Melting and Recrystallization during Mesophase Transitions of a Thermotropic Liquid Crystalline Polymer

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ABSTRACT: Wide-angle X-ray diffraction (WAXD), polarized optical microscopy, and differential scanning calorimetry (DSC) have been employed to elucidate the mesophase transitions in a thermotropic liquid crystalline polymer (LCP) prepared by copolymerization of Bisphenol E diacetate, isophthalic acid, and 2,6-naphthalenedicarboxylic acid. A single glass transition temperature (T_g) and double endotherms were discerned in the DSC scans of the neat LCP. The dual melting peaks, commonly attributed to the fast and slow melting transitions, manifest strong dependence on thermal history. Annealing slightly above the T_g transition temperature has shown the occurrence of a solid–solid crystal transformation. However, annealing in the vicinity of melting temperatures exhibits a loss of positional ordering of solid crystals, then reorganization occurs due to the large anisotropy of rod-like macromolecules. Finally, the terminal melting transition takes place. This kind of order–disorder transition of mesophase structures is similar to the phenomenon of melting–recrystallization in some flexible chain crystals and will be discussed based on new evidence from isothermal WAXD studies.

Introduction

In recent years, the phenomenon of premelting transitions in thermotropic liquid crystalline polymers (LCP) has received considerable attention in the polymer community. The appearance of dual melting endotherms has been reported for a number of LCPs.[1,2] These dual peaks have been originally assigned to the fast and slow transitions associated with the melting of two types of crystals to a mesomorphic state.[3] Winter and co-worker[4] observed a high-temperature melting peak during isothermal annealing just above the original melting endotherm. Later, Cheng et al.[5] found the occurrence of solid–solid crystal transformations in the isothermal WAXD scans of a polyester-based LCP as well as Vectra (a copolymer of hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid), namely the phase transitions from hexagonal to a more stable orthogonal structure. In the case of hydroquinone-based LCP (Granlar), a transformation was found from monoclinic I to monoclinic II[6] when LCPs were annealed at temperatures appreciably lower than those melting transitions. The authors concluded that it is this solid-to-solid crystal transformation which is responsible for the dual melting peaks. There are also numerous rheological studies[4,7–10] in the vicinity of the melting transitions of thermotropic LCPs, indicating the flowability of rigid chains during the crystal-phase transformations. Wissbrun[9] demonstrated that melt viscosity and dynamic shear modulus of an LCP increase with increasing shear rate, which has been inferred as shear thickening. The presence of new crystals may be responsible for this enhanced viscosity with shear rate or temperature.

An alternative interpretation for the dual melting transitions of LCP is a melting–recrystallization phenomenon commonly observed in some flexible chain crystals;[11,12] however, there is no experimental evidence yet to support this concept in rigid chain crystals. Conceptually, it is quite plausible that some structural changes might occur during the melting transition in which the original crystals would melt first, either partially or completely, then reorganization of stiff LCP chains would take place to form a new type of crystal due to the large anisotropy of the LCP chains. During the course of manuscript revision, a paper by Lin and Winter[13] appeared in which a high-temperature recrystallization process was reported for the copolymer of HBA-HNA. The detailed methodology and LCP materials used in their study were different from the present work, but we reached the same conclusion that recrystallization of LCP phase occurred during annealing in the vicinity of melting transition. In this paper, a direct evidence of the melting–recrystallization in a thermotropic LCP is presented on the basis of the time-dependent WAXD results.

Experimental Section

The thermotropic LCP used in this study was kindly supplied by Monsanto Co. It was prepared by copolymerization of Bisphenol E diacetate, isophthalic acid, and 2,6-naphthalenedicarboxylic acid in a monomer ratio of 50:40:10 (BPE:I:N).[14] DSC scans were acquired at 20 °C/min under nitrogen circulation using a Du Pont thermal analyzer (Model 9900) with a heating module (Model 910). Indium standards were used for temperature calibration. Wide-angle X-ray diffraction scans were acquired on a 12-kW Rigaku rotating anode with a pin hole collimator. The generator was operated at 150 mA and 40 kV using a Ni-filtered Cu Kα line. The wavelength of X-rays was 1.5406 Å. The 2θ scans were conducted from 10 to 40° at a scan rate of 10°/min in an early part of time resolved studies, but at 0.5°/min for the longer time and static measurements.

