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Solidification-induced and shear-induced band texture in thermotropic liquid crystalline polymer films

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It has been observed that the band texture of thermotropic liquid crystalline polymers (LCPs) is formed at the shearing temperature during the relaxation of shear. The band spacing increases with increasing shearing temperature between T_m and T_i , but is independent of shearing rate within the range of our experiments. The angle of zigzag orientation of the molecular chain fibrils with respect to the direction of shear is independent of the shearing temperature. The relaxation rate of the shear-induced band texture depends on the width of the bands formed. The wider the band spacing is, the slower the relaxation. When specimens with shear-induced bands of different spacings are annealed at a certain temperature for 10 min, they are all converted to a new band texture of the same spacing of around $1\ \mu\text{m}$. These bands with a small spacing generated during cooling are termed the solidification-induced band texture. When the specimen with shear-induced bands is annealed for a short time, so that the bands have not relaxed, and is then quenched, solidification-induced bands with a smaller spacing than the original bands appear. In this way, both shear-induced and solidification-induced bands could be seen in the same polarizing micrograph. The solidification-induced bands could be used as a kind of decoration to show that the chain orientation field follows the changes during relaxation of a shear-induced texture, at a given temperature, into walls, loops and sinusoidal wave textures which eventually relax to a thread texture.

1. Introduction

It is well known that both lyotropic and thermotropic liquid crystalline polymers (LCPs) show a band texture, as observed by microscopy with crossed polarizers, on being subjected to a shear or elongational flow. During the past decade, many experimental results concerning the factors affecting band texture formation of lyotropic LCPs have been reported [1-6]. It has been proved that the bands form during relaxation of the shear [1-4]. The induction period needed for the formation of an observable band texture after cessation of shearing varies over a wide range from a few seconds to several minutes, depending on the shear rate, duration of the shearing, the layer thickness and the solution concentration. The bands have a width or periodicity ranging from 0.5 to $10\ \mu\text{m}$, mainly depending on the nature of the polymer, apart from a few cases dependent on the shear rate. Some thermotropic LCPs have been found to exhibit the band texture during quenching, after being sheared between glass slides [7-10]. The high temperatures needed to obtain the mesophase rendered more extensive studies difficult. A model based on Frank's elastic energy has been proposed to interpret the appearance of the band texture

[11]. Besides the molecular elasticity, texture elasticity has been suggested as another principal source of elastic energy that could drive the formation of bands after shearing ceases [12]. Even so, the molecular mechanism leading to the formation of the band texture has not yet been satisfactorily explained.

Recently, it has been noticed that the band texture can also be formed in a nematic polymer without being subjected to a shear, if mesomorphic domains had grown to a sufficient size and then been quenched to room temperature [13, 14]. We shall refer to this kind of band formation as the solidification-induced band texture. The band spacing is usually about $1\ \mu\text{m}$. Differently oriented band in different regions of the film specimen imply a nematic multidomain texture. These bands decorate the mesogen director orientation, showing different types of disclination [15]. The mechanism of formation of this kind of band texture without shearing remains to be explored.

In this paper, relaxation behaviour after cessation of the shear was observed in several thermotropic liquid crystalline polymers at different shearing temperatures. The effects of shearing condition and thermal treatment on the band texture were studied.

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Table 1. The properties of nematic polymers **Pa**, **Pb**, **Pc**, **Pd**.

Polymer	T_m /°C	T_i /°C	M_n	$[\eta]/\text{dl} \times \text{g}^{-1}$
Pa	92	219	4600†	—
Pb	123	149	8460†	—
Pc	164	not measured	—	0.513‡
Pd	110	197	—	0.289§

† From reference [16].

