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

Direct observation of director fields of disclinations in the nematic mesophase of a main chain thermotropic aromatic polyester by surface microcrack decoration

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Online publication date: 06 August 2010

LIQUID CRYSTALS, 2001, VOL. 28, NO. 3, 451–455

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(*Received 17 March 2000; in final form 11 July 2000; accepted 21 August 2000*)

For a main chain thermotropic aromatic polyester with a flexible spacer, Cr 194 N 245 I (°C), the director fields around disclinations in the nematic mesophase can be decorated by both the solidification-induced band texture and surface microcracks. Director fields of various types of disclinations, including inversion walls, in the nematic mesophase of this semi-rigid polyester have been observed directly by polarizing optical microscopy. It was found that when the polymer was pre-sheared in the nematic state and then quenched to room temperature, a shear-induced band texture was observed, which relaxed slowly during annealing at 200°C, and then on quenching the solidification-induced band texture and surface microcracks appeared, displaying the pattern of the disclination fields. Pre-shearing is a necessary condition for the appearance of microcracks. On annealing, disclinations of various types were generated, quite often connected by inversion walls in the direction of pre-shearing. In some areas of the specimen where the shear-induced bands had not been completely relaxed during annealing, the shear-induced band texture was shown by the birefringence and surface microcracks to have a supermolecular structure of sinusoidal chain fibrils.

1. Introduction

Surface microcracks which can be observed by optical microscopy will appear in nematic polymers with highly rigid chains when the nematic melt of a thermotropic liquid crystalline polymer (LCP) is frozen rapidly [1, 2] or when a solution-cast film of a lyotropic LCP is formed after evaporation of the solvent [3]. This is understandable, as the rigid chains tend to form aligned molecular chain bundles or fibrils in the nematic domains and the lateral interchain cohesion is weak. Therefore it is easy for a break to occur along the fibrils or in the chain direction. This behaviour is analogous to the well-known technology of split fibre fabrication from highly oriented polymeric materials, such as partly crystallized flexible chain polyethylene. The microcracks are along the direction of the chain, and hence these microcrack patterns display the director field around disclinations, since the direction of the director coincides with the backbone chain in the case of main chain nematic polymers. This method of surface microcrack decoration for mapping the director field is applicable to thin or very thin films and the microcracks can be seen using an optical microscope, with or without polarizers, or even by reflection.

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An example reported by Wang *et al.* [3] is the surface microcrack formation during evaporaton of the solvent from a solution-cast film of polydiacetylene with urethane side groups. The film was cast from a nematic solution of the polymer in chloroform, and was then put aside at room temperature for 200 h under a controlled atmosphere of the solvent. A schlieren texture was observed. After complete evaporation of the solvent, surface microcracks appeared while the schlieren texture remained. These microcracks revealed the director fields of the $S = \pm 1/2$ and $S = \pm 1$ disclinations.

Hudson *et al.* [2] reported the observation of the director field by surface microcrack decoration in their study of an aromatic copolyester with flexible side groups which had a glass transition temperature $T_g = 120°C$ and was nematic between 180 and 224°C. The film, quenched from its nematic state, showed both a schlieren texture and surface microcrack decoration, revealing the director field in the polymer.

A solution-cast film of poly(2,5-didodecyl-1,4-phenylene) was melted at its melting temperature 187°C, then annealed first at 150°C and then at 135°C. Afterwards it was rapidly cooled. Then surface microcrack-decorated director fields of disclinations of $S = \pm 1/2$, ± 1 and $\pm 3/2$ were observed by Witteler *et al.* [1]. It is to be noted

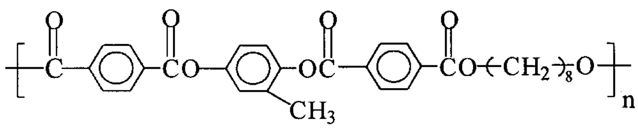
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010008205

that these three cases of surface microcrack decoration involve polymers with very rigid backbones in the main chains, that is poly(1,4-phenylene terephthalate), polyphenylene and polydiacetylene. These are the only cases yet known for very rigid main chains. However, microcrack decoration of semi-rigid main chain polymers has not yet been reported.