Optical micrographs were obtained on a Nikon polarized microscope (Model Optiphoto Pol XTP-11) using a heating stage (TH-600 Type, LINKAM Scientific Co.) controlled at an arbitrary heating and cooling rate of 10 °C/min.

Results and Discussion

Figure 1 depicts the DSC traces of the as-received LCP annealed at various temperatures. A glass transition temperature (T_g) is located at about 110 °C while the dual melting endotherms appear in the vicinity of 270–290 °C in the as-received LCP.[15] When the LCPs were annealed for 30 min at various temperatures, the T_g remains fairly stationary, but the low-temperature endothermic peak shifts drastically to higher temperatures with increasing annealing temperature, whereas the higher melting peak shows little or no movement. Consequently, the two peaks merge together with increasing annealing temperature.

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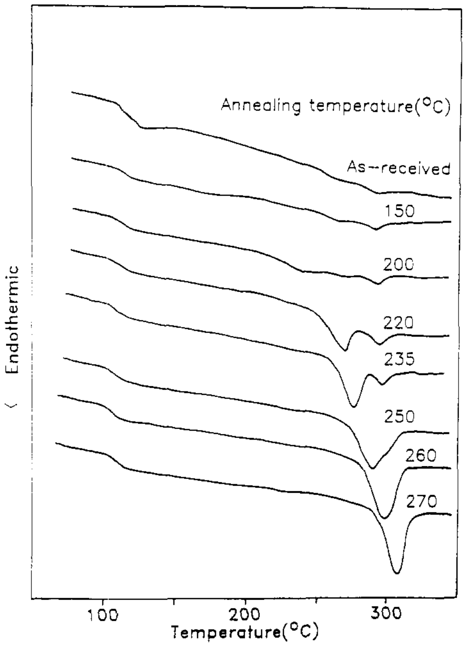


Figure 1. DSC traces of a thermotropic LCP annealed for 30 min at various temperatures.

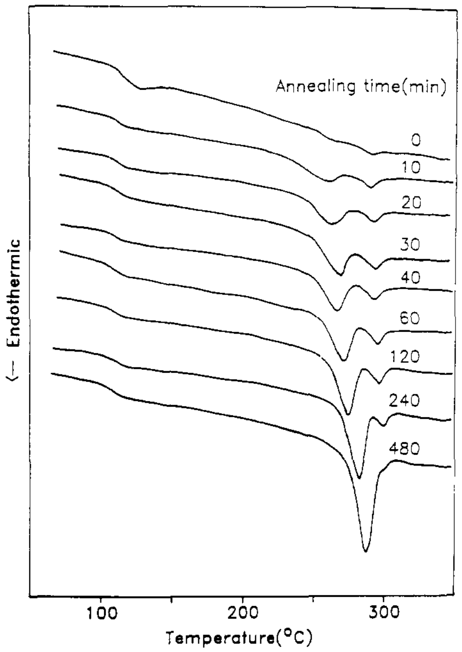


Figure 2. DSC traces of a thermotropic LCP at 220 °C for various annealing time.

This trend can also be discerned in the isothermal annealing at 220 °C for various times (Figure 2), except that the merged peak temperature is appreciably lower compared to that of the high-temperature annealing (Figure 1). Although the revelation of pronounced dual endotherms with annealing time and temperature appears similar, the movement of the low temperature is more remarkable in the case of the high-temperature annealing. These observations suggest that the low-temperature annealing and high-temperature annealing may have some differences in their premelting behavior.

Isothermal WAXD studies were undertaken by a temperature jump method, i.e., rapidly transferring the specimen from ambient to 270, 300, 310, and 320 °C. The evolution of WAXD peaks were followed as a function of elapsed time. As shown in Figure 3, three small but distinct peaks corresponding to d spacings of 5.7, 4.0, and 32. Å appear in the equatorial WAXD scan of the original LCP. These equatorial (*hk*0) planes cannot be indexed without knowing its unit cell structure. However, these WAXD peaks correspond to the (010), (200), and (210) reflections of a monoclinic crystal of this LCP fiber. The detailed analysis of the unit cell determination using highly oriented LCP fiber will be presented in a future publication.[14] The (110) peak is not distinct as it is hidden under the amorphous halo. The three crystalline peaks disappear completely in 4 min during the *T* jump to 300 °C. An amorphous-like scattering halo revealed by annealing at a lower angle than those of the diffuse halo of the as-received LCP which may be attributed to the increase of the average intermolecular distances associated with thermal expansion of the materials. The revelation of amorphous-like scattering halo suggests a complete destruction of the long-range positional order, but orientational order could persist in such stiff LCP systems because the random arrangement of rod-like molecules would be thermodynamically unfavorable in a condensed phase. As shown in Figure 4, the light scattering studies showed the "+" type four-lobe pattern in the H_v (horizontal polarizer with vertical analyzer) configuration, suggestive of the presence of orientation fluctuations during premelting transition.[17] This observation has led us to believe that the amorphous-like scattering halo may be due to the anisotropic mesophase structure rather than the random amorphous phase.

