

## 열방성 주축 액정 폴리 에스터의 Isotropic상에서의 비평형 Excess Order와 이들과 Banded Texture와의 상관 관계에 대한 연구

제 갈 중 건<sup>†</sup> · 이 규 호 · A. Blumstein<sup>\*</sup>

한국화학연구소, 고분자 소재부, 분리소재팀

(1994. 3. 9 접수)

## Study on the Non-Equilibrium Excess Order in the Isotropic Phase and Its Correlation with Banded Textures of the Thermotropic Main Chain Liquid Crystalline Polyester

Jonggeon Jegal<sup>†</sup>, Kew-Ho Lee, and A. Blumstein<sup>\*</sup>

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

<sup>\*</sup>Polymer Science Program, Department of Chemistry, University of Massachusetts, Lowell,  
Mass 01854, USA

(Received March 9, 1994)

**요 약 :** 4,4'-Dihydroxy- $\alpha$ -methyl stilbene을 mesogen으로 이용하여 제조된 상대적으로 높은 분자량( $M_n=56,500$ g/mol)을 가진 주사슬 열방성 폴리에스터를 이용해서 isotropic phase에서의 잔여 nematic order를 연구하였다. Isotropic phase에서 냉각 되면서 다시 생성되어지는 banded texture의 재현성(memory 효과)을 연구 하였으며 이와 isotropic phase에서의 잔여 nematic order와의 상관관계를 또한 연구 하였다. 고분자 샘플들은 isotropic phase인 247°C에서 일정시간 동안 annealing 후 빠른 속도로 0°C까지 냉각되어졌다. 그 고분자의  $T_{n/i}$ ,  $T_{k/n}$ ,  $\Delta H_{n/i}$  그리고  $\Delta H_{k/n}$  들은 annealing 시간이 길어짐에 따라 감소 하였다. 그러나 이들 감소한  $T_{n/i}$ ,  $T_{k/n}$ ,  $\Delta H_{n/i}$ , 그리고  $\Delta H_{k/n}$  들은 nematic mesophase에서 10시간동안 annealing함으로써 원상 복귀 되었다. Banded texture도 isotropic phase에서 사라졌다가 냉각 도중에 다시 나타났다.

**Abstract :** The excess nematic order in isotropic phase of the thermotropic liquid crystalline polymer was studied with a polyester based on the 4, 4'-dihydroxy- $\alpha$ -methylstilbene as mesogen with a relatively high molecular weight( $M_n=56,500$ g/mol). The reproducibility (memory effect) of the banded texture on the cooling from the isotropic phase was studied and correlated with excess nematic order in isotropic phase. The polymer samples were annealed at the isotropic phase(247°C), followed by quick cooling to 0°C, for different periods of time. The  $T_{n/i}$ ,  $T_{k/n}$ ,  $\Delta H_{n/i}$  and  $\Delta H_{k/n}$  of the polymer were decreased with the increasing annealing time. However, the decreased  $T_{n/i}$ ,  $T_{k/n}$ ,  $\Delta H_{n/i}$  of the polymer were recovered by the annealing at the nematic mesophase of the polymer for 10 hours. The banded texture of the polymer sample, disappeared at the isotropic phase, also reappeared on the cooling.

## INTRODUCTION

The thermotropic liquid crystalline main chain polymers show many interesting thermal behaviors and morphological changes according to the different thermal history. Especially, those polymers with high molecular weights exhibit different thermal behaviors from low molecular weight one. In the previous paper published by Keller and coworkers<sup>1</sup>, interesting results on the non equilibrium excess order in the isotropic state of main chain liquid crystal forming polymers, as a new phenomenon, from the random copolyether containing  $\alpha$ -methylstilbene mesogen were published. They only speculated that the memory of the preceding nematic order is stored in the isotropic state for some periods of time.