In the present paper, we report simultaneous occurrence of surface microcrack and band texture decoration along with the schlieren texture in the nematic state of a semi-rigid thermotropic aromatic polyester containing flexible spacers, allowing observation of a director orientation image using the polarizing optical microscope (POM). Also, the supermolecular structure and molecular director associated with the band texture formed by this polyester after pre-shearing were studied, using the decoration by sinusoidal microcracks along the pre-shearing direction.

2. Experimental

The sample used in this work is a thermotropic aromatic polyester with a flexible octamethylene spacer. The repeating unit is:



The value of $[\eta]$ is 0.37 dL g^{-1} measured for a solution in the mixed solvent phenol and 1,1,2,2-tetrachloroethane (1:1 by wt) at 30°C. The transition temperatures determined by DSC were $T_{Cr\rightarrow N} = 194$°C and $T_{N\rightarrow I} = 245$°C.

The specimen was prepared by shearing the nematic melt at 210°C followed by quenching to room temperature. The resultant specimen with a shear-induced band texture was annealed on a hot stage at 200°C for 30 min and then quenched to room temperature for observation by optical microscope (Olympus BH-2) with crossed polarizers.

3. Results and discussion

For thermotropic liquid crystalline polymers, the banding can be observed not only after the specimen has been sheared [4, 5], but also without subjection to shearing. In the latter case the specimen is annealed to let the ordered domains grow to a sufficient size and then quenched to room temperature [6, 7]. This band texture is the solidification-induced band texture, which has a band width usually of about 1 µm. Differently oriented bands in different regions of the specimen imply a nematic multi-domain texture. In fact, the band texture is an optical effect arising from alternating deviations of the molecular chain direction from an axis normal to the bands, in opposite senses for neighbouring bands. The average molecular chain direction is perpendicular to the long axes of the bands. These bands have been used to decorate the molecular director field of various types of disclinations in the specimen [8].

Figure 1 shows the POM micrograph of a specimen of the main chain thermotropic aromatic polyester with a shear-induced band texture which was annealed at 200°C and then quenched to room temperature. During annealing the shear-induced band texture in some areas of the specimen has relaxed to a multi-domain texture, while the solidification-induced band texture that appeared on quenching is clearly seen in the micrograph showing the schlieren pattern of dark core and brushes and the director field around an $S = +1$ disclination. The direction of the director should be perpendicular to the long axes of the bands. It is marvellous to observe that the surface microcracks that emerged during solidification of the specimen are exactly in the directions perpendicular to the long axes of the solidification-induced bands. This is perhaps the first example of simultaneous observation of the schlieren texture, the solidification-induced band texture and surface microcracks around the same central core of a disclination. Thus the relations between the director trajectory, the long axes of the solidification-induced bands and the microcracks are firmly established, and the surface microcracks give a direct mapping of the director field around a disclination. It is interesting to note that the microcracks were not observed in a specimen without pre-shearing even after annealing at 200°C for more than 30 min and then quenching to room temperature. Apparently pre-shearing and subsequent annealing are necessary for the appearance of surface microcracks.

An inversion wall is a defect created usually in an oriented nematic state. In fact, the wall is a manifestation of defects in an otherwise uniform director alignment. The molecular director is supposed to turn through an angle of 180° on going across the wall. Numerous inversion walls are easily observed in the thermotropic aromatic polyester specimen studied here, and these inversion walls are much longer than those observed in the specimen without pre-shearing. Presumably pre-shearing reduces the disclination density. Figure 2 shows POM micrographs of inversion walls decorated by solidification-induced band texture and surface microcracks in the specimen. It was found that there are two types of inversion walls—the splay and the bend types as shown in figures 2(*a*) and 2(*b*), respectively. Walls are predominantly along the pre-shearing direction. The director orientations across the wall are directly mapped by the surface microcracks perpendicular to the solidification-induced bands. In the case of figure 2(*a*), the director orientations in the close vicinity of the wall are parallel to the direction of the wall. In figure 2(*b*), one can find the director trajectories perpendicular to the direction of the wall as indicated by the arrow in the figure. Furthermore, numerous junctions of two inversion walls are found in the specimen. There are generally two kinds of junctions. One is the junction of two antiparallel walls, figure 3 (*a*); the other is the junction of two parallel walls, as indicated by the arrow in figure 3 (*b*).

