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Simultaneous Observation of Disclination and Texture by Optical Microscopy of a Thermotropic Aromatic Polyester

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An aromatic copolyester (m.p.148°C) film quenched from 180°C melt showed a schlieren texture. The birefringent domains increased in size with increasing temperature of the melt before it was quenched. The polymer film quenched from the melt after being heating above 240°C for 10 min showed both disclinations and a banded texture of random orientation on the same picture, although the banded texture can not be directly observed in the heated melt. However, the banded texture of the quenched film persisted on heating to a melt up to 200°C and began to vanish above this temperature, but the banded texture reappeared on being requenched into a solid film. The banded texture could also be seen in the localities displaying brushes. Consequently schlieren brushes are optical effects but not isotropic material regions.

Keywords: optical microscopy, disclination, schlieren texture, aromatic polyester

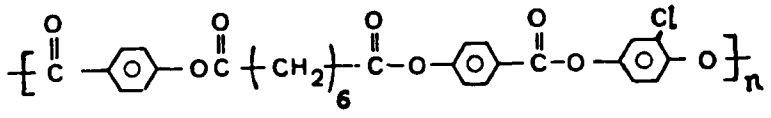
INTRODUCTION

The schlieren texture has been commonly used as a criterion of a nematic liquid crystalline state and attributed to the boundaries of nematic domains. When a nematic liquid crystalline polymer film is sheared a banded texture will develop which has been shown to be an optical effect due to periodic bending of fibrils of polymer chain aggregates at $\pm\theta$ from the direction of shear,[1,2] where θ lies in the range of 15°–30°. Thomas and his coworkers[3–5] made an important step forward to reveal the relation between disclination and texture by direct electron microscopy of an aromatic polyester using the crystalline lamellar decoration technique in which the nematic state was frozen and then annealed to result in lamellar crystallization. Disclination is a molecular aggregational defect showing the singularity in the

orientation of molecular directors, while texture shows the polymer chain orientation in whole region. In this paper we shall show that on the same polarizing optical micrograph both the disclinations and banded texture could be clearly seen.

EXPERIMENTAL

The sample used in this investigation was an aromatic copolyester containing a spacer and the substitution of the phenylene ring and having the following chemical structure:



It has a M.P. Tm = 148°C by DSC; $[\eta]$ = 52 ml/g at 25°C in phenol-1,1,2,2,-tetrachloroethane (1:1). A solution of the polymer in phenol-1,1,2,2,-tetrachloroethane (4:6) of 1 wt% was made. The solution was dropped to a glass slide held at a constant temperature of 180°C. The solvent gradually evaporated and a thin polymer film of 10 μm thickness was obtained. Such polymer films were heated above Tm and held separately at 180, 200, 220, 240 and 260°C each for 10 min and subsequently air quenched to room temperature for polarizing optical microscopy (POM). For depolarization light intensity measurement a film quenched from 180°C melt was heated at 5°C/min and the variation of depolarizing light intensity with the temperature was recorded. For scanning electron microscopy (SEM) the same procedure as above was followed to prepare the polymer film but using stainless steel plate instead of a glass slide. The films were vacuum dried for 24h to remove the residual solvents, and then they were argon-plasma-etched and a gold layer was evaporated on each film.

The polarizing microscope used was Olympus Model BH-2 and the scanning electron microscope used was Hitachi Model S-530. A laser small-angle-light scattering instrument (Model SL-1 made in this Institute) with a He-Ne laser of 6329Å was used for the observation of Hv scattering patterns of the polymer films.