With further increase of annealing time, the rod-like chains probably would self-associate and align themselves due to their large aspect (length/diameter) ratio, resulting in the reappearance of some distinct WAXD peaks. These WAXD peak positions are located at smaller angles than those at ambient temperature due to thermal expansion of crystal lattices. The peaks concurrently intensify with elapsed time due to the continued crystallization as rigid chains have sufficient mobility to flow and reorganize. The phenomenon is suggestive of recrystallization.[13] It is, however, unclear whether the new WAXD peaks arise from solid crystals or from smectic liquid crystals. It should be pointed out that shear modulus as well as melt viscosity increase with increasing annealing time and temperature in our recent dynamic rheological studies.[18] The increase of melt viscosity suggests that some ordered structures develop, eventually leading to a situation that rheological measurements become almost impossible with continued annealing time. Judging from the large amorphous-like scattering halo and the small crystalline peaks, the amount of solid crystals thus formed must be very low. The large fraction of nematic mesophase can certainly provide some flowability of rigid chains, but the new crystal formation would make such flow difficult.

In general, WAXD peaks from smectic mesophase are expected to be broader than those arising from solid crystals. Thus, the formation of smectic structure is highly unlikely as the observed WAXD peaks are not necessarily broader than those at ambient temperature. Moreover, no scattering peak was observed in our preliminary small-angle X-ray scattering experiments (Figure 5), thus suggesting the lack of smectic mesophase. The increase in viscosity and the reappearance of WAXD peaks at elevated temperatures may be due to high-temperature recrystallization,[13] in which the crystals thus formed may be of insignificant amount. Upon cooling to room temperature, the original three WAXD peaks are recovered, while a new peak, corresponding to a d spacing of 3.5 Å, appears which is probably frozen-in during cooling.

