Studies on the Morphology of the Oriented Films of the Liquid Crystalline Polyesters Based on the 4,4'-Dihydroxy-α-Methyl Stilbene

Jonggeon Jegal* and A. Blumstein*

Membranes and Separation Lab, Advanced Polymer Division, Korea Research Institute of Chemical Technology, P. O. Box 107, Daejeon Korea

*Polymer Science Program, Department of Chemistry University of Massachusetts, Lowell, Mass 01854, USA

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Abstract: The banded textures of the oriented liquid crystalline thermotropic polyesters were studied by polarized optical microscopy and X-ray diffractometry. The driving forces for the formation of the banded textures were studied by the examination of the processes for the banded texture formation on the liquid crystalline polymer films; In the case of the polymer with a relatively low molecular weight (polymer-3), the banded textures were observed after cessation of the shear application on the melted polymer sample in its mesophase; However, in the case of the polymers with relatively high molecular weights (polymer-1 and polymer-2), the shear application technique was not successful in the production of banded textures. The cold drawing and heat treatment in the mesophases of the solution cast films were necessary for the formation of the banded textures. The thermal stabilities and memory effects of
the banded textures were also studied; Formed banded textures were stable and did not change at temperatures below the crystal melting but disappeared with crystal melting. The disappeared banded textures reappeared on cooling their mesophase or isotropic phase. The regularity of the banded textures, reproduced on cooling, depended on the heat treatment conditions. The banded textures reproduced from the isotropic phase were less regular than those formed from the mesophase.

INTRODUCTION

A number of investigations have been performed on the unique characteristics in optical, rheological, and other physical properties of liquid crystalline polymers. Interest has been taken in characterization of films and fibers prepared from the polymer liquid crystals, exhibiting distinct supramolecular structures and physical properties not expected in conventional flexible polymers.

A banded texture appears to be one of the structural and morphological characteristic features of sheared or elongated liquid crystalline polymers. Both lyotropic and thermotropic polymers have been shown to exhibit banded textures when subjected to shear or elongational flow.\textsuperscript{1-3}

Studies on the formation process of the banded texture were reported only in few cases.\textsuperscript{4-8} Usually a cone and plate rheometer was used and the texture changes were monitored by an optical method during the experiment. Optical texture of thermotropic copolymers was observed under shear of oscillatory mode by Graziano and Mackley\textsuperscript{5} and banded texture was observed for high molecular weight fraction during the relaxation process after shear cessation. The mechanism and details of the formation process of the banded texture are still not clear and more experimental facts about this banded texture are needed.

So far many people used sheared-thin films on the glass plate in its mesophase, but free standing thermotropic liquid crystalline polyester films, oriented by elongation, were not used widely to study banded textures. In this paper, the driving forces for the formation of the banded textures and the influence of the thermal history on the banded textures were studied with free standing liquid crystalline polyester films.

EXPERIMENTAL

Materials. The liquid crystalline polymers and copolymers based on the 4,4'\textsuperscript{-dihydroxy-\textit{a}-methylstilbene as mesogene and azelaoyl chloride and 10, 12-docosadiynediyl chloride as spacers were used. The structures of these polymers are shown in Fig. 1. The molecular weights of these polymers and their transition temperatures are given in Table 1.\textsuperscript{14}

Preparation of the Oriented Films. The oriented films were prepared by two different methods. The oriented films from a polymer with a relatively low molecular weight such as polymer 3 were prepared by the rapid shearing with a razor blade of the melted polymer at its mesophase on the glass plate followed by rapid

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\begin{align*}
\text{Polymer-1: } X &= 0.0, \ Y = 1.0 \\
\text{Polymer-2: } X &= 0.5, \ Y = 0.5 \\
\text{Polymer-3: } X &= 0.7, \ Y = 0.3
\end{align*}
\]

Fig. 1. Chemical structures of the polymers used for the study on the banded textures.
Morphology of the Oriented Films of the Liquid Crystalline Polyesters

<table>
<thead>
<tr>
<th>Table 1. Physical Properties of Polymers</th>
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<tr>
<td>Polymer</td>
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<td>Polymer-1</td>
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<td>Polymer-3</td>
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*Thermal transition temperatures were taken from the 2nd cycle on DSC Heating and cooling rates were 20°C/min.

cooling to 0°C on an aluminum cold plate.

The oriented films from polymers with relatively high molecular weights such as polymer-1 and polymer-2 were prepared by the following procedure: The polymer films were prepared by casting of the polymer solutions in chloroform followed by drying at room temperature. The films were heat treated in their nematic mesophases (184°C for polymer-1 and 137°C for polymer-2) for 5 minutes and quenched to 0°C on an aluminum cold plate. These heat-treated films were then elongated by cold drawing to 3 times extension.