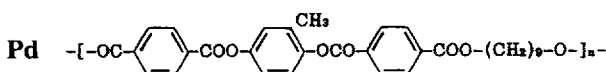
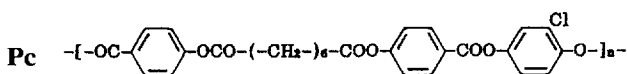
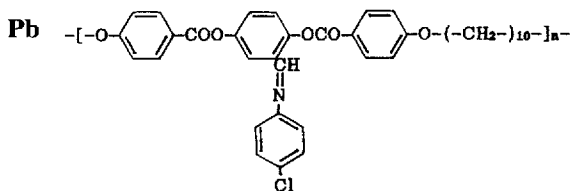
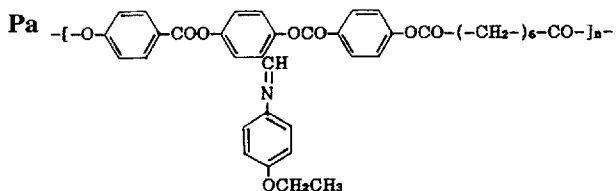
‡ Inherent viscosity measured at 25°C for a phenol/1,1,2,2-tetrachloroethane (1:1) solution at a concentration of 0.5 wt%.

§ Inherent viscosity measured at 25°C for a 1,1,2,2-tetrachloroethane solution at a concentration of 0.5 wt%.

2. Experimental

2.1. Materials

The LCP samples used in this study were nematic aromatic copolyesters, containing different side groups and different lengths of flexible spacers in the main chain, having the following molecular structures:



Their transition temperatures (determined by DSC at a heating rate of 20°C min⁻¹) and molecular weights (or inherent viscosities) are listed in table 1.

2.2. Experimental procedures

The observations of relaxation were performed using a specially constructed apparatus which allowed us to shear a thin layer of a LCP sample at elevated temperature while observing the film using an optical microscope. The nematic melts were sheared at a temperature between T_m and T_i , sometimes above T_i and then directly observed at the shearing temperature. In the meantime, a modified, rotating parallel-plate shearing apparatus [4] was used to observe the influence of shear rate. The range of shear rates $\dot{\gamma}$ used was between 0 and 3000 s⁻¹, varying with the

distance from the centre of rotation given by the following equation, assuming a uniform velocity gradient across the thickness of the thin layer:

$$\dot{\gamma} = 2\pi Rn/60h$$

where R is the radial distance of the point of observation from the rotation centre, n is the rotation speed in min⁻¹ and h is the thickness of polymer melt layer. After shearing, the glass slides containing the sandwiched nematic melt were immediately quenched to room temperature. An Olympus Model BH-2 polarizing optical microscope (POM), in conjunction with a Mettler FP-52 hot stage and a Model SL-1 small angle light scattering apparatus made in this Institute were used for texture observations.

3. Results and discussion

3.1. Formation process of the band texture in the nematic state of thermotropic LCPs

The band texture is usually observed in quenched solid films of thermotropic LCPs [7–10], because it is rather difficult to observe the texture at high temperatures in the mesophase. Recognizing this difficulty, we selected samples for study which had relatively low T_m and T_i values, so that we were able to observe the relaxation of the shear-induced band textures at the shearing temperature, after cessation of shear. For polymers **Pa** and **Pb**, the band texture appeared so quickly after cessation of shearing, at any temperature between T_m and T_i , that the induction periods of band formation were practically zero. However the relaxation of the bands, that is the gradual extinguishing of the bands, was observed to be a slow process, which could be divided into two stages. In the first stage, the straight bands perpendicular to the shear direction became wavy and short, and disappeared gradually, but the chain orientation was maintained. In the second stage, the chain orientation relaxed continuously, ending in formation of a thread texture. The first stage of the relaxation process generally occurs over a shorter time scale than the second stage. That is why one has to quench the sheared sample to room temperature as quickly as possible, in order to observe the fine band texture. The relaxation after shear cessation from the shear-induced band texture to a completely quiescent thread texture occurs in the order of 10 to 1000 s, depending on the nature of the polymer, the temperature and the shearing conditions. In general, there is more chance of observing the band texture at lower temperatures of the mesophase as the chain orientation relaxes slowly owing to the higher viscosity of the polymeric melt. At higher shearing temperatures, the relaxation time becomes short and it is more difficult to observe the band texture.