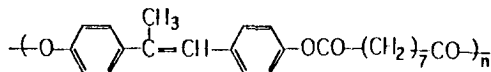
The thermal properties of thermotropic liquid crystalline polymers such as transition temperatures and enthalpy changes in the mesophase transitions will have good relationship with changes in morphology. Of changes in morphology, the banded texture is a good candidate for the study on the correlation of non-equilibrium excess order in the isotropic state with morphology because the banded texture is very closely related to the orientation of macromolecules. The banded texture is one of the structural and morphological characteristic features of oriented liquid crystalline polymers.<sup>2-5</sup> It is generally accepted idea that the banded texture is due to the highly oriented molecule with sinusoidal conformation prepared by the shear application on the liquid crystalline polymer at its nematic mesophase followed by the rapid cooling to low temperature.<sup>5</sup>

In this paper, the non-equilibrium states in transitions from nematic phase to isotropic phase and from crystal phase to nematic phase were investigated with a thermotropic liquid crystalline main chain polyester based on 4,4'-dihydroxy- $\alpha$ -methylstilbene and azelaoyl chloride. The banded texture behavior according to the temperature of the oriented films were studied and

correlated with the non-equilibrium excess nematic order in the isotropic phase of the polyester to prove the existence of the non-equilibrium excess nematic order in isotropic phase of the thermotropic liquid crystalline polymers.

## EXPERIMENTAL

**Materials.** Thermotropic liquid crystalline semiflexible main chain polyester based on the 4,4'-dihydroxy- $\alpha$ -methylstilbene as mesogen was used in this study;



The polyester was synthesized by the interfacial polymerization of 4,4'-dihydroxy- $\alpha$ -methylstilbene with azelaoyl chloride in the presence of the base catalyst.<sup>6</sup> The molecular weight of this polyester was 56,500 g/mole(Mn).<sup>6</sup> The crystal-nematic transition temperature( $T_{k/n}$ ) of this polymer was 174.5°C and the nematic-isotropic transition temperature( $T_{n/i}$ ) was 217°C.

**DSC Study.** In order to study the thermal properties of the polymer samples with different thermal histories, a Perkin-Elmer Differential Scanning Calorimeter(DSC) (model:DSC-2C) was used.

Five polymer samples were prepared as follows; Five aluminum DSC sample pans containing approximately 10 mg of the polymer sample were prepared. Each sample pan was located in the sample holder of the Perkin-Elmer DSC and heated to 247°C, which was 13°C higher than the end of the transition temperature from nematic to isotropic phase, with a heating rate of 20°C/min. At this temperature, each sample was annealed for 1, 2, 4, and 8min, respectively. After annealing, every samples were rapidly cooled to 0°C by the chiller attached to the DSC machine. The one of the samples, annealed at 247°C for 8 min followed by quick cooling, was

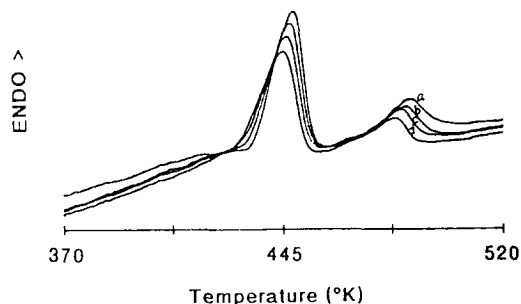
heated again to 187°C (nematic mesophase) and kept at this temperature for 10 hours for annealing. This sample was also rapidly cooled to 0°C. The prepared five samples with different thermal histories were scanned on DSC with a heating rate of 20°C/min. From the each heating scan, maximum peak temperatures of isotropization and crystal melting, and enthalpy changes ( $\Delta H$ ) of each transition were taken.

**Preparation of the Film with Banded Textures.**<sup>7</sup> The free standing cast film in the nematic glass state was elongated by the cold drawing with a draw ratio  $\lambda=3$  at room temperature. This elongated film was then positioned on a micro-hot stage equipped with a calibrated thermometer and heated up to its mesophase temperature (187°C). After keeping at that temperature for five minutes, the film was cooled down to 0°C by slow cooling and banded texture was developed in the film.<sup>7</sup>

