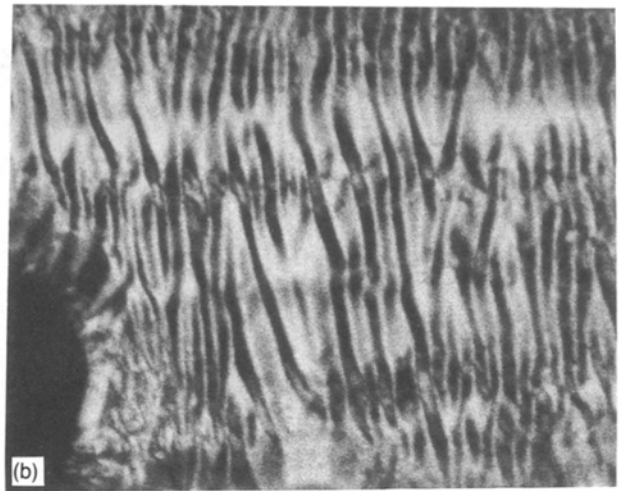
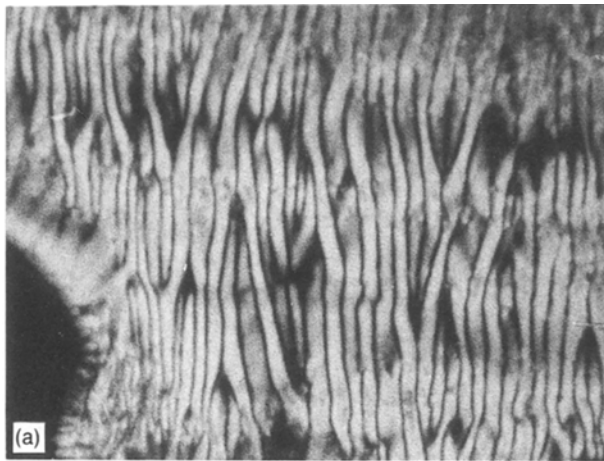


Figure 1 Optical micrographs of LCP X7G under crossed polarizers (a) angle between shear direction and polarizer  $\varphi = 0^\circ$  (b)  $\varphi = 36^\circ$ .

texture with a band period of 1 to 2  $\mu\text{m}$ . The direction of the bands is perpendicular to the shear direction.

The pretreated specimens were again heated up to 300°C and annealed for some minutes at this temperature. On the “thinner” parts of the samples no alteration of the banded structure is observed while on the “thicker” parts a new vein structure appears which is tilted by 20 to 30° to the shear direction, see Fig 2.

Other parts of the sheared specimens present a so far unobserved texture which is called “tractor texture” due to the similarity to the mark of tractor tyres on the ground, see Fig. 3. (Another possible name for this texture would be “herring-bone pattern”.) The thickness of the bands of the tractor texture varies from 4 to 24  $\mu\text{m}$ . By annealing of the samples the tractor texture is intensified, details will be discussed elsewhere [10].

The bands of the usual banded texture run perpendicular to the shear direction whereas the bands of the

tractor textures are inclined to the shear direction in a zigzag manner as outlined schematically in Fig. 4. The molecules within the zigzag bands are arranged perpendicular to the band surface in every second band section (see Fig. 4, sections a, b, c, and d, respectively). Moreover, the tractor texture is built up into the shear direction in such a way that the molecules are lying perpendicular to the band surface in every second band (see Fig. 4, sections a, e, f, and g, respectively). By rotation of the specimens under crossed polarizers the halving of the band period is observed.