For polymers **Pc** and **Pd**, especially when the shearing

temperatures were 200 and 130°C (and above), respectively, the band texture could hardly be generated, simply because the viscosities of the polymer melts decreased sharply at these temperatures. This implies that the molecular chain length may be one of the prime factors influencing the band formation. For polymer **Pd**, even if the nematic melt was sheared at a relatively low temperature (130°C), the small molar mass of the polymer made it very mobile, resembling the behaviour of a low molar mass liquid crystal. The shear orientation would then be totally relaxed before the band texture could form. Consequently no band texture could be observed. The shear-induced band texture was not observed when the LCP melts **Pa**, **Pb** and **Pd** were sheared above their nematic–isotropic transition temperatures (T_i). It is suggested that the formation of the band texture is merely a consequence of interchain order rather than of chain structure. The bands were usually formed after shearing at an intermediate viscosity of the system.

3.2. The effect of shear rate and shear temperature on the band texture

When the nematic melt was sheared in the rotating parallel-plate apparatus and then immediately quenched to room temperature, the sheared specimen showed a Maltese cross extinction pattern with a radial band texture between crossed polarizers, resembling a typical spherulite morphology, as shown in figure 1. It was found from the interference colour after inserting a compensator that the molecular orientation corresponded to a negative birefringence; that is, the molecular chains were oriented along the shearing direction, perpendicular to the long axes of the bands. Figure 1 also shows that there is no band texture in the vicinity of the rotation centre, where the shear rate was too small. From the radial distance of the demarcation circle between banded and non-banded regions, the critical shear rate $\dot{\gamma}_c$ can be calculated; the value depends strongly on temperature and the nature of the polymer. For example, the value of the critical shear rate $\dot{\gamma}_c$ is 13 s^{-1} for polymer **Pa** at 140°C and 11 s^{-1} at 160°C; however, for polymer **Pd**, $\dot{\gamma}_c$ is very low, only 1 s^{-1} at 120°C. The radial bands in figure 1 appear more distinct and straight along the radial direction with increasing radial distance, i.e. with increasing shear rate. Figure 2 shows a magnified local areas of figure 1 corresponding to shear rates from 2165 to 2169 s^{-1} . The band spacing appears to be independent of the shear rate within the experimental range up to 3000 s^{-1} .

Although the band spacing is independent of shear rate at a given temperature, it increases with the temperature at which the melt is sheared. Figure 3 shows the polarizing micrographs of polymer **Pa** subjected to shearing at different temperatures. From the photomicrographs and the values listed in table 2, the average band spacing

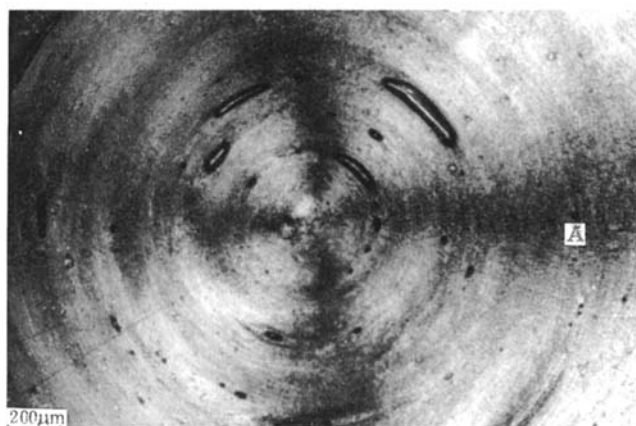


Figure 1. POM micrograph of the band texture of nematic polymer **Pd**, sheared by rotating the parallel-plate shearing apparatus at 120°C.