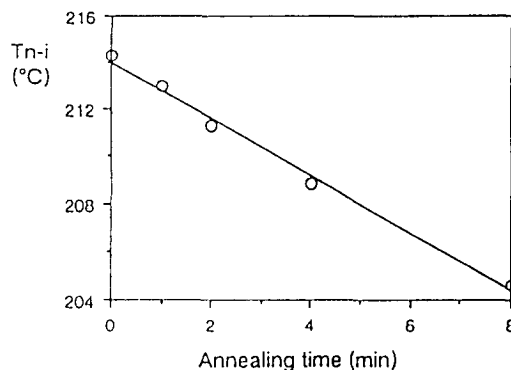
**Heat Treatment of the Banded Textured Film.** The film with banded textures was heated to 247°C (isotropic phase) and kept for three minutes at this temperature. And the film was quenched to 0°C. The banded texture of the film was studied with Leitz Ortholux II polarizing microscope equipped with a Mettler FP-5 heating stage.

## RESULTS AND DISCUSSION

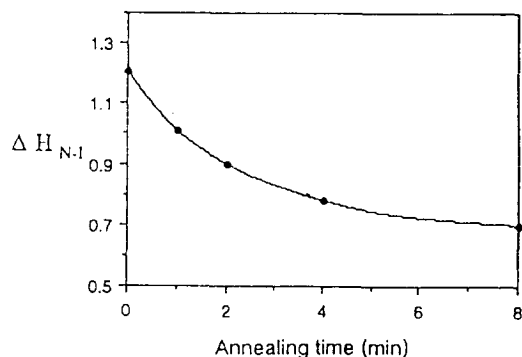
**Non-Equilibrium Excess Order in the Isotropic Phase.** Fig. 1 shows DSC thermograms of polymer samples with different holding time in the isotropic phase (247°C) followed by rapid cooling to 0°C. The isotropization temperature ( $T_{n/i}$ ) and enthalpy change ( $\Delta H_{n/i}$ ) both decreased with increasing annealing time at the isotropic phase (247°C) followed by rapid cooling to 0°C. The isotropization temperature ( $T_{n/i}$ ) and enthalpy changes ( $\Delta H_{n/i}$ ) both decreased with increasing annealing time at the isotropic phase (247°C). The trends of decreasing isotropization temperatures and enthalpy changes are shown



**Fig. 1.** DSC heating thermograms for the polyester samples with different annealing time at 247°C (above the isotropization temperature); 0 min (a), 1 min (b), 2 min (c), and 4 min (d).



**Fig. 2.** The N-I transition temperatures ( $T_{n/i}$ ) of the polyester vs. annealing time in the isotropic phase (247°C).



**Fig. 3.** The enthalpy changes ( $\Delta H_{n/i}$ ) in the N-I transition of the polyester vs. annealing time in the isotropic phase (247°C).

**Table 1.** The Transition Temperatures( $T_{n/i}$ ) and Enthalpy Changes( $\Delta H_{n/i}$ ) of the Polyester as a Function of Annealing Time

Holding time (min)	$T_{n/i}$ (°C)	$\Delta H_{n/i}$ (cal/g)
0	214.3	1.21
1	213.0	1.01
2	211.3	0.90
4	208.9	0.78
8	204.6	0.70
10hrs*	212.6	0.96

Holding at 247°C (isotropic phase)

\* Annealing at 187°C (nematic mesophase) for 10 hrs

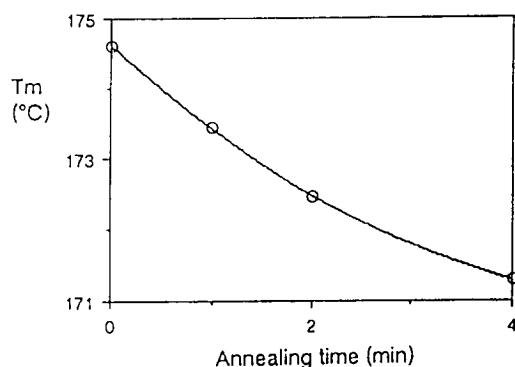
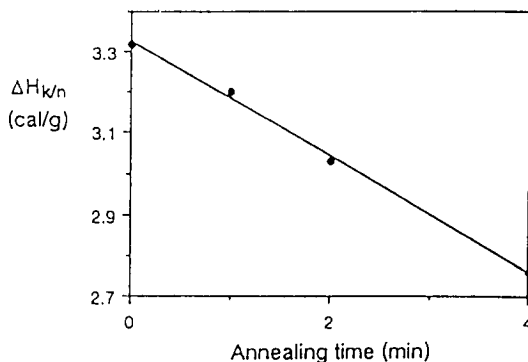
in Fig. 2 and 3, respectively. However, when the sample, annealed at the isotropic phase for 8 minutes followed by rapid cooling to 0°C, was annealed again at the nematic mesophase(187°C) for 10 hours, the isotropization temperature and enthalpy change were recovered(98% in isotropization temperature and 79% in enthalpy change of fresh sample)(see Table 1.).

