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Observation of disclinations in the nematic state of a thermotropic aromatic copolyester by lamellar decoration

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The frozen nematic state of a thermotropic aromatic copolyester exhibits a schlieren texture with two and four dark brushes emanating from a point observed under a polarizing optical microscope; these correspond to disclination strengths $s = \pm 1/2$ and $s = \pm 1$, respectively. The combined techniques of lamellar decoration and ruthenium tetraoxide staining have been used to reveal the director orientation around disclinations in the frozen nematic state of polymers by transmission electron microscopy. All six disclinations in the nematic mesophase of a single liquid-crystalline aromatic copolyester have been observed. Every disclination interacts and is connected with its neighbouring disclination so that disclination exist in pairs usually of opposite sign in their disclination strengths. Some pairs with the same sign disclination have also been observed.

1. Introduction

Under a polarizing optical microscope we observe the texture of a thin layer of liquid-crystalline polymer, which 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 of the liquid-crystalline polymer is the occurrence of disclinations. The disclinations are observed by optical microscopy as two and four extinguished brushes emanating from a nucleus, i.e. a central point, the so-called schlieren texture with disclination strengths $s = \pm 1/2$ and $s = \pm 1$, respectively. For low molecular mass liquid crystals it has been established both theoretically [1] and experimentally [2, 3] that there are two disclinations of $s = \pm 1/2$ and four disclinations of $s = \pm 1$, that is a total of six disclinations in the nematic mesophase.

The orientation of the macromolecular chain and its mesogens in the thermotropic liquid-crystalline state of a polymer can be frozen in its glassy state. In the case that the polymer is capable of being crystallized, annealing the frozen glass under suitable conditions could lead to lamellar crystallization which will show the orientation of the polymer chains as the chains usually lie nearly perpendicular to the lamellar surface. 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 [4–6] 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 with a flexible spacer where the mesogens are in the back-bone. Ford and Bassett [7] have also

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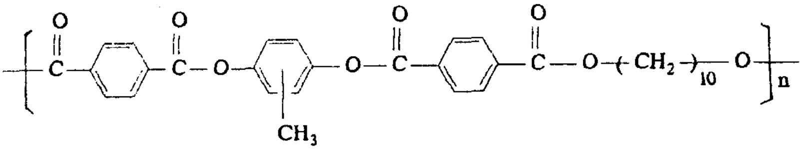
used the same technique to reveal the morphology of disclination strength $s = \pm 1/2$ in the bulk specimen of a main chain liquid-crystalline polymer containing a semi-flexible coupling chain by scanning electron microscopy. Recently Dong and Deng [8] have also used this technique to reveal the disclination strength $s = \pm 1/2$ in the bulk specimen of an aromatic copolyester without a flexible spacer by scanning electron microscopy. In this paper all six disclinations in the frozen nematic state of an aromatic copolyester with a flexible spacer have been observed by the combined technique of lamellar decoration and ruthenium tetraoxide staining. So far as we are aware this is the first time that four disclinations of $s = \pm 1$ in addition to two disclinations of $s = \pm 1/2$ could be observed experimentally in the nematic state of a single liquid-crystalline polymer.

2. Experimental

2.1. *The polymer sample and specimen preparation*

The material used in this work was an aromatic copolyester with a flexible spacer having the chemical structure:



It showed an inherent viscosity of 0·163 dL g^{-1} at 25°C in phenol-1,1,2,2-tetrachloroethane(1 : 1); $T_{CN} = 110°C$ and $T_{NI} = 217°C$ were determined by DSC, these are rather different from the data reported by Zhou [9], because the molecular weight on the polymer used in this work is lower. A solution of the polymer in 1,1,2,2-tetrachloroethane of 0·5 wt% concentration was made. A few drops of the solution were dropped on 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 100 nm thick was formed. After a few minutes the slide was put into ice-water so that a frozen nematic state of the polymer film resulted. The film was then annealed at 90°C for 2 h to ensure complete crystallization.