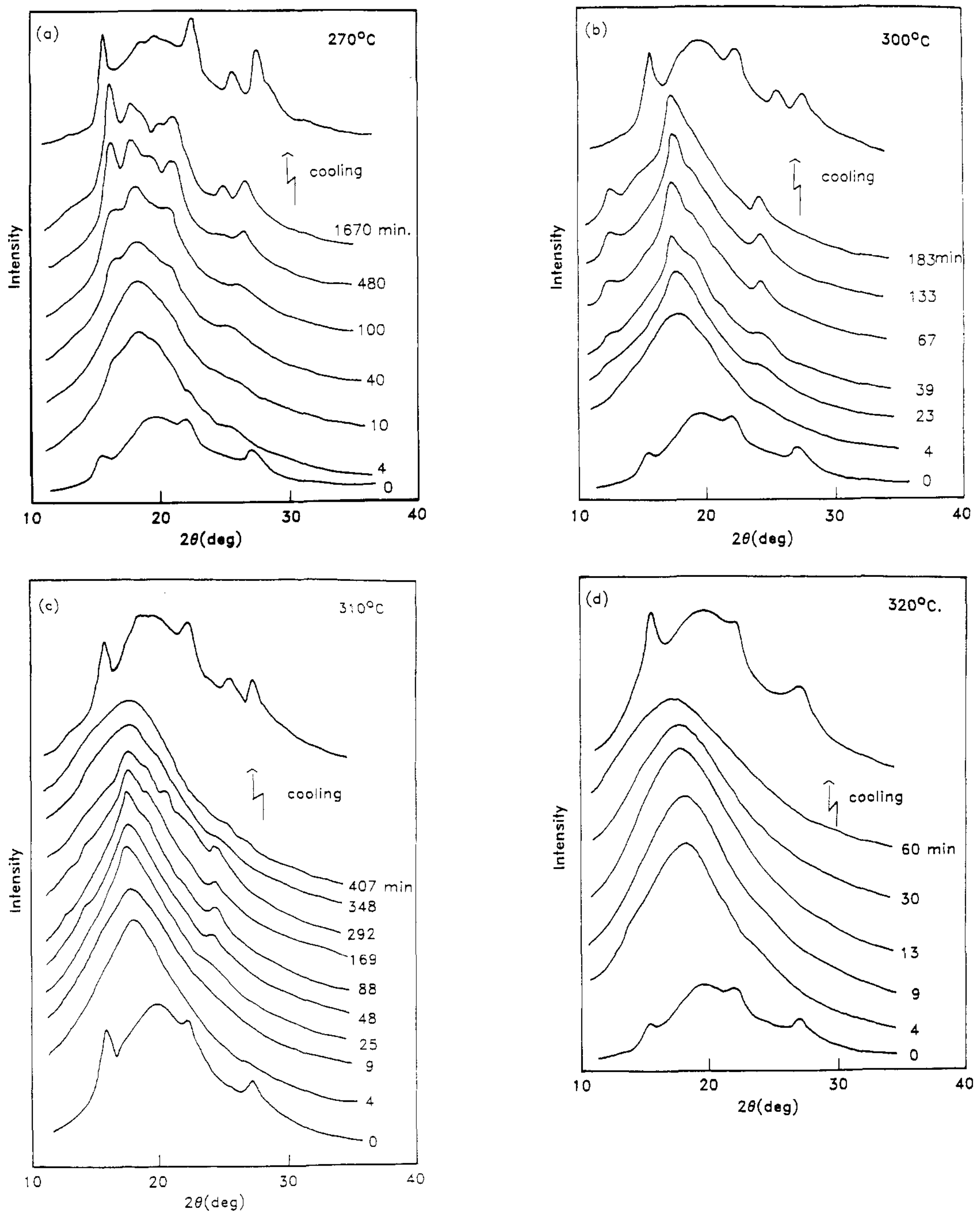
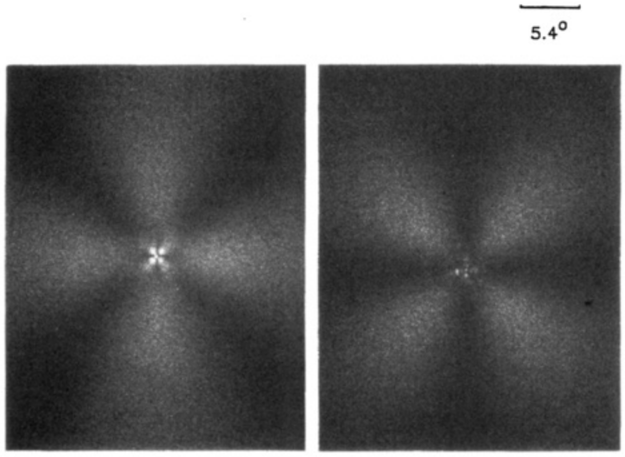


Figure 3. Time evolution of WAXD scans of bulk LCPs at 270, 300, 310, and 320 °C, exhibiting the phase transition of solid crystal–nematic–new crystal as a result of melting–recrystallization.

This behavior can be further discerned in the *T* jump to 270 °C, where the solid-crystal mesophase transition occurs as a longer time (Figure 3a). If the isothermal annealing temperature is sufficiently low, there is a possibility of incomplete melting of the original crystals. It is plausible that the partially molten amorphous rigid chains may reorganize to form a new crystalline phase as evident in the DSC scans. The partial melting of the original crystals and the subsequent formation of mesophase crystals may be reminiscent of the crystal–crystal phase transformation proposed by Cheng and co-workers[5,6] for the low-temperature annealing of other LCPs. The only difference between the low-temperature annealing of Cheng et al. and high-temperature annealing of the present study is that the positional ordering is totally lost in the latter due to higher mobility of LCP chains at elevated temperatures. It should be emphasized that the premelting transition of solid crystal–nematic–new crystal would dominate at the high-temperature annealing before the terminal melting transition takes place. Upon cooling back to ambient temperature, the original crystal structure is recovered, but an additional peak arising from a different crystal form can also be discerned. If one rescans DSC of such heat-treated samples, the presence of two types of crystals would naturally result in the dual melting endotherms. It should be cautioned that the dual endotherms cannot be assigned exclusively to the melting of two types of crystals as the melting–crystallization can also show dual peaks.