increases from 1 to $12 \mu\text{m}$ with increasing shearing temperature between T_m and T_i . In figure 3(d), zigzag fibrils can be seen under the polarizing microscope, demonstrating directly the formation of short period structure in the shear direction during the relaxation process. The orientation angles ϕ between the macromolecular chain in the band and the shearing direction are constant at around 15 degrees as shown in table 2. Same results were found for polymer **Pb**. For polymer **Pc**, the band spacing showed an abrupt change from 1 to $15 \mu\text{m}$ at 190°C. The relaxation rate of the shear-induced band texture was found to depend on the band spacing. For example, for polymer **Pa**, in a heating at a rate of 5°C min^{-1} , the narrow bands (about $1\text{--}5 \mu\text{m}$) became wider at first and then became wavy and finally disappeared as the temperature was raised to 140°C (see figure 4), while the wider bands ($6\text{--}12 \mu\text{m}$) persisted at a temperature up to 200°C, although the bands were not as straight as those at lower temperatures (see figure 5). In the isothermal case, when the oriented films were directly



Figure 2. POM micrograph of the band texture partially magnified from local area (A) of figure 1.

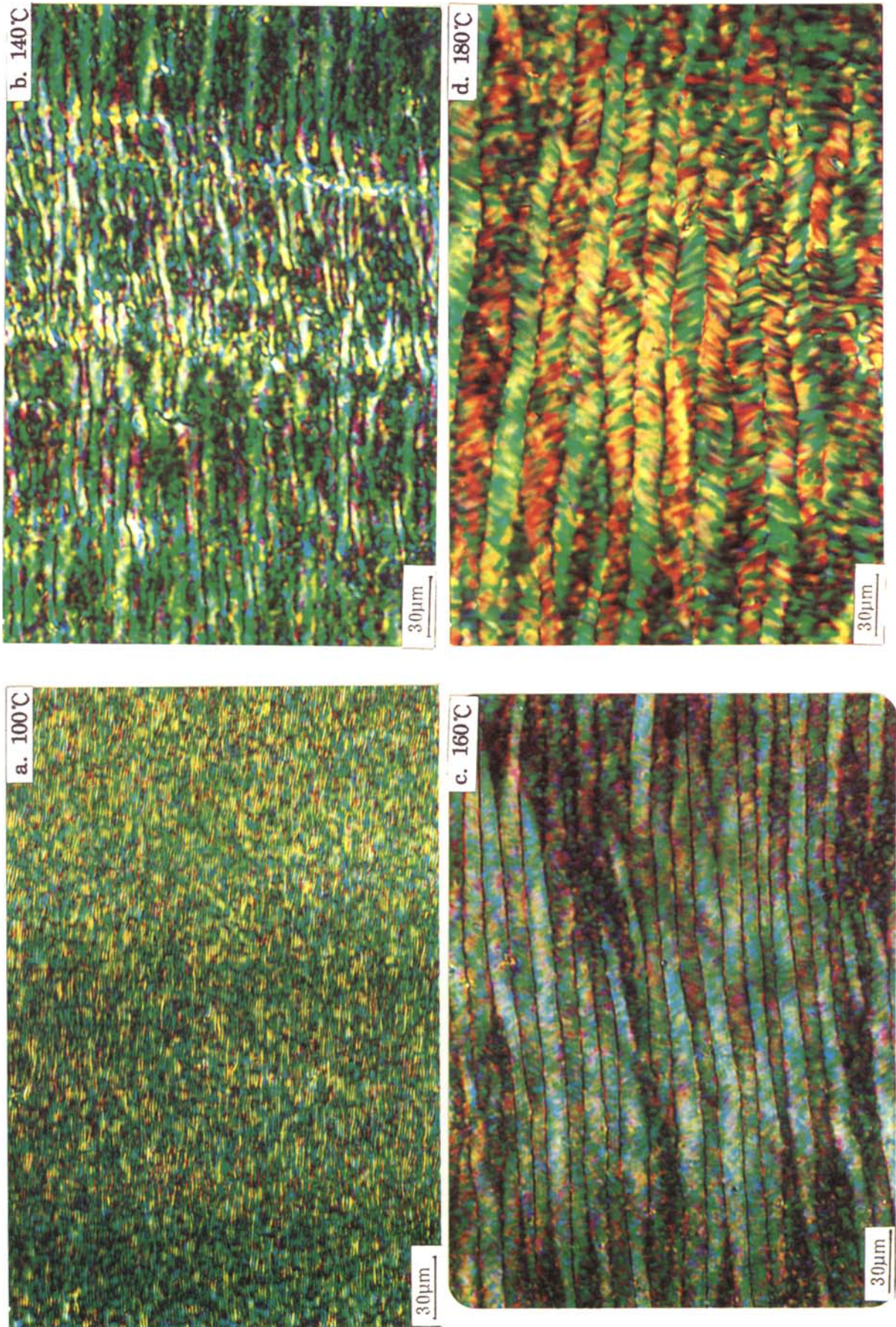


Figure 3. POM micrographs of band textures of polymer **Pa** sheared at different temperatures, and subsequently quenched to room temperature.

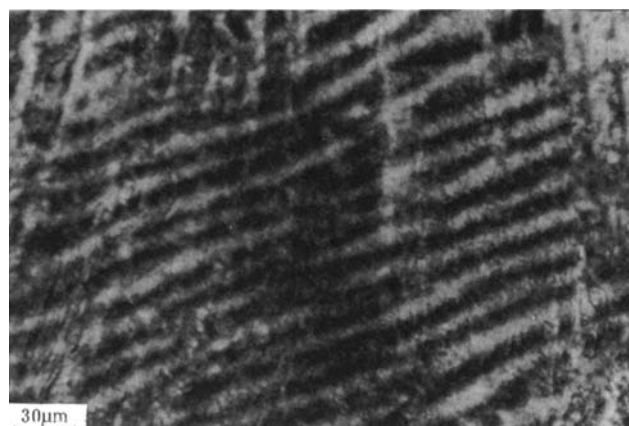
Table 2. Characteristics of the shear-induced band texture at different temperature.

Shear temperature/°C	Band spacing/ μm	ϕ degree