2.2. *Electron microscopy*

In order to improve the contrast of TEM pictures the crystallized polymer film was subjected to staining in RuO_4 vapour [10, 11] at 50°C for 1 h. The stained thin film was then floated on a water surface and was picked up by a copper grid for TEM observation in a Hitachi H-800 type transmission electron microscope.

3. Results and discussion

The nematic state of the aromatic copolyester used in this investigation was easily frozen into a nematic glass, from which the schlieren texture could be observed under a polarizing microscope as shown in figure 1. We can see that it shows two and four dark brushes emanating from a nucleus, corresponding to the dislocation strengths $s = \pm 1/2$ and $s = \pm 1$, respectively. However, after lamellar crystallization the frozen film sample was still not able to reveal the lamellar morphology in TEM because of insufficient contrast in electron beam transmission. So RuO_4 staining was essential for succesful observation of the disclinations.

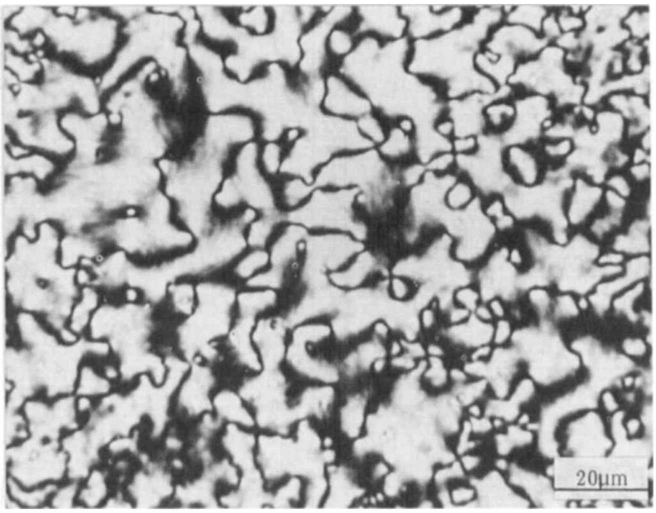


Figure 1. Optical micrograph between crossed polars of the schlieren texture of the frozen nematic mesophase of an aromatic copolyester.

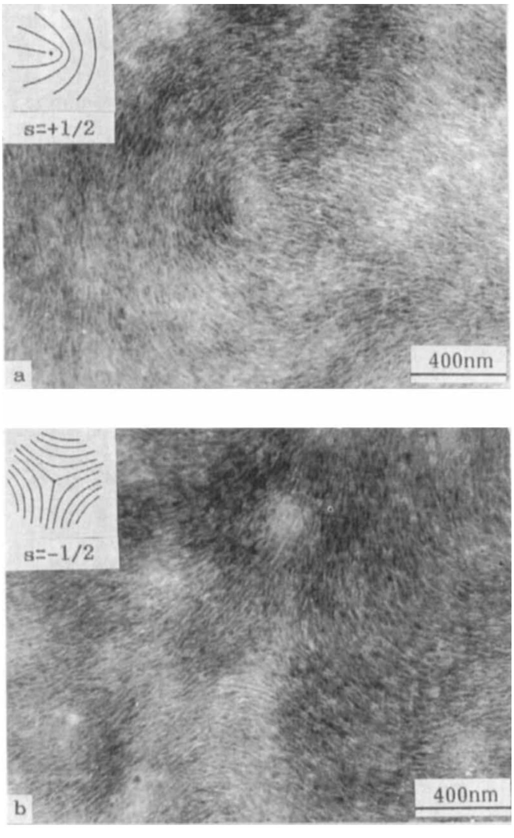


Figure 2. Lamellar decorated TEM micrographs of (*a*) disclination strength $s=+1/2$, (*b*) disclination strength $s=-1/2$, and the corresponding mapped director orientations.

