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Banded texture decoration of disclinations in a main chain thermotropic aromatic copolyester observed by optical microscopy

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A new method for the study of texture and director patterns in a main chain thermotropic aromatic copolyester with a flexible spacer is described, whereby the molecular chain or director orientation of the nematic mesophase becomes decorated by the formation of a banded texture during quenching, without being subjected to a shear. The pattern of the decorated banded texture may be observed directly by polarizing optical microscopy, revealing the complete texture of molecular chain orientation across the whole specimen. The molecular director orientation lies perpendicular to the long axis of the bands. Various types of disclination, including an inversion wall, in the nematic mesophase of a thermotropic aromatic copolyester have been observed. This decorating technique is particularly suited for non-crystallizable main chain liquid crystalline polymers, where the lamellar decoration technique fails.

The texture of a thin layer of a liquid crystalline polymer (LCP) is produced by disclinations present in the mesophase and is characteristic of different mesophases. For a nematic mesophase, the most common feature in the texture is the occurrence of disclinations and inversion walls [1]. The schlieren texture as observed by polarizing optical microscopy (POM) takes the form of two and four extinguished brushes emanating from a central point and corresponding to disclination strengths of $s = \pm 1/2$ and $s = \pm 1$ respectively. The orientation of the macromolecular chain in the thermotropic liquid crystalline state of a polymer can be frozen in its glassy state and annealing of the frozen glassy state under suitable conditions can lead to lamellar crystallization. This technique of lamellar decoration to explore the orientation of crystalline polymer chains by transmission electron microscopy (TEM) was first used by Wood and Thomas [2–4] to show the singularities in the chain orientation around the disclinations of $s = \pm 1/2$ in the frozen nematic state of an aromatic copolyester. Recent studies of Ford [5] and Dong [6] have also used the technique to reveal the disclination strength $s = \pm 1/2$ in the bulk specimen of a main chain liquid crystalline polymer by scanning electron microscopy (SEM). In a previous paper we have reported [7] that in addition to disclinations of $s = \pm 1/2$, disclinations of $s = \pm 1$ have also been examined by TEM using the combined technique of lamellar decoration and ruthenium tetroxide staining for the frozen nematic state of an aromatic copolyester with a flexible spacer. All the above results are limited to a very local picture of the molecular organization representative of the liquid crystalline state. In the present communication, we shall describe a new technique to reveal the complete molecular

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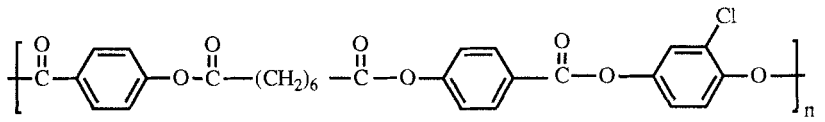
director pattern across the whole sample in the optical polarizing microscopic field of view by banded texture decoration. So far as we are aware, this is the first time that banded texture decoration has been used to show the disclinations in the nematic state of LCPs by POM. This technique of banded texture decoration not only saves a lot of trouble in preparing specimens for TEM observation, but also avoids the possibility of damage by the electron beam. It is particularly suited to observing the disclinations in the nematic mesophases of non-crystalline main chain LCPs, where the lamellar decoration technique fails.

The LCP used in this work was an aromatic copolyester with a flexible hexamethylene spacer. The synthesis has been described elsewhere [8]. The chemical constitution of the molecular chain is



The inherent viscosity of a 0·5 g dl^{-1} solution of the polymer in 50/50 (w/w) phenol/1,1,2,2-tetrachloroethane at 30°C was 0·52 dl g^{-1}. The transition temperature to the nematic mesophase was 148°C measured by DSC. No clearing temperature could be observed before the onset of decomposition. The polymer sample was dissolved in a 40/60 (w/w) mixture of phenol/1,1,2,2-tetrachloroethane to obtain a 1 wt% solution. A few drops of the solution were dropped on to a glass slide preheated and maintained at a constant temperature of 180°C. When the solvent had evaporated at this temperature, a thin polymer film of *c.* 10 μm thickness was obtained. Then the polymer film was transferred on to another hot-stage maintained at a constant temperature of 250°C for annealing for 10 min to induce the growth of domains of ordered molecular chains [9]. Subsequently, the polymer sample was quenched to room temperature to form the banded texture. The texture formed was observed using an Olympus Model BH-2 polarizing optical microscope.

