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Direct decoration of disclinations by solidification-induced band texture for a nematic side chain liquid crystalline polymer

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For a nematic polymethacrylate side chain liquid crystalline polymer, g 154 N 298 I (°C), the solidification-induced band texture has been observed aligned along the disclination under a polarizing optical microscope, when the specimen was quenched from 280°C to room temperature. The decoration technique of solidification-induced band texture, which is usually reported for main chain liquid crystalline polymers, was then introduced to reveal the director field pattern along a disclination for this side chain liquid crystalline polymer. It was found by infra-red dichroism measurements that the director orientation is parallel with the direction of the band. On this basis, disclinations with strength $s = \pm 1/2$ and $s = \pm 1$ were mapped according to the corresponding pattern of solidification-induced band texture. In addition, two types of inversion wall, loop-like and splay-type walls, were also found to be decorated by the solidification-induced band texture.

1. Introduction

For main chain liquid crystalline polymers (MCLCPs) several decoration techniques have been developed to reveal the director field along a disclination, such as the lamellar decoration [1, 2], the solidification-induced band texture decoration [3, 4] and the surface microcrack decoration [5–7]. By contrast, few decoration techniques have been reported for side chain liquid crystalline polymers (SCLCPs). The reasons for this are: (a) SCLCPs are usually amorphous and, therefore, lamellar decoration cannot be considered; (b) although band texture can usually be observed in both lyotropic [8–12] and thermotropic main chain liquid crystalline polymers [13–15], the properties of SCLCPs are similar to those of low molar mass liquid crystals (LMMLCs) and so the band texture is rarely seen in SCLCPs; (c) surface microcracks usually appear in nematic polymers with highly rigid chains when the nematic melt of a thermotropic liquid crystalline polymer is frozen rapidly [5, 16], but for SCLCPs the backbone is usually flexible and it is difficult to form microcracks. Therefore, the literature describing the observation of director fields of disclinations by decoration methods is mainly limited to MCLCPs and not to of SCLCPs except for the report of the focal-conic texture decoration method proposed by Hu *et al.* [17] In the work of Hu *et al.*, the polyacrylate SCLCP studied shows two mesophases, namely, smectic and nematic. When the specimen is in the temperature range of the nematic mesophase, a typical schlieren texture can be observed under polarizing optical microscopy (POM). Once the temperature is decreased to the nematic-to-smectic, transition temperature the focal-conic texture of the smectic mesophase starts to grow gradually around the corresponding schlieren texture core, taking the existing defects as template, and therefore the focal-conic texture decoration can be utilized to reveal the director field around disclinations for the studied SCLCP.

In the present work, the solidification-induced band texture was found to occur along with the nematic schlieren texture when the polymethacrylate SCLCP studied was quenched from the nematic melt to room temperature. Therefore, along with the focal-conic texture decoration, the decoration technique of solidification-induced band texture can also be used to reveal the director field of a SCLCP, which is very important in the study of disclinations in SCLCPs. As far as we know, the solidification-induced band texture has only

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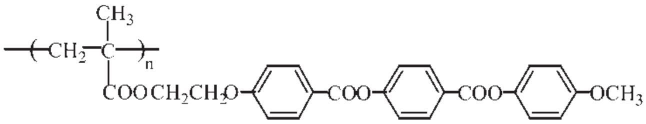
been observed in a few MCLCPs [3, 4, 6, 18, 19] and not previously found in nematic SCLCPs.

2. Experimental

The polymer studied in this work was a thermotropic polymethacrylate with mesogens consisting of three benzene rings attached longitudinally to the backbone through a short flexible spacer,