RESULTS AND DISCUSSION

The polymer film obtained by quenching from 180°C melt showed between crossed polarizers a clear schlieren texture as shown in Figure 1 with singularities of four and two schlieren brushes, characterized as disclinations of $s = \pm 1$ and $s = \pm 1/2$ respectively. As the temperature of the melt was increased the quenched film showed a smaller density of disclination, while the birefringent areas (domains) between the schlieren brushes showed growth. The growth of the birefringent domains of ordered molecular chains is analogous to the growth of spherulites of usual crystalline polymers and the kinetics of growth follows the Avrami relation.[6,7]

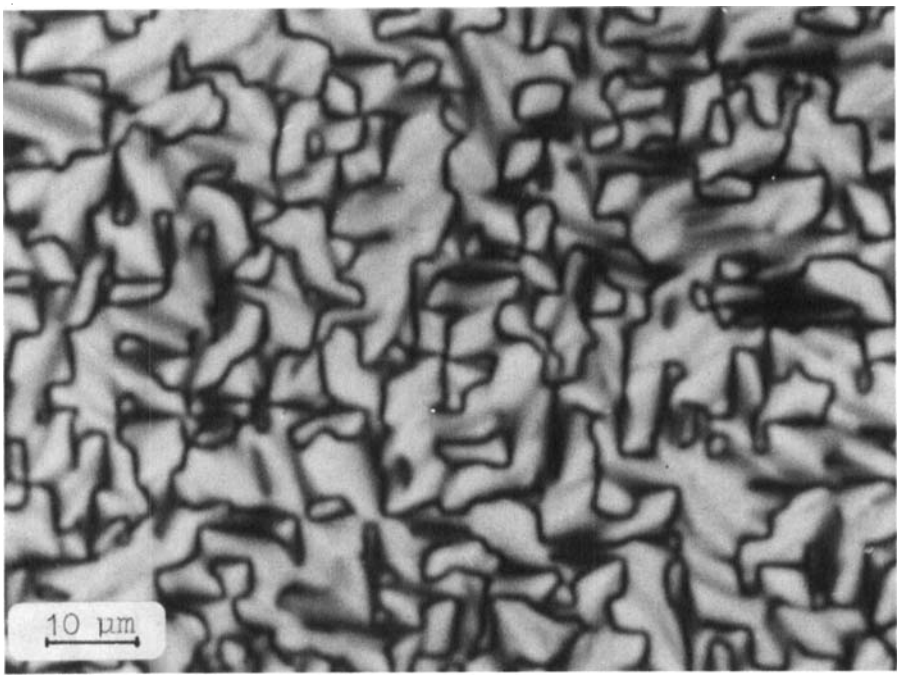


FIGURE 1 Schlieren texture of thermotropic aromatic polyester film quenched from 180°C melt, crossed polars. See Color Plate VI.

In fact this growth of ordered domains can be observed by small-angle laser light-scattering (SALS) patterns.[8] Figure 2 shows the Hv SALS patterns of the films quenched from 180, 220 and 260°C. The four-leaf Hv scattering pattern at the polarizer and analyzer directions, shrinking in scattering angles with increasing melt temperature, is clearly seen. This indicates the increasing correlation length for SALS of the ordered domains with increasing temperature of the melt. At the same time the depolarization intensity of a light beam passing through the sample film between crossed polarizers increased with temperature during heating of the film as shown in Figure 3. The increase of depolarization intensity means the growth of the ordered nematic domains which started at 176°C and showed two steps with a small plateau between 185–200°C and finally approaching a limited value above 240°C. The meaning of the appearance of a small plateau is not clear at the moment. The film quenched from 10 min heating of the melt at a temperature higher than 240°C showed both the disclinations and banded texture of random orientation on the same POM photograph as shown in Figure 4. The banded texture however, can not be directly observed in the heated melt. Apparently the banded texture developed during quenching. Once the banded texture developed in the quenched film, the banded texture persisted on heating to a melt up to 200°C. Two pictures of Figure 4 were taken at the same position of the quenched film but at two different