The formation of banded textures after shearing is nearly ubiquitous for both lyotropic and thermotropic main chain liquid crystalline polymers. For main chain thermotropic aromatic copolyesters, the banded texture can be observed not only after shearing [9, 10], but also during quenching from the nematic state [11, 12]. In both cases, these bands have a width of the order of microns, and they can be observed easily by POM. The nematic phase of a thermotropic aromatic polyester exhibits a schlieren texture between crossed polarizers. As the temperature of the nematic melt was increased, neighbouring disclinations of opposite sign in their disclination strength interact and merge to form new disclinations. As the ordered domain size grows and reaches a sufficient size, the banded texture developed during air quenching [11]. This banded texture, as seen by POM between crossed polarizers, is an optical effect of slight alternating deviations of the molecular chain direction from a fibre axis normal to the bands, in opposite senses for the neighbouring bands. The average of the molecular chain direction, for example the average director **n** orientation in the bands, is perpendicular to the long axis of the bands as shown in figure 1 for the copolyester studied.

Figure 2 (*a*) shows the banded texture-decorated POM picture of the disclinations of $s = +1/2$. The abrupt changes in molecular chain orientation around the point of disclination can be clearly seen. The width of the bands is *c.* 1 μm. The director orientation was mapped in figure 2 (*b*) by constructing sets of lines perpendicular to the long axes of the bands. A similar texture of the disclination of $s = -1/2$ is shown in

figure 3. Disclinations of $s = \pm 1/2$ are fairly stable defects and are the ones most commonly observed.

Shown in figure 4 are three disclinations of $s = +1$. This type of disclination can exhibit three different types of director orientation, i.e. different angles of $c = 0$, $c = \pi/2$ and $c = \pi/4$ between the orientation axis of the molecular director and the main optical axis. The mapped director orientations are sketched in the cuts of the figure. The disclination of $s = -1$ has not yet been observed.

It is known that an isolated disclination would lead to an infinite strain energy. Consequently every disclination interacts and is connected with its neighbouring disclination of opposite sign in disclination strength, so that disclinations exist usually in pairs. Figure 5 and 6 demonstrate such pairs of disclinations with $s = +1/2$ and $s = -1/2$, as well as $s = +1$ and $s = -1/2$, respectively. These are comparatively stable textural features for a nematic state. The total sum of the disclination strengths in a system should be zero.

The observations described above offer an important clue in our understanding of the nature of the nematic texture. The banded texture decoration technique provides a direct visualization of the relationship between the schlieren texture and the disclinations in a nematic mesophase. Shown in figure 7 is the banded texture-decorated POM picture of the disclinations present in the aromatic copolyester studied in the film frozen from its nematic state. It is clear that the disclinations decorated by banded texture also cover localities displaying schlieren brushes. When all locations, where the director orientation coincides with the polarizer or the analyser directions of the POM, the four or two brushes are shown with a nucleus. It is obvious that when the crossed polarizer and analyser are rotated, the shape and positions of the dark brushes will change, but the nucleus (dark centre point) of the disclination will remain stationary. Therefore the schlieren texture usually observed by POM for a nematic LCP is really an optical effect of the disclinations [13].

An inversion wall is created as a line defect in which the molecular director is supposed to turn through an angle π across the defect. Figure 8 (*a*) shows the banded texture-decorated POM picture of an inversion wall in the nematic phase of the thermotropic aromatic polyester studied. The molecular directors are mapped in figure 8 (*b*). The curvature of the director orientation as the wall is approached will depend on the elastic constants of the material [5].

We would like to thank Professor Q. X. Zhou for the LC copolyester sample. This work was supported by National Basic Research Project–Macromolecular Condensed State.