110	1.0–1.5	15
120	1.0–1.5	15
135	1.5–2.0	15
140	4.0–5.0	15
160	6.0–8.0	15
180	8.0–10.0	15
200	8.0–12.0	15

annealed at 160°C, the narrow bands (sheared at 120°C) vanished immediately, but the wide bands (sheared at 180°C) remained for 30 min. At this temperature, the wide bands faded out gradually as time progressed. It is presumed that the band texture formation of a LCP is related to its thermal history, in the sense that the band spacing might be related to the domain size in the nematic melt before shearing. It is known that the density of disclinations becomes smaller, or in other words, the nematic domains become larger, when the melt is heated to higher temperatures. Consequently, the shear-induced band texture generated from high temperature shearing has a wider spacing. Therefore the band texture has the memory of the nematic domain state before shearing, and the structural units of the band could be considered to be these nematic domains. Presumably these nematic domains are also the kinetic units of molecular motion in the band. The bands with wider spacing have a smaller relaxation rate owing to the larger kinetic units of the nematic domains.

3.3. Solidification-induced band texture and shear-induced band texture

It is interesting to mention here that all these band textures with different band widths became narrow after

Figure 4. POM micrograph of an oriented film of polymer **Pa** (sheared at 140°C) and annealed at 140°C for 10 min.Figure 5. POM micrograph of an oriented film of polymer **Pa** (sheared at 160°C) and annealed at 180°C for 10 min.