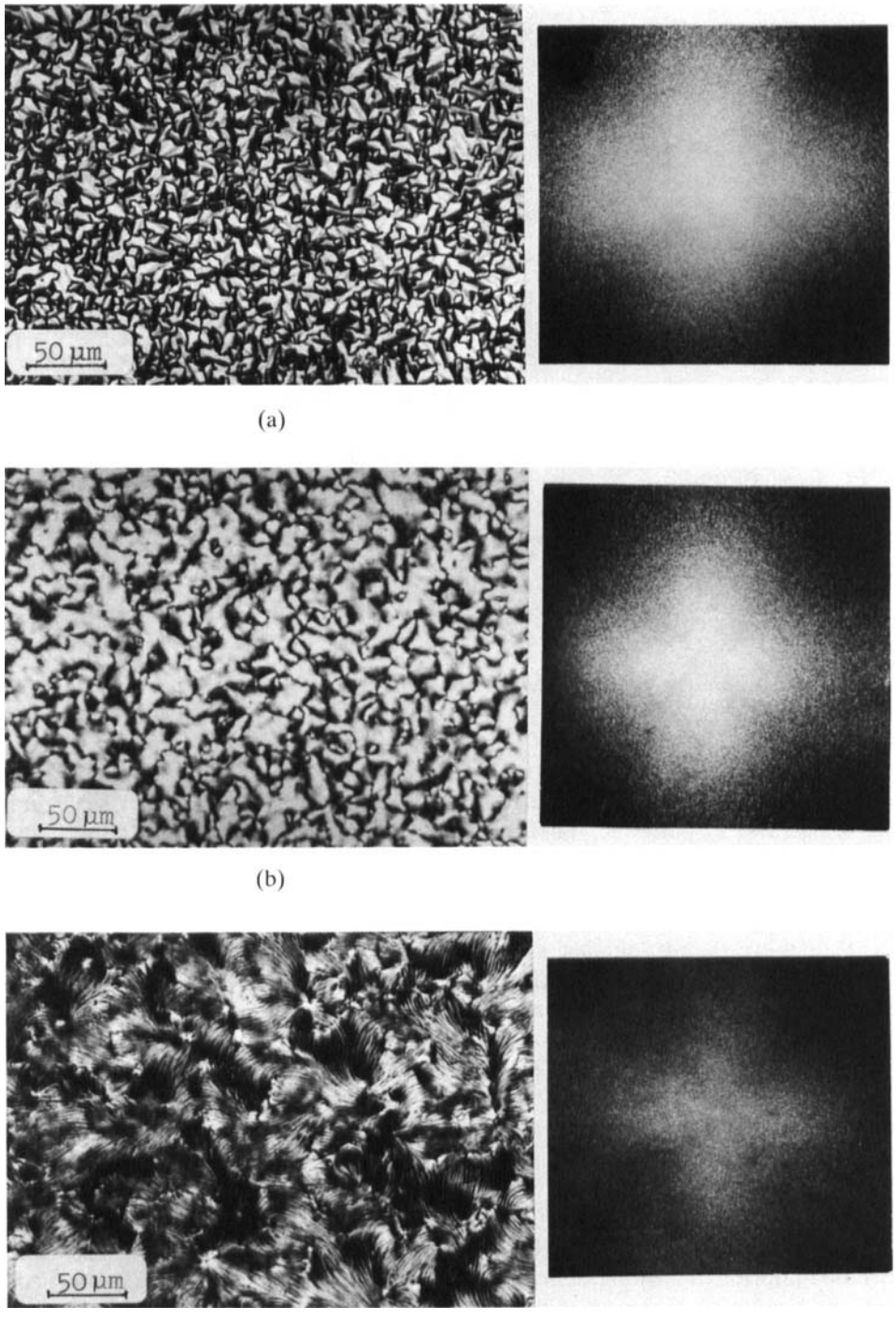


FIGURE 2 Optical polarizing micrographs and corresponding Hv small-angle-light-scattering patterns of the films quenched from the melt at different temperatures, a) 180°C; b) 200°C; c) 260°C, crossed polars.