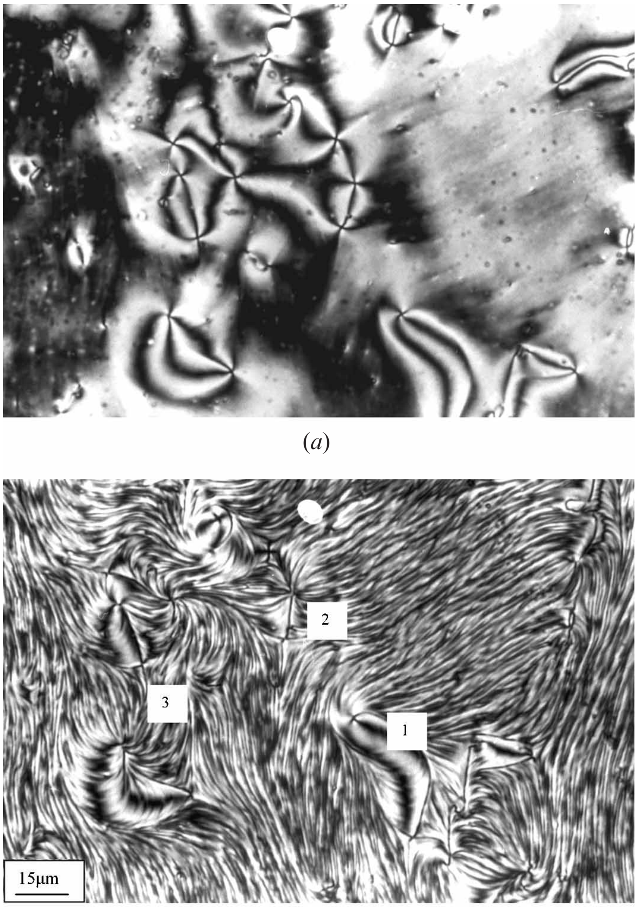
The polymer was denoted PMA-2-TP. Its apparent number average molecular weight was 3.2×10^4 measured by GPC (PL-GPC 210 model) with tetrahydrofuran as solvent and polystyrene as standard samples for calibration. PMA-2-TP showed a glassy-to-nematic transition temperature ($T_{\mathrm{g\ N}}$) at 154°C and a nematic-to-isotropic transition temperature ($T_{\mathrm{N\ I}}$) at 298°C determined using differential scanning calorimetry (Perkin-Elmer DSC-7).

To prepare the film specimens containing the solidification-induced band texture, the powder sample was first pressed into a thin film between two glass slides at 280°C and held for 4 min. Then the film specimen was quenched to room temperature as rapidly as possible. The observation of solidification-induced band texture was carried out by polarizing optical microscopy (POM), using an Olympus BH-2 model, equipped with a Mettler FP-52 hot stage and an automatic camera.

To prepare highly-oriented specimens for infrared dichroism measurements, the polymer melt was mounted between two KBr single crystal slides and sheared by hand at 280°C on a hot stage. The oriented film was then annealed at the same temperature for 2 min to relax the orientation partially and the film subsequently quenched in air. The infrared dichroism measurements were performed on a Bruker IFS-113V Fourier transform IR spectrometer at a spectral resolution of $2\,\mathrm{cm}^{-1}$.

3. Results and discussion

As shown in figure 1 (*a*), a typical schlieren texture containing four brushes was observed clearly under POM when the PMA-2-TP specimen was annealed at 280°C. After annealing for about 4 min the specimen was cooled to room temperature as rapidly as possible, and the solidification-induced band texture was then found along with the schlieren texture under POM, as shown in figure 1 (*b*). The width of the band was about 1 μm. To our knowledge, this is the first time that a SCLCP has been reported to form a solidification-induced band texture. It can be seen clearly from figure 1 (*b*) that the morphological patterns of the solidification-induced band texture around the schlieren 1, 2 and 3 differ considerably from each other, indicating a different type of disclination. This indicates that the disclinations in the PMA-2-TP nematic mesophase can be revealed by the morphological pattern of the solidification-induced band texture, which is a decoration technique developed in MCLCPs. Solidification-induced band texture has been described as a crystallization-induced band texture by Hoff *et al.* because crystallization is thought to be the source of its formation [4]. By contrast, Chen *et al.* termed a similar band texture as solidification-induced since they found that it could also be formed in the frozen amorphous state of an aromatic copolyester [3, 18]. Presently, the designation solidification-induced band texture is thought to be more universal.



(*a*)

(*b*)

Figure 1. POM micrographs of the same region of (*a*) nematic schlieren texture at 280°C and (*b*) the corresponding solidification-induced band texture formed after quenching to room temperature.

It must be mentioned here that the properties of SCLCPs are usually considered to be similar to those of low molar mass liquid crystals and that band texture is hardly formed in SCLCPs. Why is solidification-induced band texture observed in PMA-2-TP? We suggest that the conformation of the flexible backbone of PMA-2-TP is mainly influenced by the rigid side chains containing three phenylene rings. For a monomeric unit of PMA-2-TP, the rigid side chain is much longer than the flexible backbone unit; therefore the influence of the side chain on the backbone is very significant and makes the backbone more rigid. Thus the properties of PMA-2-TP are more similar to those of MCLCPs than to those of LMMLCs and solidification-induced band texture can therefore be formed in PMA-2-TP. Thus, band texture can be obtained not only in MCLCPs but also in SCLCPs if the SCLCP backbone is sufficiently rigid in nature.