The molecular orientation in the shear direction was obtained using the polarized microscope by measuring the angle of maximum extinction as a function of position. From Fig. 5 it can be recognized that the orientation of the molecules within a given tractor band remains constant. The alteration of the orientation between two neighbouring bands occurs in a small intersection of about 1  $\mu\text{m}$  thickness. Thus, the course of the orientation within the tractor texture has

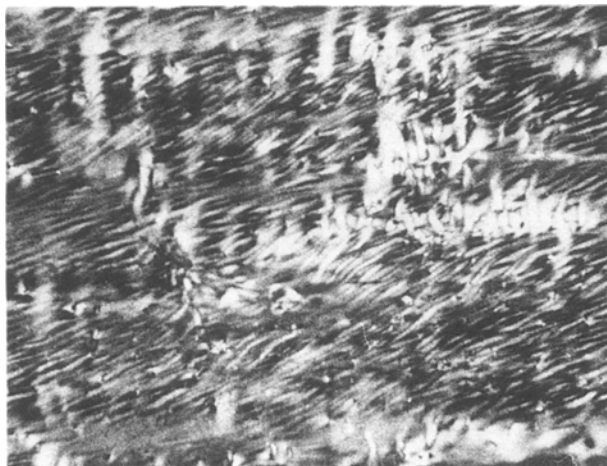


Figure 2 Optical micrograph of LCP EPE 240 under crossed polarizer. The sheared specimens were heat-treated at 300°C for 10 min prior to microscopical observation.

Figure 3 Optical micrograph of LCP EPE 240 under crossed polarizers showing the so-called tractor texture.

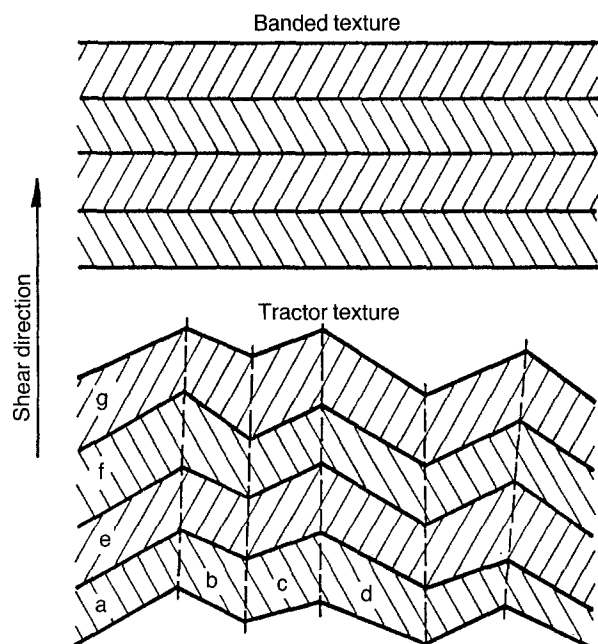


Figure 4 Schematic drawing of banded texture and the tractor texture shown in Fig. 3. The fine lines represent the molecular orientation within the bands. The letters a, b, c, d, e, f, and g characterize different parts of the zigzag bands.

a box-type design instead of a sinusoidal shape for the usual banded texture.

### 3.2. LC 10108 (X 7 G) (Kodak)

Specimens which have been sheared at 300°C and subsequently quenched down to room temperature exhibit the usual banded texture with a band thickness between 1 and 8 μm (depending on the local conditions of shearing).

The following annealing procedure at 300°C gives rise to different morphologies of the heat-treated samples: on the "thinner" parts the banded texture remains unaltered and a new domain structure without macroscopical orientation appears. The difference in this behaviour has its origin in the strength of interaction: the bonding of the macromolecules onto the substrate (glass plate) is much stronger than the