Figure 4 is a POM micrograph of a disclination of strength $S = -1$ decorated by surface microcracks and solidification-induced band texture. This type of disclination is rarely observed in liquid crystalline polymers. As we know, disclinations tend to exist in pairs with neighbouring disclinations having opposite signs to decrease the elastic distortion energy. Figures 5 and 6 show typical paired disclinations of $S = (+1/2, -1/2)$ and $S = (+1, -1)$, respectively, with their corresponding director fields.

As mentioned earlier, the relaxation of the shear-induced band texture formed after pre-shearing to the multi-domain texture during annealing was not always complete; in some parts of the specimen the shear-induced band texture remained after annealing, as shown

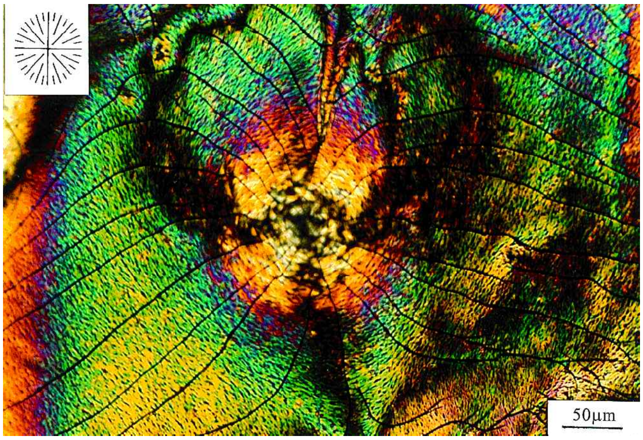


Figure 1. Director field of disclination of strength $S = +1$, $\phi_0 = 0$ decorated simultaneously by surface microcracks and solidification-induced band texture in the aromatic polyester observed by POM.

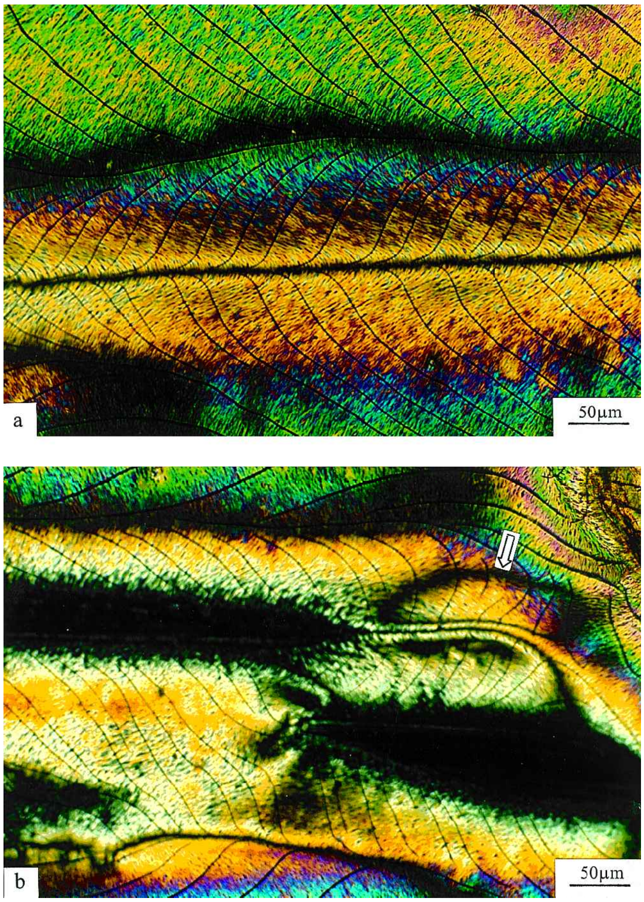


Figure 2. Two types of inversion walls observed simultaneously in the aromatic polyester by surface microcracks and solidification-induced band texture—see the text.