As discussed already, the director field around a disclination can be revealed by the morphological pattern of the solidification-induced band texture for PMA-2-TP. But in order to map the director field orientation and determine the type of a disclination, the direction relationship between the mesogen and the band texture must be ascertained. Infrared dichroism measurements are thought to be an effective means of confirming the direction relationship between them [17, 19]. Uniformly oriented specimens for IR dichroism measurements are obtained by shearing the specimen in the melt between two KBr single crystal slides at 280°C. Figure 2 shows POM micrographs of the shear-induced band texture formed in PMA-2-TP. The arrow represents the shearing direction. It should be noted here that in order to form shear-induced band texture the sheared sample must be held at 280°C for 2 min and then quenched to room temperature. If the sample is quenched directly to room temperature after the cessation of shearing the shear-induced band texture cannot be formed. It is well known that the formation of the shear-induced band texture is due to relaxation of the oriented molecules after the cessation of shearing. For a given polymer, the relaxation rate depends mainly on temperature. The relaxation rate for PMA-2-TP, is too slow at room temperature to form the band texture. Annealing at a higher temperature is thought to be a better method to accelerate the relaxation process and then the band texture can be formed. It is important to choose an appropriate annealing temperature and time to avoid complete relaxation of oriented macromolecular chains.

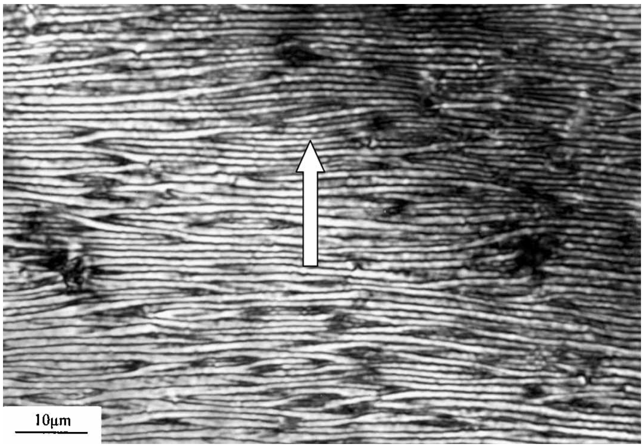


Figure 2. POM micrographs of the shear-induced band texture; the arrow indicates the shearing direction.

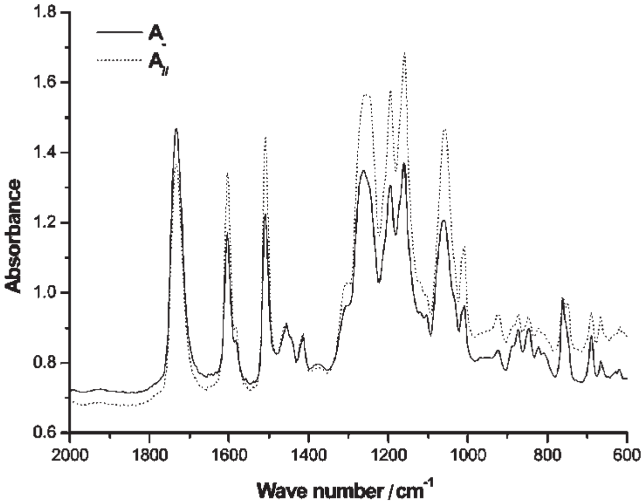


Figure 3. Polarized IR spectra of the oriented region shown in figure 2.

The polarized IR spectra for the shear-induced band texture of figure 2 is shown in figure 3, where $A_{\|}$ and $A_{\perp}$ denote absorbance parallel to and perpendicular to the band direction. It can be seen from figure 3 that the oriented film shows distinct IR dichroism. The main characteristic absorption bands are given in the table. The C–O–C stretching bands at 1059, 1159, 1194 and

Table. Some IR absorption band assignments and values of their dichroic ratios for PMA-2-TP.