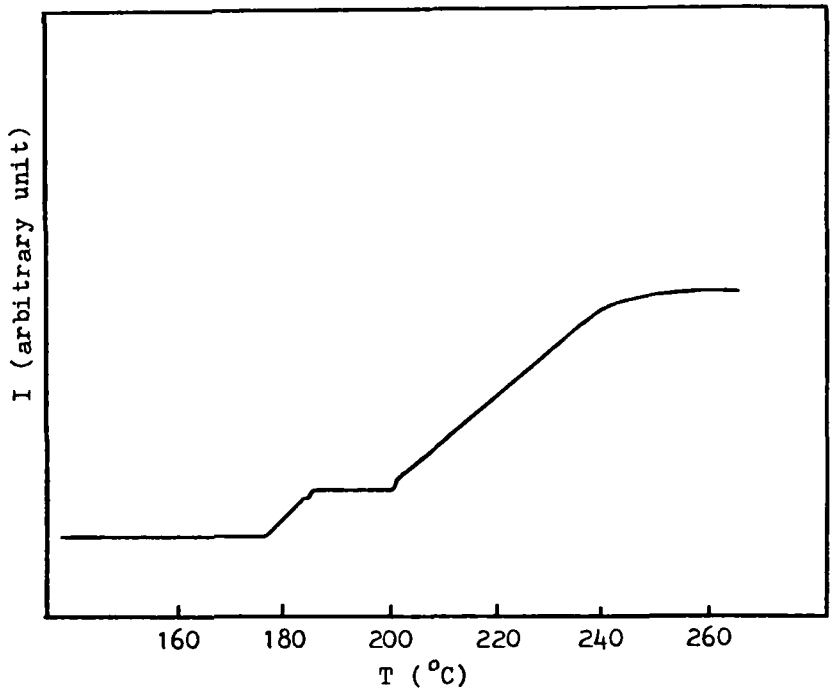


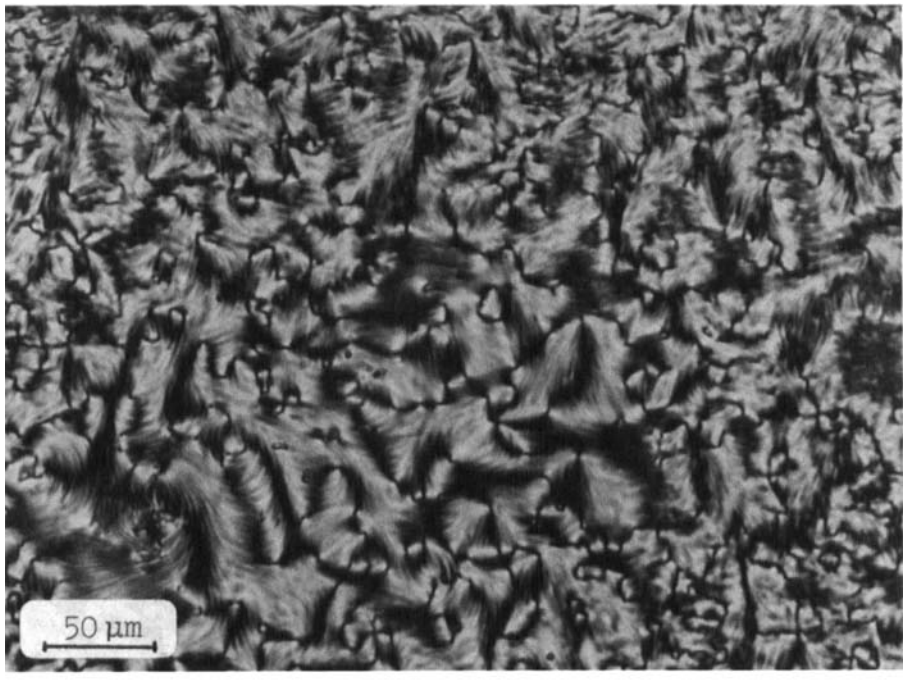
FIGURE 3 Variation of the depolarization intensity of a light beam passing through the sample film between crossed polarizers during heating at 5°C/min.

depths of focusing in the film. It is clear that the banded texture covers also the localities displaying schlieren brushes. Consequently, schlieren brushes are optical effects but not isotropic material regions.