Heat Treatment of the Films. The polymer films were heat treated at different temperatures for different period of time on a micro-hot stage equipped with a calibrated thermometer.

Characterizations. The morphologies of the films were studied on a Leitz Ortholux II polarizing microscope with a Mettler FP-5 heating stage.

X-Ray diffraction patterns of oriented films were obtained from a Laue camera mounted on a Rigaku generator operation at 40 KV and 25 mA using nickel filtered Cu-K alpha radiation with wavelength as 1.54 Å.

RESULTS AND DISCUSSION

Banded Texture Formation. The banded textures of the oriented films of polymer-1, polymer-2, and polymer-3 are shown in Fig. 2, showing periodic alternation of dark striation and bright layer along the direction of extension or shear.

In the case of the polymer with a relatively low molecular weight such as polymer-3(η =

![Orientation Direction](attachment:image)

Fig. 2. The polarizing photographs of the banded textures of the oriented films: polymer-1(a), polymer-2(b), and polymer-3(c). (Magnification: ×500)
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**Solution Cast Film**
- Heating at 184°C for 5 min
- Quenching to 0°C

**Nematic Glass Film**
- Cold drawing at room temp. ($\lambda=3$)

**Oriented Film with Elongated Nematic Domain Textures**
- Heating at 184°C for 2 min
- Rapid Cooling to room temp.

**Oriented Film with Banded Textures**

**Scheme 1**

The banded textures were developed in the film after cessation of rapid shearing the sample in its mesophase followed by rapid cooling to 0°C as shown in other papers. However, in the case of the polymers with relatively high molecular weights, the banded textures could not be prepared by the same preparation method as mentioned in the case of the polymer with a low molecular weight in this experiment due to the high melt viscosities of the polymers with high molecular weights.

Scheme 1 shows the procedure of banded texture formation with polymer-1 film. In this experiment, solution cast films were used to study the factors affecting the banded texture formation. The thicknesses of the cast films were about 30 µm.

The wide angle X-ray diffraction pattern of the cast polymer-1 film is shown in Fig. 3(a) and suggests that this film is semicrystalline and unoriented. This film did not show any banded textures(Fig. 4(a)).

In order to make the nematic glass films, heat treatment was done at the mesophase as mentioned at the experimental part. The heat treated film was turbid and became nematic glass. The film in nematic glass state was then stretched ($\lambda=3$) to orient molecular chains and the resulting film became transparent.

The wide angle X-ray diffraction pattern (WAXD) and a polarized light photograph of the polymer-1 film, oriented by the stretching

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**Fig. 3.** The wide angle x-ray diffraction (WAXD) patterns of the films of polymer-1; (a) solution cast film, (b) oriented film by stretching in nematic glass state(c) films with banded textures after heat treatment.
as mentioned above, are shown in Fig. 3(b) and Fig. 4(b), respectively. The WAXD shown in Fig. 2(b) presents a typical oriented nematic state with good orientation of molecular chains. However, the oriented film did not show any banded textures. The oriented film showed only elongated domain textures along the elongation direction as shown in Fig. 4. The elongated domain textures might be resulted from the elongated nematic domains. The nematic domains, produced in the film by the heat treatment at the nematic mesophase could be changed into rodlike shapes due to the stretching of the film. In the elongated nematic domains, molecules formed oriented fibrils and this was also confirmed by the x-ray diffraction pattern (Fig. 3(b)).

In order to study the effect of the relaxation of the oriented macromolecules on the banded textures formation, the oriented film with elongated domain textures were heat treated. First of all, the films were heated up to nematic mesophase, these films did not show banded texture but elongated domain texture. After holding at their nematic mesophase mentioned above for about 30 seconds the elongated domain texture began to disappear and banded textures were developed slowly, but during the holding at this temperature for 2 min., banded texture formation was not completed and some of the elongated domain textures were still remained. After holding for 2 min., these films were cooled down to room temperature by two ways, slow cooling and rapid cooling. Interestingly, banded textures formation, shown in Fig. 4, was completed on those films during the cooling by either slow or rapid cooling.

However, when stretched films with elongated domain textures were heated up to just below their crystalline melting points, 165°C for polymer-1 film, no banded texture was developed on the films on the cooling.