Figure 1. POM micrograph of banded texture formed after shearing the nematic mesophase of the aromatic copolyester, (*a*) crossed polarizer and (*b*) average molecular director orientation *n*.

Figure 2. Banded texture decorated POM micrograph of disclination strength $s = +1/2$, (*a*) crossed polarizers and (*b*) mapped molecular chain or director orientations.

Figure 3. Banded texture decorated POM micrograph of disclination strength $s = -1/2$, (*a*) crossed polarizers and (*b*) mapped molecular director orientations.

Figure 4. Banded texture decorated POM micrographs of three disclinations of strength $s = +1$, crossed polarizers and corresponding mapped molecular director orientations, (*a*) $s = +1$, $c = 0$; (*b*) $s = +1$, $c = \pi/2$; (*c*) $s = +1$, $c = \pi/4$.

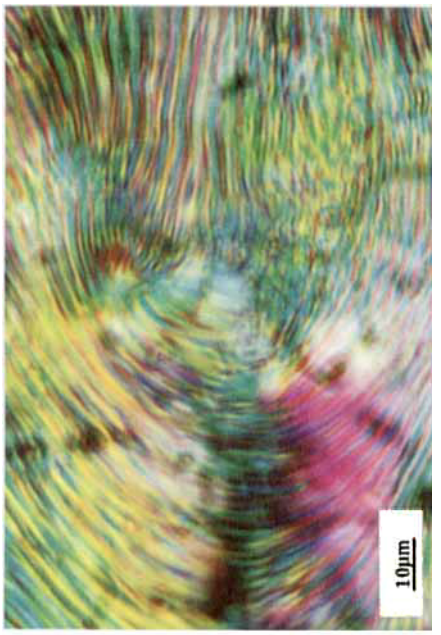


Figure 2 (*a*)

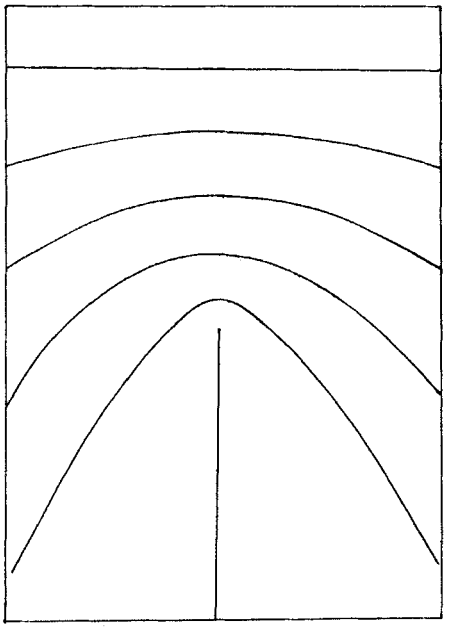


Figure 2 (*b*)

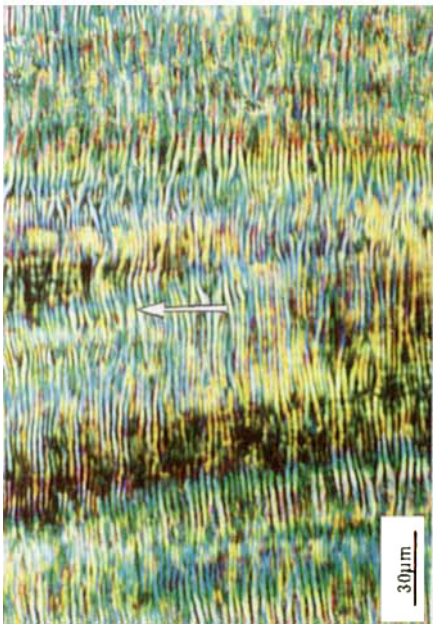


Figure 1 (*a*)

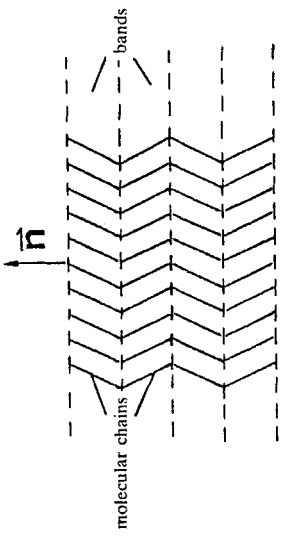


Figure 1 (*b*)