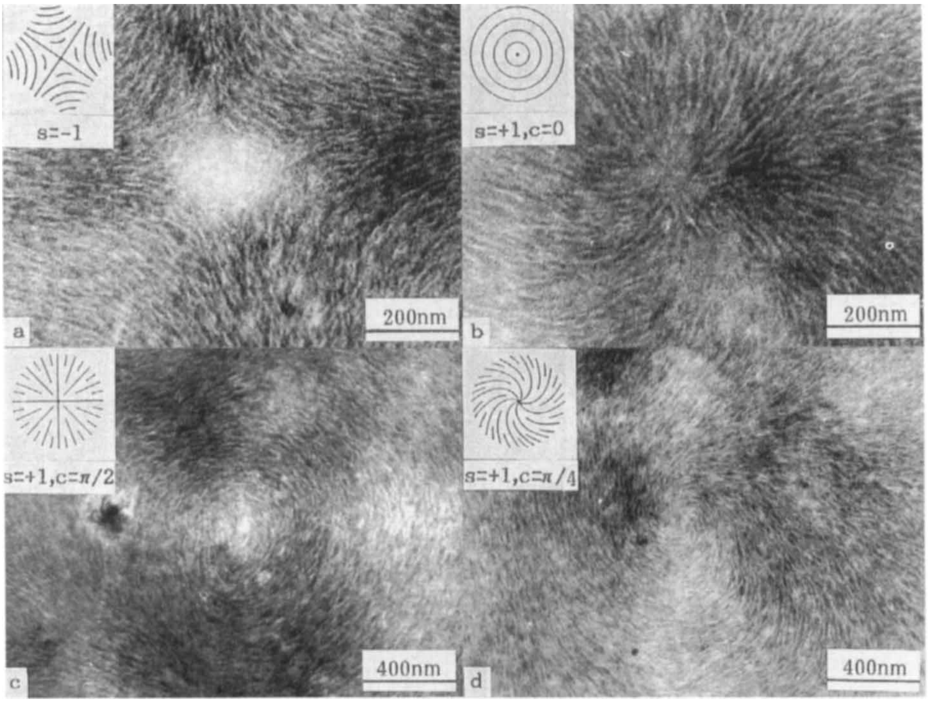


Figure 3. Lamellar decorated TEM micrographs of the types of (*a*) disclination strength $s=-1$, (*b*–*d*) disclination strength $s=+1$, and the corresponding mapped director orientations.

Figure 2(*a*) shows the lamellar decorated TEM picture of the disclinations with $s=\pm 1/2$. It can be clearly seen that crystalline lamellae grow around the disclination. The lamellar thickness was about 10 nm. The polymer chains were perpendicular to the long axis of the lamellae, which was checked by selected area electron diffraction pattern. As the directors of the mesogen lie in the direction of the polymer chain, the chain or director orientation is mapped as sketched in the cut of the figure. It is clearly a disclination of $s=+1/2$; the similar texture of the disclination with $s=\pm 1/2$ is shown in figure 2(*b*). This type of disclination with $s=\pm 1/2$ is a line disclination which is a fairly stable defect and the most commonly observed.

In figure 3 are shown four disclinations with $s\mathrm{T}\pm 1$ as indicated by the mapped chain or director orientation sketched in the cuts of the figure. The disclinations with $s=\pm 1$ can exhibit three different types of director orientation because of the different angles c, of 0, $\pi/2$ and $\pi/4$ between the director orientation and main optical axis [1]. The mapped director orientations are sketched in the cuts of the figure. This type of disclination with $s=\pm 1$ is point disclination which is a rather unstable defect, it has not been observed in the nematic mesophase of a liquid crystal polymer before.

It is known that an isolated disclination would lead to an infinite strain energy [12]. Consequently every disclination interacts and is connected, therefore, with its neighbouring disclination of opposite sign in their disclination strength so that disclinations usually exist in pairs. Figures 4 and 5 demonstrate such pairs of disclinations with $s=\pm 1/2$ and $s=\pm 1$, respectively. These are comparatively stable textures for a nematic and the total sum of the disclination strengths in the system should be zero.