From these results, it was found that after orientation of polymer films by stretching, heating up to their nematic mesophase, above the crystal melting points, and cooling to below crystal melting temperatures by either slow or rapid cooling were necessary for the formation
Fig. 5. The polarizing photographs of the polymer-2 films with banded textures at different temperatures; (a) 132°C (mesophase), (b) 125°C (after cooling from nematic mesophase), (c) room temperature (after cooling from nematic mesophase), (d) room temperature (after cooling from isotropic phase). (Magnification: × 500)

of the banded textures on the oriented films. In the literature, most of the results indicate that banded textures are formed immediately or in a short period of time after shear cessation. But in our experiment, mentioned above heating and cooling after elongation are necessary for the formation of banded textures. Mao Xu and co-workers\(^9\) mentioned in their paper that banded
texture could hardly be the result of free thermal relaxation from the shearing orientation state, but is probably the result of forced thermal relaxation due to elasticity in the sheared specimens.

From our results, it can be suggested that the straight arrangement of molecular chain in fibrils, produced by the elongation, can be relaxed thermally enough to form zigzag rearrangement of fibrils only by the heating above crystal melting temperature. And this zigzag rearrangement of fibrils was confirmed by the WAXD as shown in Fig. 3(c). When this x-ray diffraction pattern was compared with that of oriented polymer-1 film without banded texture, two patterns of x-ray diffraction are much different. Two diffused spots in the wide angle region of x-ray diffraction pattern of the film without banded textures, which were characteristic pattern of oriented nematic glass, were disappeared by the heat treatment for the development of the banded textures, and 4-broken solid lines in the wide angle region were developed on the x-ray diffraction pattern of the film with banded textures.

Windle et al. also obtained the similar x-ray diffraction pattern to ours from the films with banded textures. They claimed that a faint four point on the x-ray picture may be observed in the case of the banded texture which is consistent with the almost regular sinusoidal trajectory of the molecules.

From those two x-ray diffraction patterns, it was found that orientation of molecular chains of stretched film without banded texture was higher than that of film with banded texture and also it is not negligible to form the oriented crystallite by the strain induced oriented crystallization. It can be suggested from all these results that strain-induced crystallization will be one of the important factors of banded texture formation.

Thermal Stability of the Banded Textures. The produced banded textures of the films of the polymer-2 were very stable in the wide temperature range from room temperature to high temperature just before the crystal melting point.

When polymer-2 film with banded texture was heated up to its nematic mesophase, banded textures started to disappear with crystal melting and completely disappeared at the mesophase (132°C Fig. 5(a)). At this temperature, there was no specific morphological pattern but high birefringence with polarized light and the brightness of this birefringence was changed and repeated from black to white with 45° rotation angle under crossed polarizer. From this phenomenon, it can be suggested that the orientation of the molecular chains was sustained at this temperature.

This film was cooled down slowly with 5°C/min and when the temperature was right below the crystal melting point, banded textures began to appear again and this banded texture became apparent, sharp and regular at 125°C as shown in Fig. 5(b). Further cooling of this sample to room temperature resulted in the formation of the less regular banded texture in Fig. 5(c) than that at 125°C as described above.

Also after heating the polymer-2 film with banded textures to its isotropic phase, banded textures were reappeared on the cooling to room temperature. However, the regularity of produced banded texture became less than that of the banded textures produced on the cooling from the mesophase as shown in Fig. 5(d).

From this thermal stability study of banded texture, it was found that banded texture is very stable at high temperature just below crystal melting point and reproducible with cooling from the mesophase as well as from the isotropic phase. This reproducibility of banded texture with a variation of the temperature means some kind of memory effect, which was also mentioned but could not be proved by the Mao Xu et al.9

The reproducibility of the banded texture by
the cooling from isotropic phase suggests that the macroscopic order of parallel aligned molecules was sustained even at isotropic phase. This phenomenon may be explained or may support the non-equilibrium residual short-range nematic like order in the isotropic phase up to several minutes after the nematic to isotropic transition has occurred. The residual short range nematic like order may act as trigger to form the banded texture during the cooling to room temperature.

CONCLUSIONS

For the formation of the banded textures from the thermotropic liquid crystalline polymers, the zigzag arrangement of macromolecules produced by the annealing of the stretched film is one of the major factors. The zigzag arrangement of macromolecules could be resulted from the forced thermal relaxation of the straight oriented macromolecules due to the elasticity.

Another factor for the formation of the banded textures will be the oriented crystallites formation in the oriented films. Because banded textures were always developed and completed by the cooling from the crystalline melting temperature and the banded textures were not completed at the nematic mesophase temperature, the oriented crystallite, produced by the orientation induced crystallization is not negligible in the banded texture formation.

REFERENCES