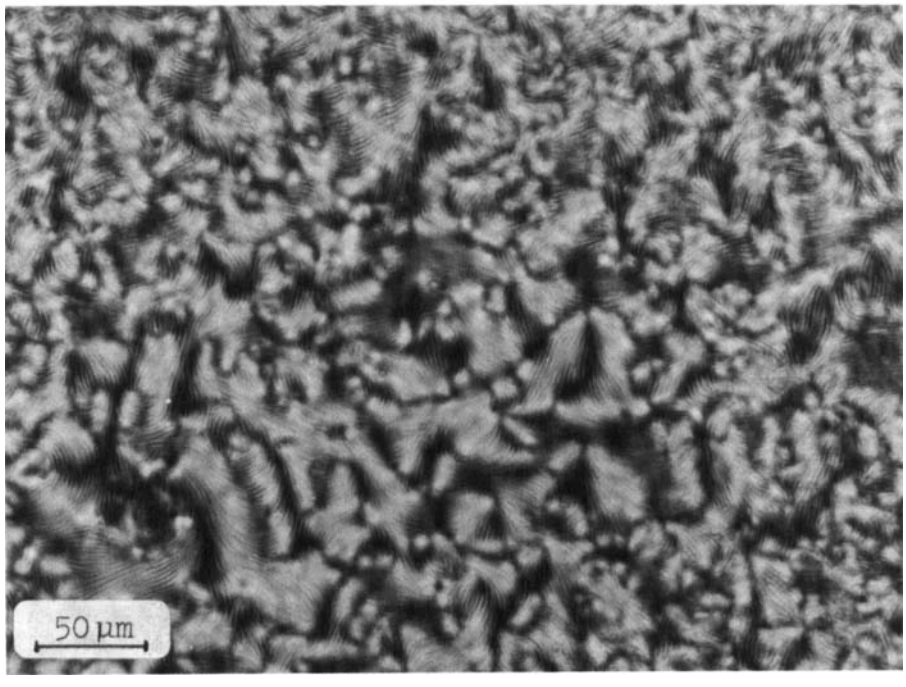
In the banded texture the band observed is around 1 μm in width on the same order of magnitude with the width of the band observed in the mat morphology of oriented nematic aromatic polyamides.[9,10] When the film was rotated with respect to the polarizer-analyzer directions the bright and dark bands interchanged indicating different molecular chain orientations in the adjacent bands. From these optical observations the molecular chains in the adjacent bands are estimated to lie in ±30° with the band normal direction. It seems reasonable to consider the mat morphology of an oriented nematic mesophase as a monodomain free from disclination.

Figure 5 shows POM pictures of the film quenched from 250°C melt exhibiting different densities of disclinations at different areas. Figure 6 is the scanning electron micrographs of the film of Figure 5 etched by argon plasma. In the SEM photographs the less ordered interfibrillar regions were etched by argon plasma to show up the fibriles of molecular chain aggregates with the molecular chains in the long dimension of the fibrile which is roughly normal to the band.