Band/cm^{-1}	Tentative assignment	$R = A_{\|}/A_{\perp}$
690	Out-of-plane phenylene ring bending	<1
762	Out of plane phenylene ring C–H bending	<1
1059	C–O–C stretching	>1
1159	C–O–C stretching	>1
1194	C–O–C stretching	>1
1263	C–O–C stretching	>1
1508	Phenylene ring stretching	>1
1605	Phenylene ring stretching	>1

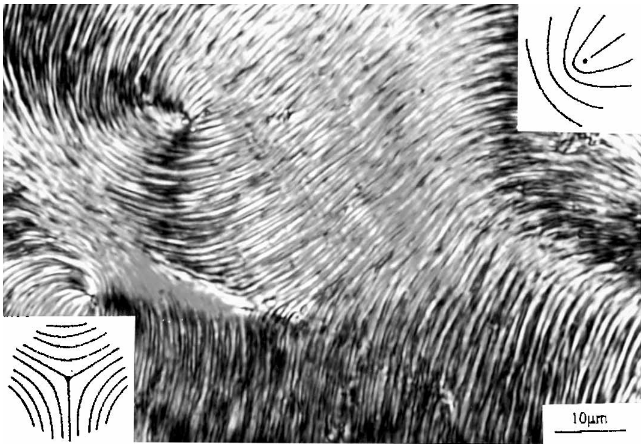
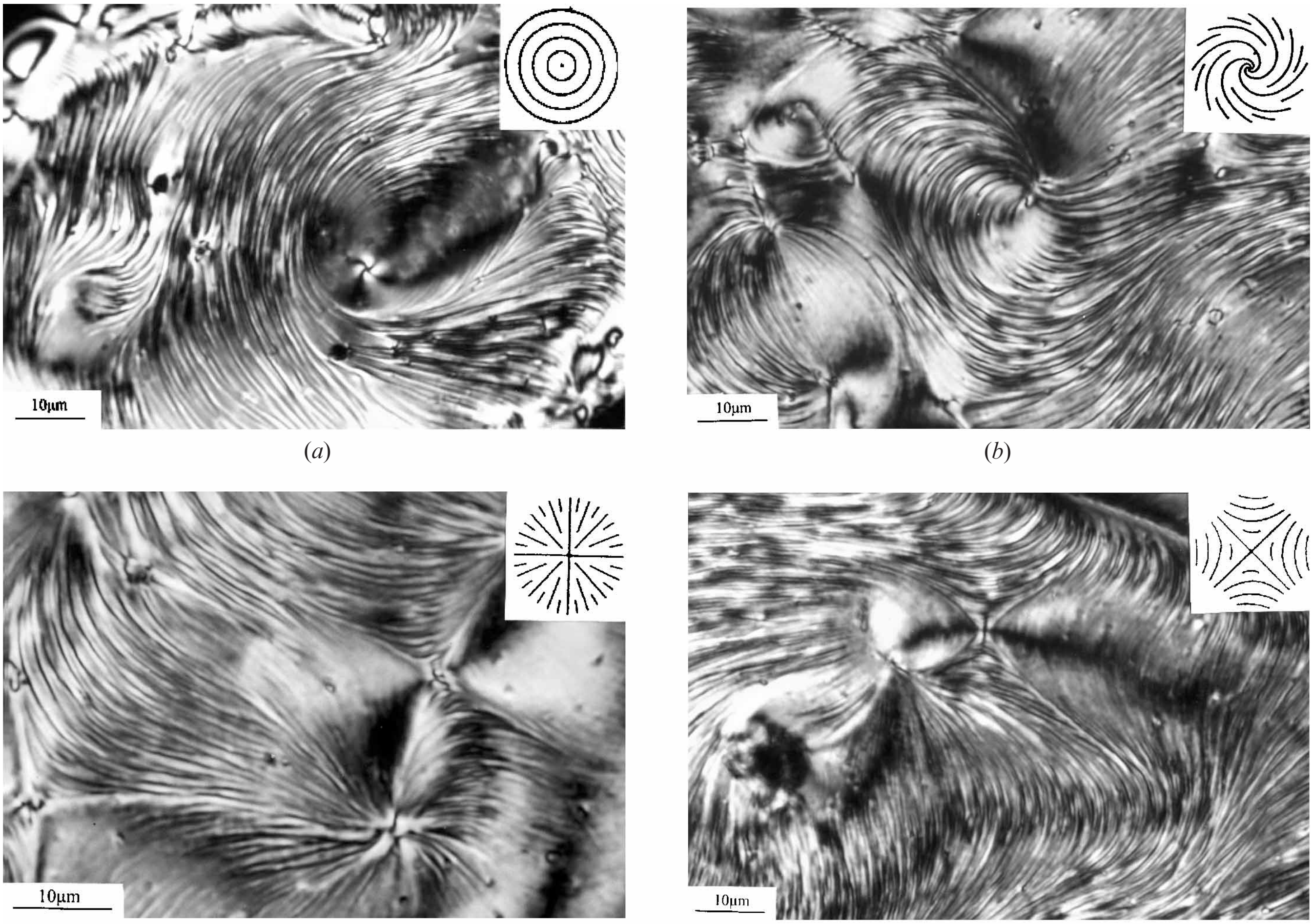