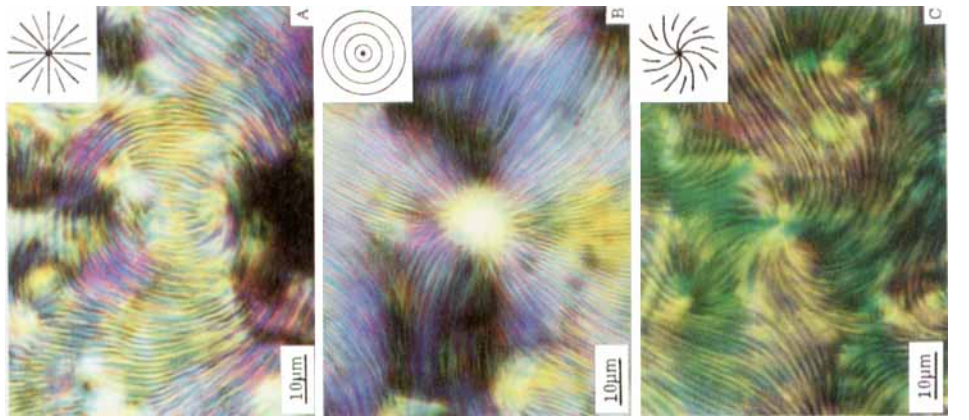


Figure 4 (*a, b, c*)

Figure 3 (*a*)

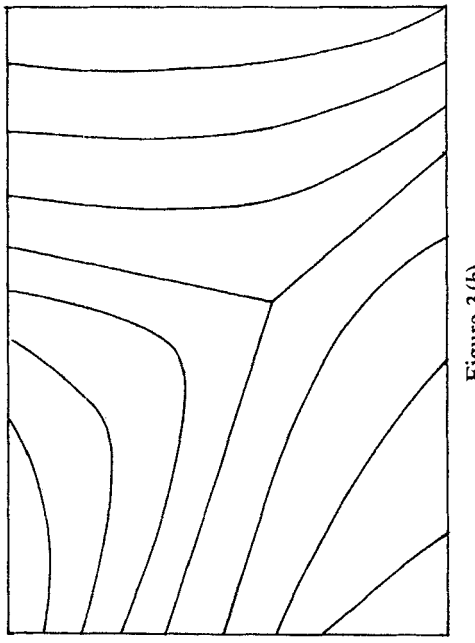


Figure 3 (*b*)

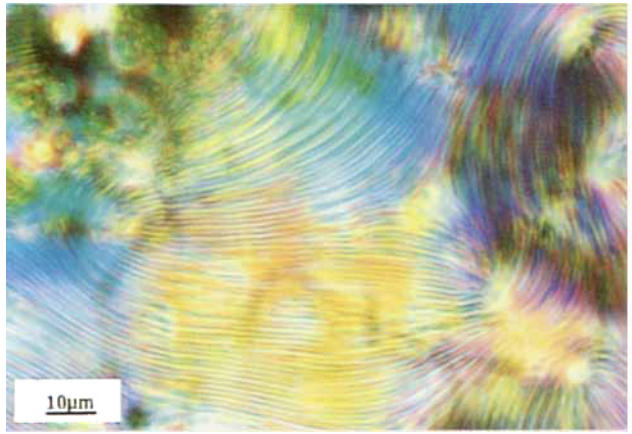


Figure 5 (*a*)