It is interesting to mention here that when a quenched film with banded texture was heated above 200°C the banded texture began to vanish. However, on quench-

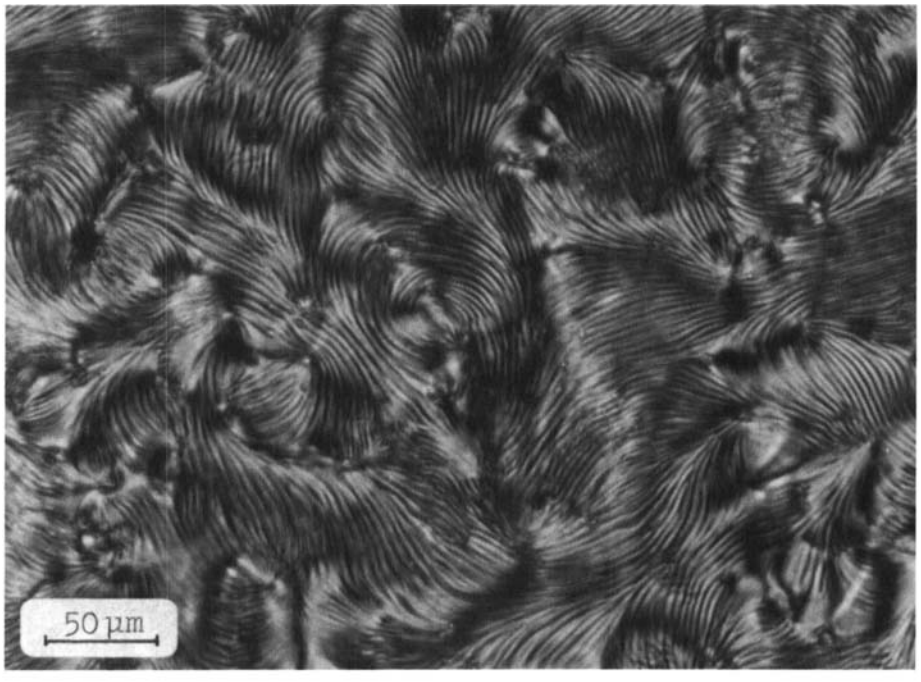


(a)

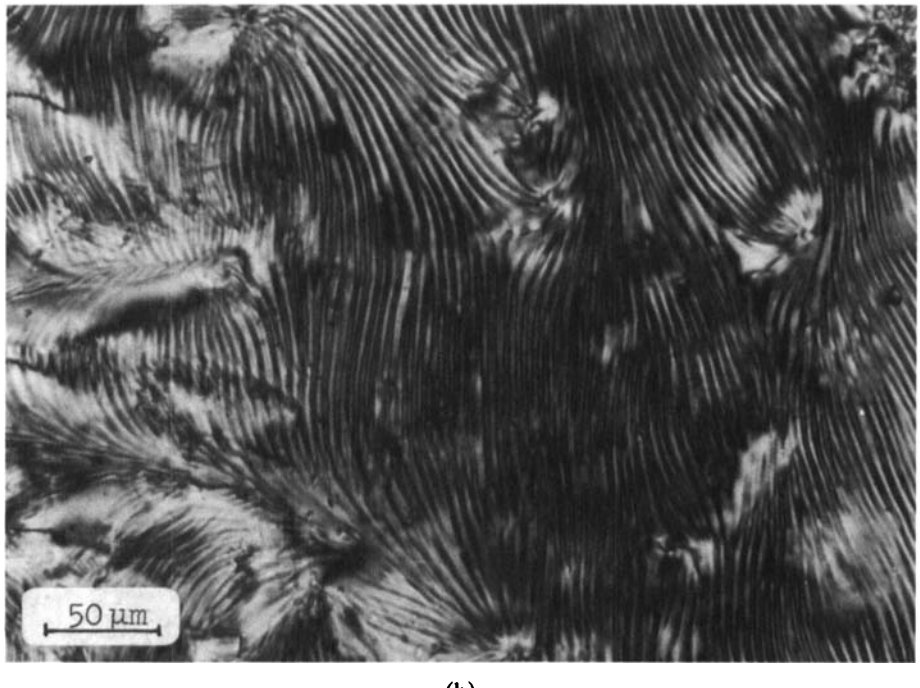


(b)

FIGURE 4 A set of optical polarizing micrographs of the film quenched from 250°C melt taken from the same position at different focusing depths. See Color Plate VII.