Figure 4. POM micrograph of a pair of disclinations with $s = \pm 1/2$.

1263 cm^{-1}, as well as the phenylene ring stretching bands at 1508 and 1605 cm^{-1}, exhibit distinct parallel dichroism, i.e. $A_{\|}/A_{\perp} > 1$. On the other hand, the out-of-plane vibrations of phenylene ring C–H bending and phenylene ring bending at 762 and 690 cm^{-1} exhibit perpendicular dichroism, i.e. $A_{\|}/A_{\perp} < 1$. It is well known that the C–O–C and the phenylene ring stretching vibrations have their transition moments parallel to the long axes of the mesogen. Therefore, the mesogens are arranged parallel to the band direction, which means that the orientation of the director is parallel to the direction of the band texture and perpendicular to the shearing direction. In addition, it is well known that the backbones are oriented parallel with the shearing direction and, hence, the orientation of the backbone of PMA-2-TP is perpendicular to the band direction. Therefore, the orientation of the side group is normal to the direction of the backbone in the case of shearing.

Since the direction relationship between the director and the band is now clarified, the director field around a disclination can be revealed according to the morphological pattern of the solidification-induced band



(a) (b)

(c) (d)

Figure 5. POM micrographs of disclinations with strength (a) $s = +1$, $c = 0$; (b) $s = +1$, $c = \pi/3$; (c) $s = +1$, $c = \pi/2$; (d) $s = -1$.

texture. Figure 4 shows the typical paired disclinations of $s=(+1/2, -1/2)$ decorated by such band texture. As mentioned already, the direction of the mesogens of PMA-2-TP, that is, the orientation of the director, is parallel to the direction of the band. On this basis, maps of the director field with strength $s=+1/2$ and $s=-1/2$ are shown in the top right and bottom left of the micrograph in figure 4, respectively.

As well as the line disclination with strength $s=\pm 1/2$, point disclinations with $s=\pm 1$ are also observed in PMA-2-TP. POM micrographs of the disclinations with $s=\pm 1$ decorated by solidification-induced band texture are shown in figure 5. The sketched map of the director field is illustrated in the top right corner of each micrograph. It can be seen from figure 5 that there are three types of disclination for $s=+1$, corresponding to different angles (angle c) between the orientation axis of the director and the main optical axis. The three types of disclination for $s=+1$ can be distinguished by angle c as 0, $\pi/3$ and $\pi/2$ according to the sketch map of director field: thus figure 5 (*a*) corresponds to $s=+1$, $c=0$; figure 5 (*b*) corresponds to $s=+1$, $c=\pi/3$; and figure 5 (*c*) corresponds to $s=+1$, $c=\pi/2$. The typical paired disclinations of $s=(+1, -1)$ can also be found decorated by solidification-induced band texture, as shown in figure 6.

Another special disclination decorated by solidification-induced band texture is also observed in the sample, as shown in figure 7. The sketched map of the director field in the top right corner of figure 7 is elliptic and the morphology of the band texture aligned along with the disclination is similar to the fingerprint.

Inversion walls are another kind of defect in liquid crystalline phases: two types of inversion walls are decorated by solidification-induced band texture in PMA-2-TP, namely loop-like walls, figure 8 (*a*), and splay-type walls, figure 8 (*b*). The molecular director lies in the film plane and is assumed to turn through an angle π across the singularity line in both types of wall.