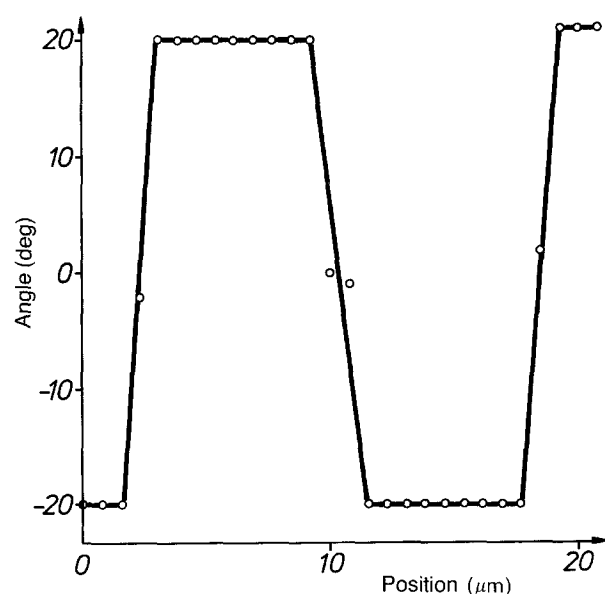


Figure 5 Angle of maximum extinction as a function of position along the shear axis.

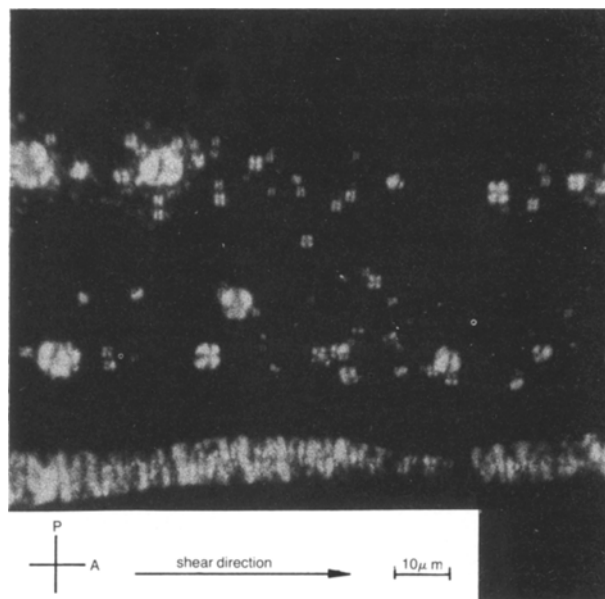


Figure 6 Optical micrograph of annealed LCP X7G under crossed polarizers showing spherulites.

mutual interaction of the macromolecules. Therefore, the adsorbed surface layer of the LCP has different physical properties than the volume layer. During the annealing the structure of the adsorbed layer is stable and the orientation within this layer remains unaltered. On the other hand, within the volume layer the previous texture is changed into the domain structure mentioned above.

In some cases a different morphological behaviour in very thin sheared specimens was observed after annealing. At those parts where there is very little substance the banded texture does not keep area-covering but remains in stripes of 5 to 10 μm width. After a short annealing at 300°C the original banded texture within the stripes is converted into spherulites with a diameter of 2 to 10 μm.

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### References

1. M. G. DOBB, D. J. JOHNSON and B. B. SAVILLE, *J. Polym. Sci., Polym. Phys. Edn* **15** (1977) 2201.
2. G. KISS and R. S. PORTER, *ibid.* **18** (1980) 361.
3. A. M. DONALD, G. VINEY and A. H. WINDLE, *Polymer* **24** (1983) 155.
4. C. VINEY, A. M. DONALD and A. H. WINDLE, *J. Mater. Sci.* **18** (1983) 1136.
5. R. CURTIS and J. R. FINCHER, *Mol. Cryst. Liq. Cryst.* **155** (1988) 559.
6. G. MARUCCI, N. GRIZZUTI and A. BUONAURO, *ibid.* **153** (1987) 263.
7. S. SHEN, Y. JIN, S. HU and M. XU, *Polym. Commun.* **28** (1987) 208.
8. A. M. DONALD and A. H. WINDLE, *J. Mater. Sci.* **19** (1984) 2085.
9. C. VINEY, A. M. DONALD and A. H. WINDLE, *Polymer* **26** (1985) 870.
10. M. KWIATKOWSKI and G. HINRICHSEN, in preparation.

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