At a *T* jump temperature of 310 °C (Figure 3c), the solid crystal–nematic–new crystal formation occurs in a similar fashion at 300 °C. As time proceeds further, terminal melting occurs suggestive of a total loss of positioning ordering. In the case of 320 °C *T* jump (Figure 3d), there is no memory of melting recrystallization of LCP, thus the WAXD peaks simply disappear with isothermal annealing



(a) (b)

Figure 4. (a) H_v and (b) V_v scattering patterns from nematic liquid crystalline state (300 °C) of LCP.

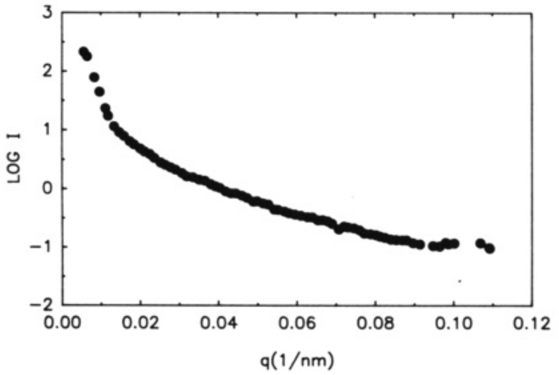
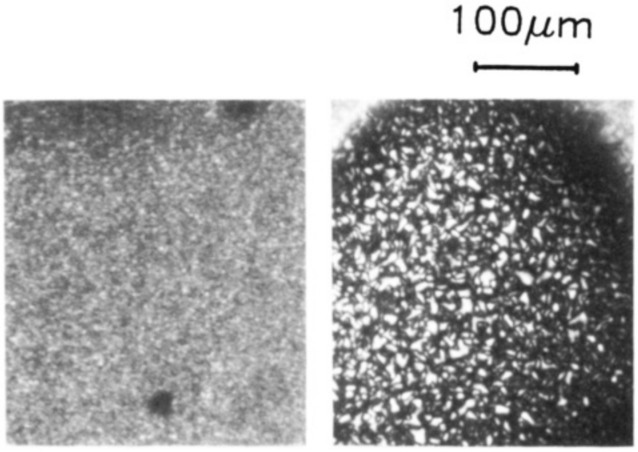


Figure 5. Small-angle X-ray scattering profile of LCP obtained at 300 °C.

time. When the LCP is quenched to room temperature, only the original crystalline WAXD can be discerned without a new peak. These WAXD results are reproducible in subsequent heating cycles.

Above the terminal melting temperature (320 °C), it is essential to find out whether LCP molecules are in isotropic melt or in nematic mesomorphic states. We therefore heat a thin LCP specimen up to 370 °C under polarized optical microscope. Isotropic phase appears around 360–370 °C. Upon cooling back to 330 °C, some disclination textures develop and the size grows with time, thus confirming the nematic structure (Figure 6). Since the isotropic phase transition temperature is very close to thermal degradation temperature of 370–380 °C, a prolonged heating at such temperatures is not recommendable. In a heating scan up to 300 °C, no Schlieren texture developed, but anisotropic entities can be seen under a polarized microscope, suggesting the existence of disordered crystals.



(a) (b)

Figure 6. Polarized optical micrographs obtained (a) during heating to 300 °C and (b) after cooling from 370 to 330 °C. The heating and cooling rate was 10 °C/min.

In summary, we observed that the premelting transition in this thermotropic LCP is a melting–recrystallization process. At high-temperature annealing near the melting transition, the solid crystals lost the positional ordering. Then the rigid macromolecules reorganize to form a new crystal structure and finally terminal melting to a mesophase occurs. This kind of solid crystal–nematic mesophase–new crystal phase transition is similar to the melting–recrystallization observed in some conventional linear flexible crystalline polymers. Annealing far below the melting temperatures may lead to incomplete melting of solid crytals, and then the partially molten LCP chains may form a new crystal phase. This process may be similar to the crystal–crystal phase transition claimed by Cheng et al. In our opinion the melting–recrystallization may be responsible for the dual DSC endotherms in this thermotropic LCP.

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