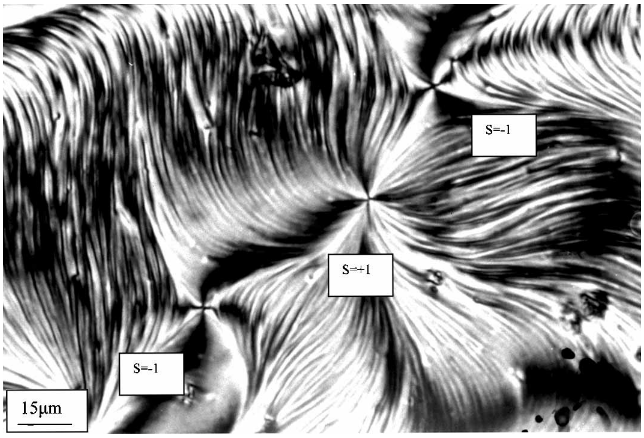


Figure 6. POM micrograph of paired disclinations with $s=\pm 1$.

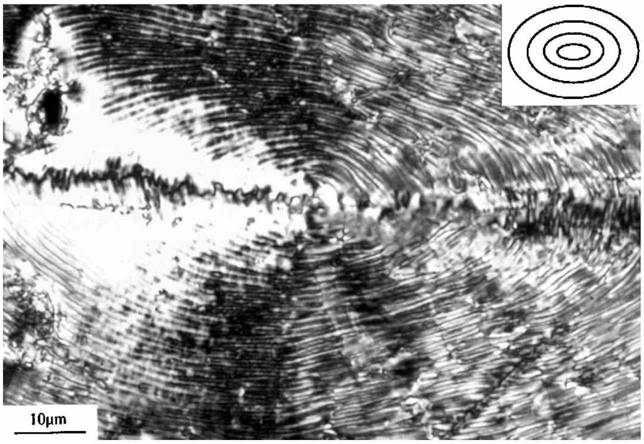
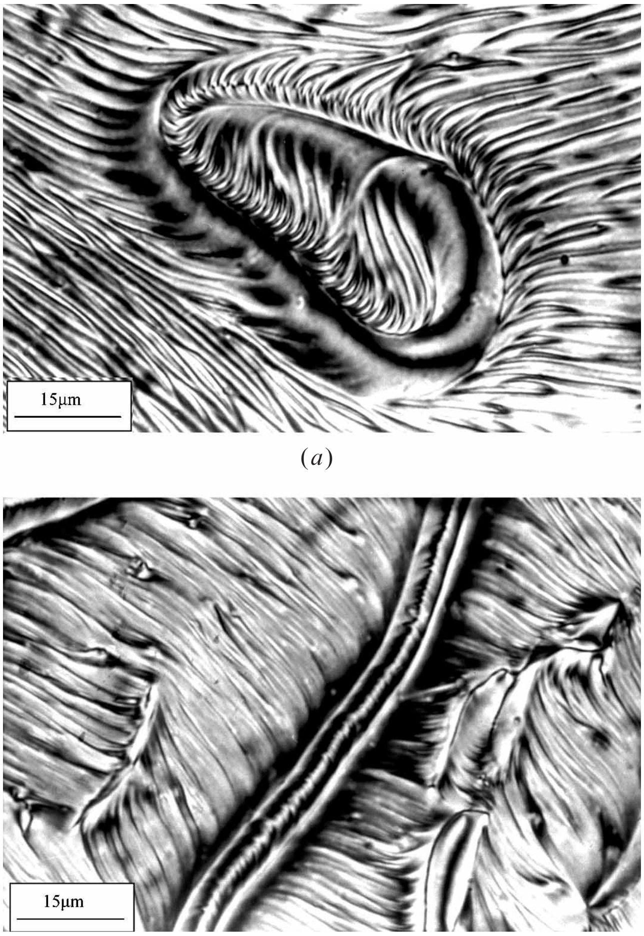


Figure 7. POM micrograph of a fingerprint-like disclination.



(*a*)

(*b*)

Figure 8. POM micrographs of two types of inversion wall decorated by solidification-induced band texture: (*a*) loop-like, (*b*) splay-like.

4. Conclusion

By quenching the SCLCP PMA-2-TP from 280°C to room temperature as rapidly as possible, solidification-induced band texture can be observed to be arranged along with the schlieren texture. The decoration technique of solidification-induced band texture, which has only previously been applied to MCLCPs, has been used to reveal the director field around disclinations of a SCLCP. Disclinations with strengths $s = \pm 1/2$ and $s = \pm 1$ are observed by this decoration technique. In addition, a special disclination with elliptic director field pattern, and two types of inversion wall, namely loop-like and splay-type walls, are also observed to be decorated by this technique.

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