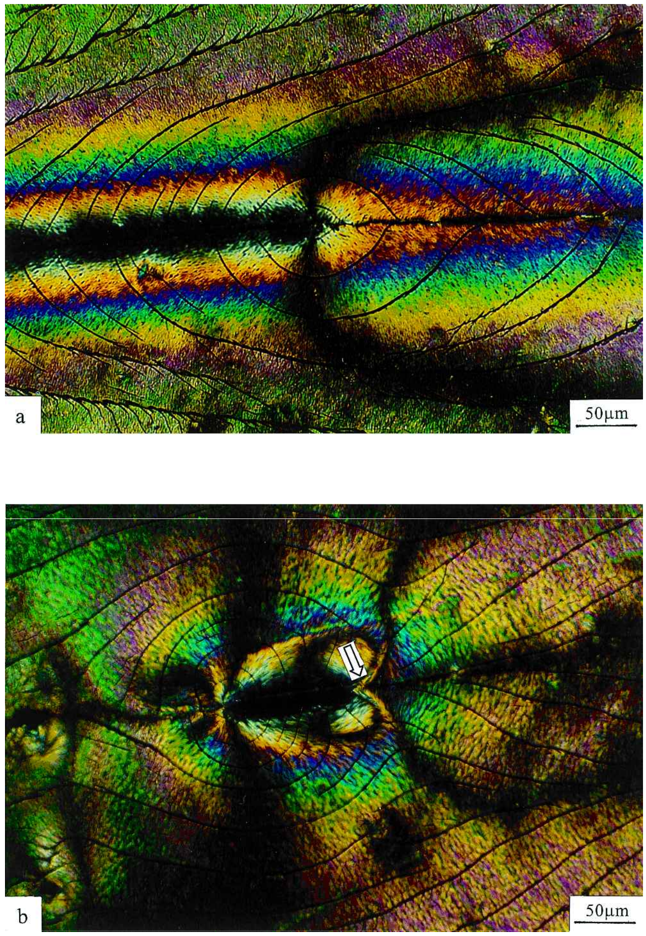


Figure 3. POM micrographs of the junctions of (*a*) two antiparallel inversion walls and (*b*) two parallel inversion walls (as indicated by the arrows) decorated simultaneously by surface microcracks and solidification-induced band texture in the aromatic polyester.

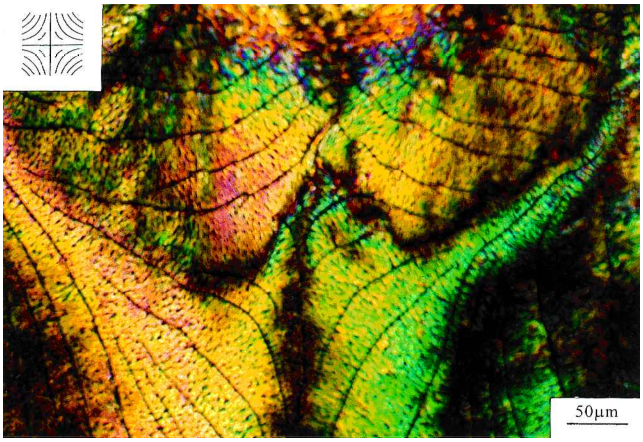


Figure 4. POM micrograph of a disclination of strength $S = -1$ decorated simultaneously by surface microcracks and solidification-induced band texture in the aromatic polyester.

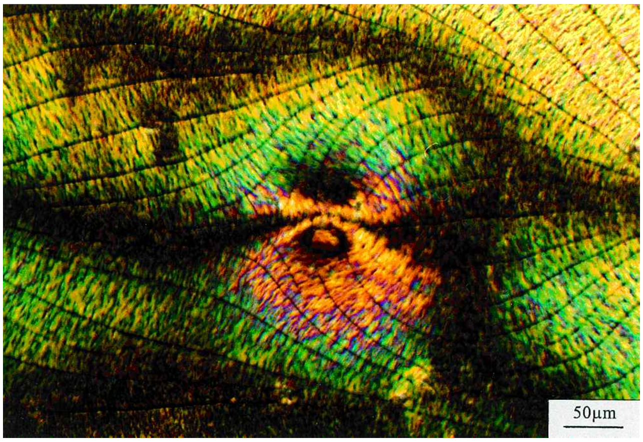


Figure 5. A pair of disclinations of $S = +1/2$ and $-1/2$ as observed by POM through surface microcracks and solidification-induced band texture decoration in the aromatic polyester.