The behavior of melting temperatures and enthalpy changes are shown in Fig. 4 and 5, respectively. The crystal to nematic transition temperature( $T_{k/n}$ ) and the enthalpy change( $\Delta H_{k/n}$ ), associated with this transition, both decreased with increased annealing time at the same condition mentioned above.

However, when the polymer sample was cooled to 0°C slowly(20°C/min) instead of the quick cooling after annealing in isotropic phase(247°C) for a certain period of time, the  $T_{n/i}$  and  $T_{k/n}$  were unchanged and independent of the holding time at the isotropic phase(247°C). The enthalpy changes( $\Delta H_{n/i}$  and  $\Delta H_{k/n}$ ) of each transition were not changed either.

The decrease in  $T_{n/i}$ ,  $T_{k/n}$ ,  $\Delta H_{n/i}$  and  $\Delta H_{k/n}$  with the annealing time(followed by the quick cooling) can be due to a "memory of order" in the isotropic phase and "memory of disorder" in the nematic phase.

From the results of this experiment, it appears that annealing in the isotropic phase followed

**Fig. 4.** The K-N transition temperatures( $T_{k/n}$ ) of the polyester vs. annealing time in the isotropic phase(247°C).**Fig. 5.** The enthalpy changes( $\Delta H_{k/n}$ )in the K-N transition of the polyester vs. annealing time in the isotropic phase(247°C).

by quick cooling lowers the degree of the crystallinity and the degree of crystal perfection(decrease in  $T_{k/n}$  and  $\Delta H_{k/n}$ ). The decrease of melting point and the corresponding  $\Delta H_{k/n}$  with increasing annealing time at the isotropic phase can be explained by the slow transition rate from nematic mesophase to the isotropic phase. It can be speculated that because the rearrangement of macromolecules from nematic order to isotropic order is slow, some elements of the nematic order still persist in the isotropic state at 247°C only 13°C higher than  $T_{n/i}$ . This "excess" nematic order will be transformed to isotropic disorder during annealing and the randomness of the

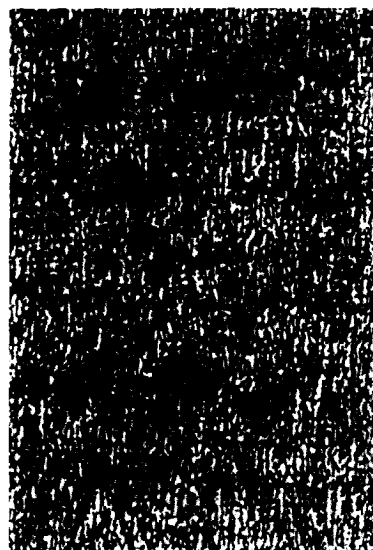
resulting isotropic phase will be increased with increasing annealing time at this temperature. Conversely, the "memory" of randomness in the isotropic phase will disturb the melt crystallization during the rapid cooling, leading to the less crystallinity and less perfection of produced crystals. This phenomenon may result in the decrease of the  $T_{k/n}$  and  $\Delta H_{k/n}$  as shown in Fig. 4 and 5.

The decreasing isotropization temperatures and lower enthalpy changes with increasing holding time at the isotropic phase also may be due to the slow arrangement of macromolecules to give a nematic order in the nematic mesophase. Because the arrangement rate of macromolecules to form nematic order after crystal melting is slow, some of the isotropic order resulting from the amorphous phase may remain in the nematic mesophase and this excess isotropic order will decrease the isotropization temperature and enthalpy change. Similarly, an amorphous phase results from the quenching of the isotropic phase for increasing periods of time. The degree of the nematic mesophase will increase and  $T_{n/i}$  and  $\Delta H_{n/i}$  will decrease.