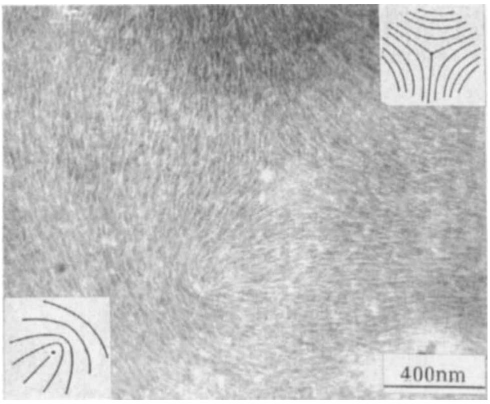


Figure 4. Lamellar decorated TEM micrograph of a pair of disclinations $s=+1/2$, $s=-1/2$, and the corresponding mapped director orientations.

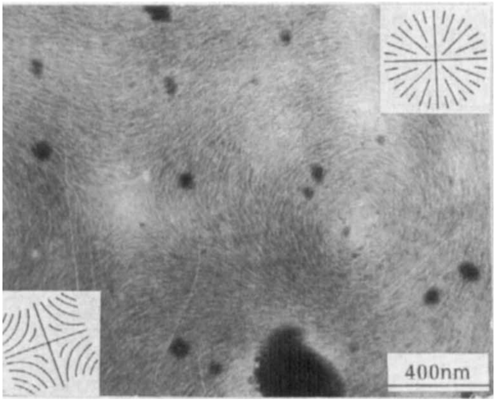


Figure 5. Lamellar decorated TEM micrograph of a pair of disclinations with $s=+1$, $s=-1$ and the corresponding mapped director orientations.

It is interesting to point out here that we could also observe two disclinations of different types connected to each other to form a pair. For example, a pair of disclinations with $s=\pm 1$, $c=\pi/2$ and $s=-1/2$ is shown in figure 6(*a*) and a pair of disclinations with $s=+1$, $c=\pi/4$ and $s=-1/2$ is shown in figure 6(*b*). In some cases we could even observe pairs of disclinations of the same sign for their strengths. For example, a pair of disclinations with $s=+1$, $c=\pi/4$ and $s=+1/2$ are shown in figure 7(*a*) and a pair of disclinations both with $s=-1/2$ are shown in figure 7(*b*). These disclination pairs with the same sign for their strengths correspond presumably to a non-equilibrium state and to an unstable texture. Owing to the long relaxation time needed for polymer chains to reach equilibrium these unstable disclinations present in the nematic as fluctuations are frozen into the glass. Of course, over a larger field of view the sum of the disclination strengths should vanish.

These observations offer an important clue to our understanding of the nature of the nematic texture. As the polymer chains are, of course, continuous throughout the region of the nematic domains, the chain direction is subjected to abrupt changes across the domain boundaries. In this sense nematic domains of a liquid crystal