in figure 7. The spacing of the bands is about 20 μm, approximately the same as the original value before annealing. It was found that the contrast ratio of the band texture was strongly dependent on the relative angle between the shearing and polarizer directions of the crossed polarizers. It is interesting to note that the bands appear in pairs and the number of bands changes with rotation of the sample with respect to the crossed polarizers. When the specimen is rotated about 28° clockwise from the shearing direction, the width of the bands is double that before rotation. Figure 7 shows the extinction behaviour described above for the band texture of the present polyester. According to the theoretical birefringence images for the sinusoidal model calculated by Ding *et al.* [9], the supermolecular structure associated

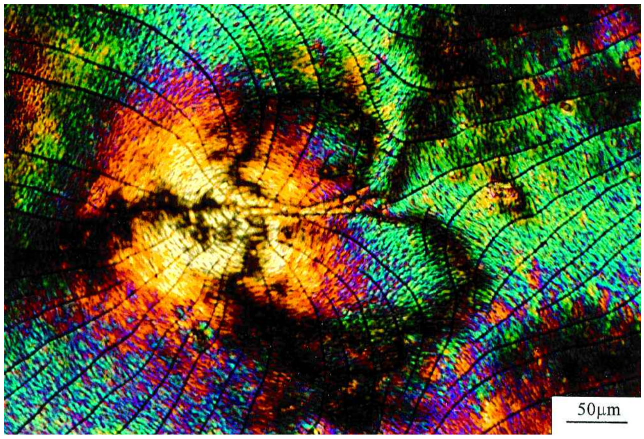


Figure 6. A pair of disclinations of $S = +1$ and -1 as observed by POM through surface microcracks and solidification-induced band texture decoration in the aromatic polyester.

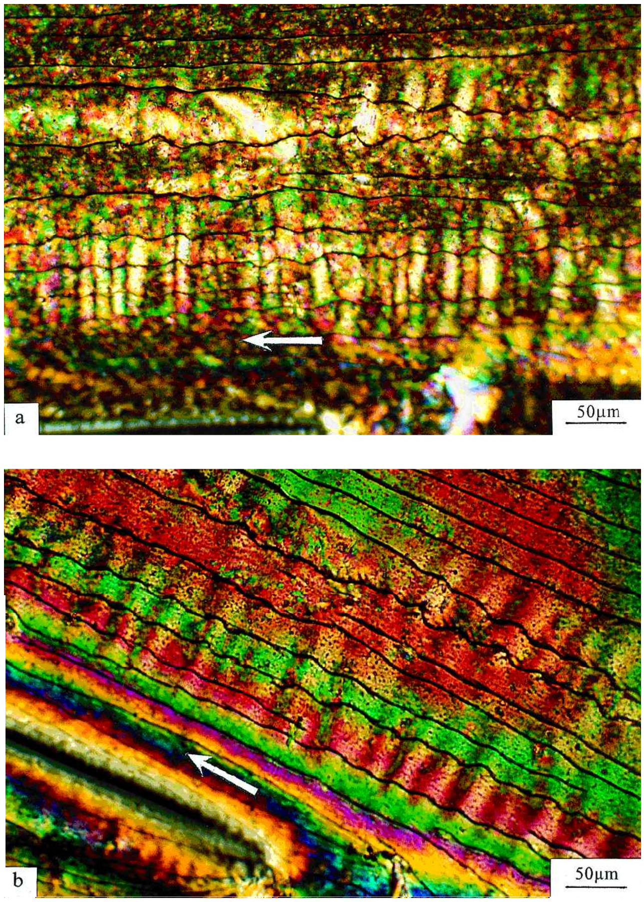


Figure 7. POM micrographs of the aromatic polyester film with the shear-induced band texture annealed at a temperature of 200°C and then quenched to room temperature. (*a*) The pre-shearing direction along the polarizer direction; (*b*) the specimen has been rotated about 28° clockwise from the polarizer direction. Arrows in the figure indicate the pre-shearing direction.

with the shear-induced band texture in the specimen is sinusoidal. The maximum angular divergence between the director and the shearing direction is about 28°. The surface microcracks actually show the sinusoidal chain structure in the shear-induced bands.

This work was supported by the National Key Project of Fundamental Research—'Macromolecular Condensed State', Ministry of Science and Technology, PR China.

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