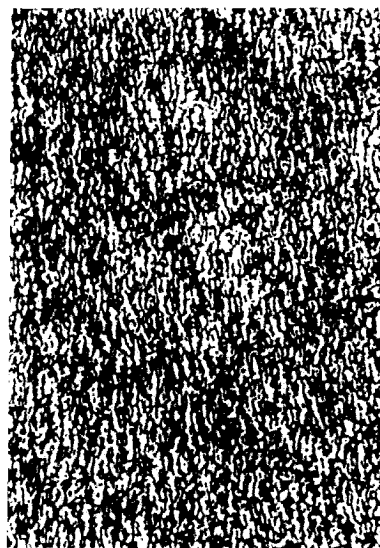
This phenomenon of "memory" becomes more apparent with high segmental relaxation times. The high segmental relaxation times are a characteristic of polymers of high molecular masses producing media of high viscosity such as described in this study.

**Banded Texture Behaviors with Temperature Changes.** Banded textures have been found in a wide range of liquid crystalline polymers including aromatic polyamides, cellulose derivatives, and aromatic polyesters.<sup>2-5</sup> It is generally accepted that they are a general feature of liquid crystalline polymers oriented by flow.

Banded textures obtained for the polymer film were very stable in a wide temperature range (from room temperature to temperature approaching  $T_{k/n}$ ). After heating of banded textured film to  $T_{n/i}$  followed by quenching, the



(a)



(b)

**Fig. 6.** The polarizing photographs of the banded texture of the polyester (a) before heat treatment (b) after heat treatment at the isotropic (247°C) followed by the rapid cooling to room temperature. (Magnification : x 500).

banded textures persisted as shown in Fig. 6.

The persistence of banded texture on rapid

cooling from the isotropic phase indicates the existence of a memory of order in the isotropic phase. Such effects were also mentioned by the Mao Xu et al.<sup>5</sup> This phenomenon may qualitatively indicate the non-equilibrium residual short range nematic order in the isotropic phase. The residual short range nematic order may act as a trigger to form the banded texture during the cooling cycle. It is obvious that if thermodynamic equilibrium in the isotropic phase is established quickly, every macromolecules would be conformationally disordered and this randomly disordered system could not produce the banded textures with rapid cooling. Thus the formation and persistence of banded textures on quenching from isotropic state is an evidence of memory of the preceding nematic order stored in the isotropic phase. While any long range orientational order is clearly lost, as evidenced by the birefringence in the oriented sample in the isotropic phase under polarizing microscope, it would appear that a significant degree of local order is preserved after transition. Such parts of residual short range nematic order acts as unuclei for the formation of oriented nematic domains along the elongation direction of the film on the cooling.

## CONCLUSIONS

The thermodynamic equilibrium of the ther-

motropic main chain liquid crystalline(LC) polymer in the nematic mesophase and isotropic phase was not fast enough to be in equilibrium during the heating scan on DSC at a heating rate of 20°C/min. The isotropic phase of thermotropic main chain LC polymer was in a non-equilibrium state of considerable excess short-range order. This excess order was a function of time. The non-equilibrium state of the isotropic phase with the excess short-range order was responsible for the production of the banded texture during the cooling from the isotropic phase of the oriented film.

## REFERENCES

1. J. L. Feijeo, G. Ungar, A. Keller, and V. Persec, *Polymer*, **31**, 2019 (1990).
2. A. M. Donald, C. Viney, and A. H. Windle, *Polymer*, **24**, 155 (1983).
3. Y. Nishio, T. Yamane, and T. Takahashi, *J. Polym. Sci., Polym. Phys. Edn.*, **23**, 1053 (1985).
4. S. E. Bedford and A. H. Windle, *Polymer*, **31**, 616 (1990).
5. X. Liu, D. Shen, L. Shi, and M. Xu, *Polymer*, **31**, 1987 (1990).
6. J. G. Jegal, C. H. Lin, and A. Blumstein, *Polymer Prep.*, **32**, 215 (1991).
7. J. G. Jegal and A. Blumstein, in preparation.