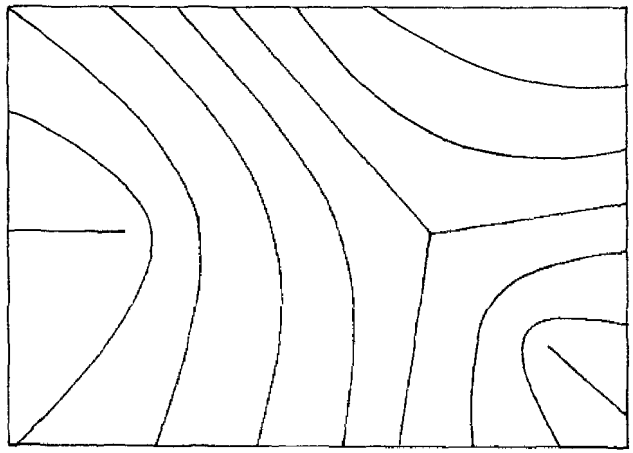


Figure 5 (*b*)

Figure 5. Banded texture decorated POM micrograph of a pair of disclinations $s=+1/2$ and $s=-1/2$, (*a*) crossed polarizers and (*b*) mapped molecular director orientations.

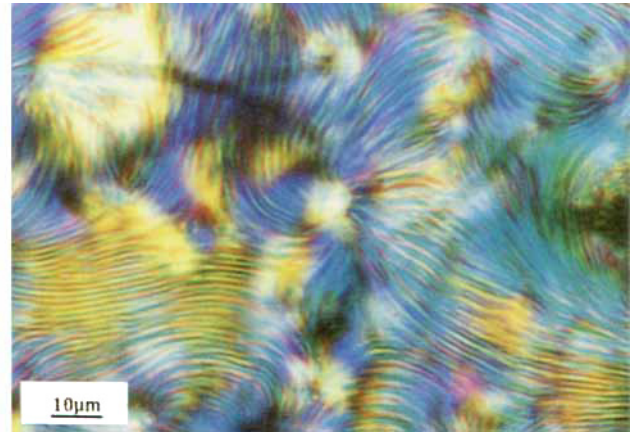


Figure 6

Figure 6. Banded texture decorated POM micrograph of a pair of disclinations $s=+1$ and $s=-1/2$, crossed polarizers.

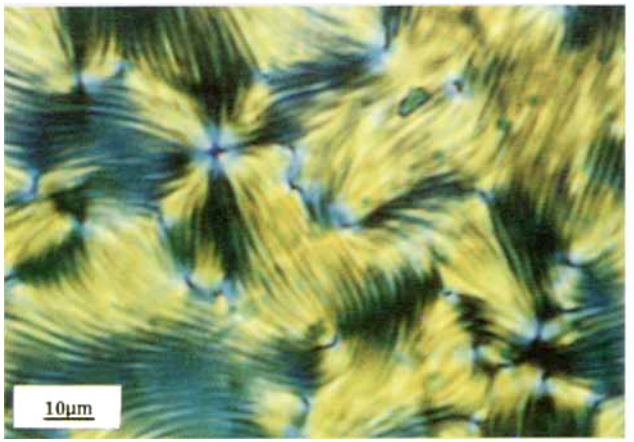


Figure 7

Figure 8(*a*)

Figure 7. POM micrograph showing both schlieren texture and banded texture-decorated disclinations.

Figure 8. Banded texture-decorated POM micrograph of an inversion wall, (*a*) crossed polarizers and (*b*) mapped molecular director orientations.

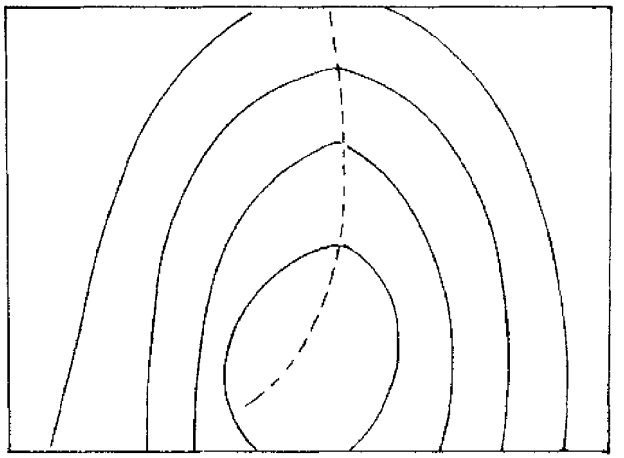


Figure 8(*b*)

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