the sample had been annealed in a certain range of temperatures for more than 10 min and then quenched or cooled naturally to room temperature. As a result, the bands, originally of different spacings, all narrowed to the same band spacing of around 1 μm (see figure 6) while maintaining the original orientation direction of the macromolecular chains. This annealing temperature was 180–200°C for polymer **Pa**, 138–142°C for polymer **Pb** and above 240°C for polymer **Pc**. These narrow bands presumably constitute the solidification-induced band texture observed in nematic polymers without shearing through a similar thermal treatment [13]. Under shearing, the mesogen directors will align the shear direction so that the multidomain texture becomes an oriented, continuous, monodomain phase with vanishing disclinations. It is evident that the solidification-induced band texture can be found in a monodomain nematic phase, contrary to the results of Hudson *et al.* [17]. When a film of polymer **Pa** with a wide band texture, generated at a shearing temperature between 160–200°C, was annealed for a short period, say a few minutes, so that the shear-induced wider bands had not entirely relaxed, the solidification-induced band texture with a narrow band spacing could appear within the original shear-induced bands during cooling, so that both shear-induced and solidification-induced bands appeared simultaneously in the field of view of the microscope, as shown in figure 7(a). The narrow bands within the wider bands give us a kind of decoration showing that the field of molecular chain orientation—the long dimension of the narrow bands—is perpendicular to the zigzag fibrils of the molecular chain along the shearing direction. The small angle light scattering (SALS) Hv pattern of this oriented film, shown in figure 7(b), shows a grating-like diffraction pattern of two pairs of lobes normal to the bands, indicating that the bands in the oriented structure have two periodicities. The sharp diffraction at small angles (see figure 7(c)) is related to

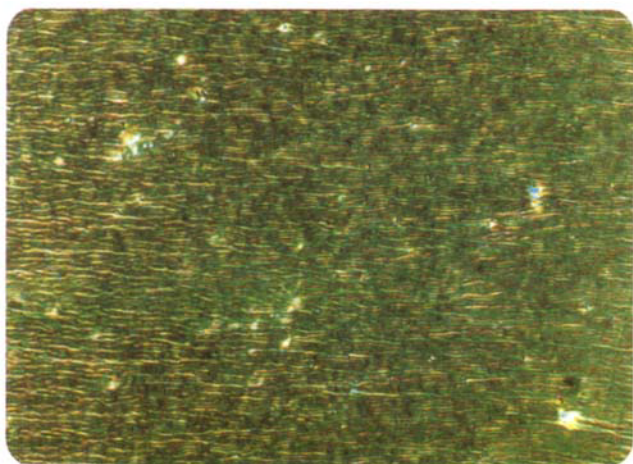


Figure 6. POM micrograph of the solidification-induced band texture of an oriented film of polymer **Pa** (sheared at 160°C) and annealed at 190°C for 20 min before quenching to RT.

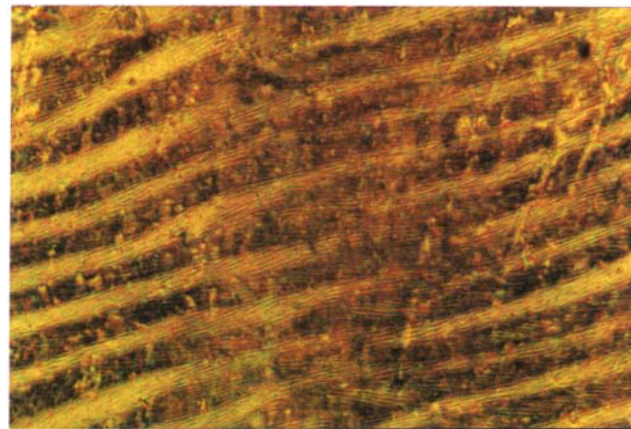
the spacing of the original shear-induced bands, while the diffuse diffraction at larger angle is related to the solidification-induced bands.

No bands could be directly observed when the film was heated at the annealing temperature. The solidification-induced band texture was generated only during quenching or rapid cooling from a high enough annealing temperature. For polymer **Pa**, this band texture could also be formed by rapidly cooling ($10^{\circ}\text{C min}^{-1}$) from 185°C to about 90°C. If the cooling rate was slow (below $3^{\circ}\text{C min}^{-1}$ for polymer **Pa**), the band texture appeared indistinct. X-ray diffraction studies have shown that polymers **Pa** and **Pb** have poor crystallinity [18], so we do not think that crystallization leads to the formation of bands as proposed by Hoff and Keller [14].