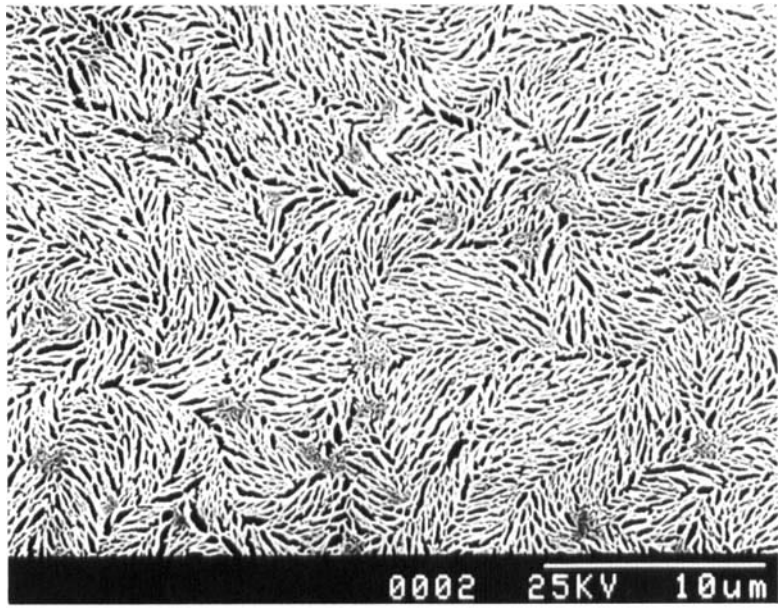


(a)

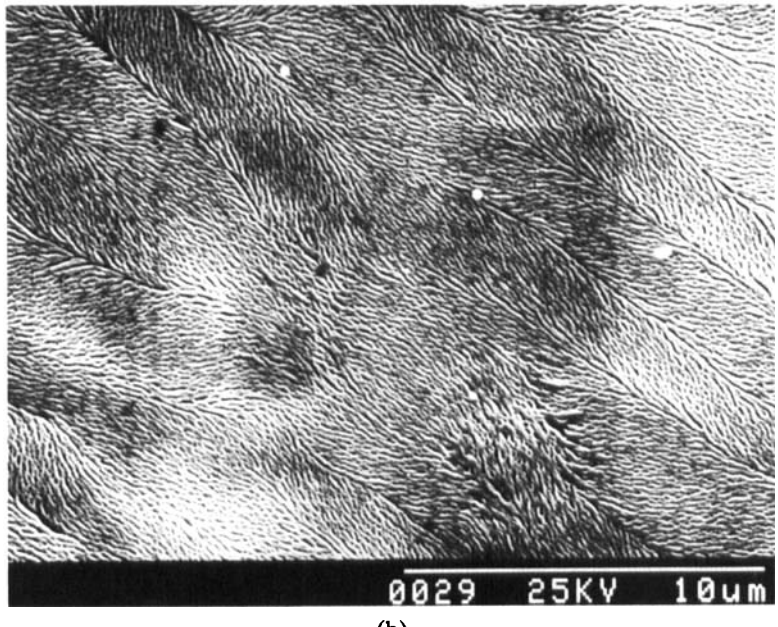


(b)

FIGURE 5 Optical polarizing micrographs of film quenched from 250°C melt showing different disclination densities at different areas, crossed polars. See Color Plate VIII.



(a)



(b)

FIGURE 6 Scanning electron micrographs of the film of Figure 5, etched by argon plasma.

ing the melt where the banded texture had disappeared, the banded texture reappeared in the quenched film. It remains to be understood why the banded texture develops only during quenching, but not in the melt as well as why the banded texture of a shear oriented nematic mesophase develops only during shear relaxation.[11,12]

Acknowledgment

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