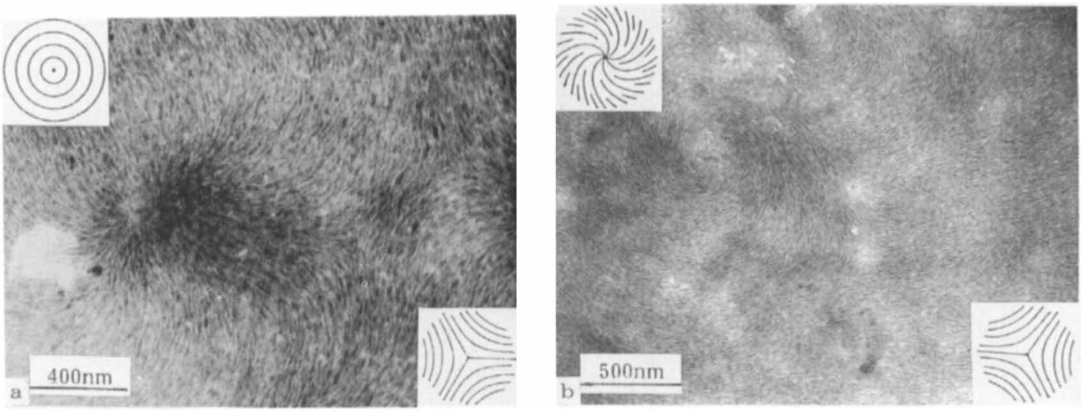


Figure 6. Lamellar decorated TEM micrographs of pairs of disclinations with (*a*) $s=+$, $c=\pi/2$ and $s=-1/2$; (*b*) $s=+1$, $c=\pi/4$ and $s=-1/2$, and the corresponding mapped director orientations.

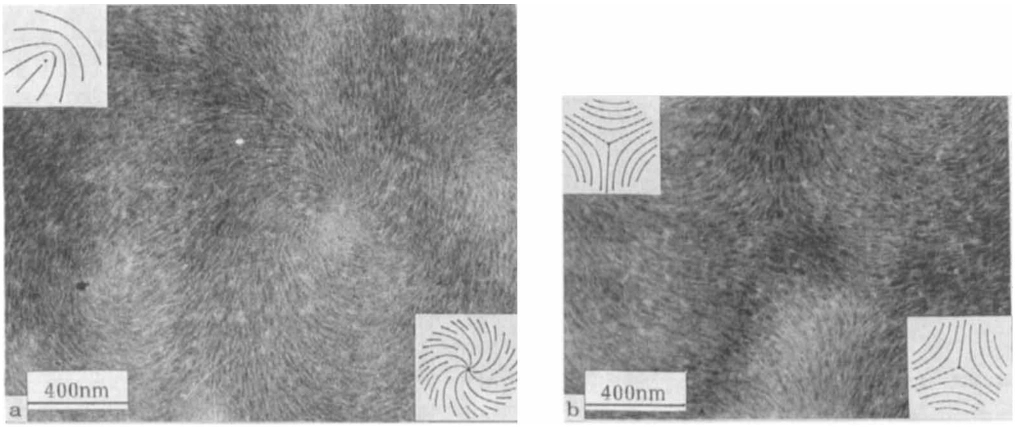


Figure 7. Lamellar decorated TEM micrographs of pairs of disclinations with (*a*) $s=+1$, $c=\pi/4$ and $s=+1/2$; (*b*) both $s=-1/2$, and the corresponding mapped director orientations.

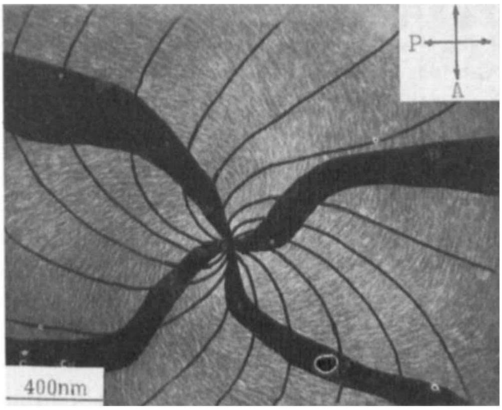


Figure 8. Schematic diagram showing the relationship between the schlieren texture and the director orientation around a point disclination.

polymer are in the precise meaning of a texture and there is no material boundary across the domains. The schlieren texture usually observed for a nematic liquid crystal polymer is really an optical effect of the disclinations [13]. Figure 8 shows the lamellar decorated TEM picture of disclinations present in the aromatic copolyester film frozen from its nematic state. The chain or director orientations are mapped on the figure. It is clear that when this film is put between crossed polarizer and analyser, all regions where the chain director orientation coincides with either the polarizer or the analyser directions will appear dark. These dark regions are mapped and marked black in figure 8 and it forms the two or four brushes of the schlieren texture. 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 (centre point) of the disclination will stay stationary.

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