We can also observe the relaxation process of the oriented nematic state of LCPs under annealing for different times using the solidification-induced band texture decoration. The shear-induced band texture was observed to relax, resulting in the gradual distortion of the chain orientations (see figures 6 and 7) and the formation of many inversion walls parallel to the original shear direction (see figure 8 (a)), loop walls (see figure 8 (b)) and a sine-wave-like texture (see figure 8 (c)) in the relaxed specimen.

4. Conclusions

We have tried in this paper to elucidate the formation and relationships of two kinds of band texture, the shear-induced and solidification-induced band textures in



(a)



(b)



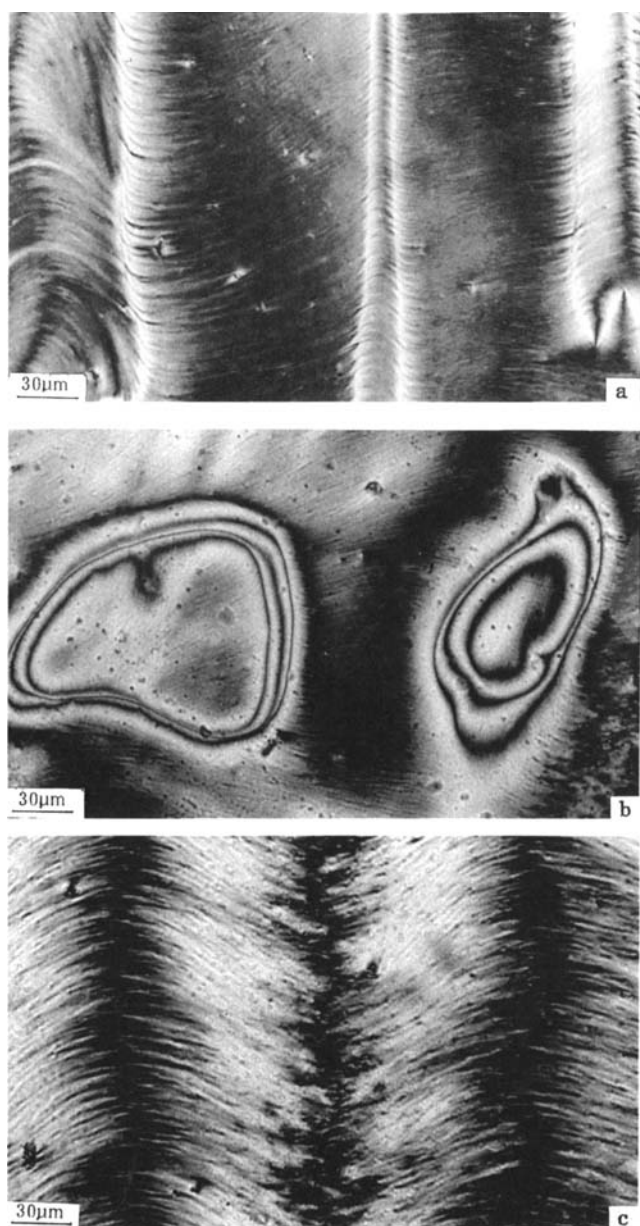
(c)

Figure 7. POM micrograph (a) and corresponding small angle light scattering Hv (b) and (c) pattern of an oriented film of polymer **Pa** sheared at 160°C annealed at 190°C for 5 min and subsequently quenched to RT. (c) Is the diffraction at small angle magnified from (b).

the nematic state of thermotropic LCPs. Here, we conclude the following:

- (1) Like lyotropic LCPs, the band texture of thermotropic LCPs can be observed at the shear temperature without quenching, while the relaxation of the shear occurs.
- (2) The band texture of thermotropic LCPs can be formed when shear rate $\dot{\gamma}$ is bigger than the critical shear rate $\dot{\gamma}_c$. The band spacing is independent of the shear rate and increases with rising shear temperature within the nematic limits defined by T_m and T_i .
- (3) The solidification-induced band texture can also be generated in the oriented nematic phase without disclinations. These two kinds of band texture induced by different mechanisms can be observed in the same sample.

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Figure 8. Micrograph of an oriented film of polymer **Pa** annealed at 190°C for 30 min and subsequently quenched to RT.