

STUDIES ON THE MORPHOLOGY OF THERMOTROPIC POLYESTER DURING TRANSITIONS BETWEEN ISOTROPIC AND ANISOTROPIC MELTS

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ABSTRACT

The morphology of a thermotropic aromatic polyester during the transitions between isotropic and anisotropic melts was studied by means of polarizing microscopy and small angle light scattering techniques. Both transition processes were found to be composed of the initiation of a new phase at local places of the old phase matrix and the growth of the new phase domains. A change of Hv scattering patterns was observed in the transition temperature ranges and was explained as the result of heterogeneity of the mesophase system, but not the change in ordering of a homogeneous mesophase.

INTRODUCTION

Thermotropic liquid crystalline polymers are characterized by the existence of one or more mesophases above their melting point. With further increasing temperature the polymers will finally become isotropic at the so-called clearing point. At this critical temperature an equilibrium exists between the anisotropic and isotropic melts. Studies on the morphological changes during the isotropization transition and its counterpart, the liquid crystallization transition from the isotropic melt, will undoubtedly give insight into the characteristic features and formation of polymeric liquid crystals.

Liquid crystal forming polymers may exist in crystalline, amorphous and mesomorphic phases. This complexity is one of the main difficulties in studying polymeric liquid crystals. However in the temperature ranges of transitions between isotropic and anisotropic melts we are only dealing with problems of two phases. Thus it is anticipated that results of these studies could be explained unambiguously and of clear scientific importance.

Polarizing microscopy and small angle light scattering (SALS) are usually used for studying the morphology of liquid crystals. Optical texture of liquid crystalline materials under polarizing microscopy is characteristic for different mesophases and has been observed for many polymer liquid crystals. Although morphological features of polymer samples at temperatures near the transitions have been shown in few cases^[1,3], no data of systematic studies concerning the morphological changes in both the isotropization and liquid crystallization processes of polymer liquid crystals were

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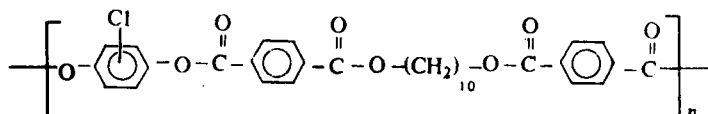
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published. The SALS studies may give information about the ordering of molecular packing within the samples. The Hv scattering patterns of nematic and smectic liquid crystals are circularly symmetric with respect to the incident beam, but usually four-leaf clover patterns are observed for cholesteric mesophase^[4, 5]. An anomaly has been reported for polymeric nematic liquid crystals. The Hv scattering patterns exhibit noncircular symmetry before the isotropization transition in a very narrow temperature range^[1, 6, 7]. This phenomenon has been observed for lyotropic and thermotropic polymers, but its cause is still not explained clearly.

In the present work the morphological features of an aromatic polyester were studied during both transitions between the isotropic and anisotropic melts.

EXPERIMENTAL

An aromatic polyester of the chemical structure:



was prepared from 1, 10-decane bisterephthaloyl chloride and chloro-substituted hydroquinone. Its synthesis has been described elsewhere^[8]. The intrinsic viscosity of the polymer is 0.5 dl/g measured in tetrachloroethane at 25 °C. Thin film specimens were prepared by solution cast. An Olympus polarizing microscope and a SALS apparatus of type LS-1, both with hot stage, were used for morphological studies. The heating and cooling rates were about 2 °C/min and 4 °C/min for the two methods respectively. Thermograms were recorded using a Perkin-Elmer DSC-4. Runs were conducted at a heating rate or cooling rate of 20 °C/min.

RESULTS AND DISCUSSION

Figure 1 shows the thermograms of the polyester sample. Two endothermal peaks were observed at 148 °C and 193.6 °C in the heating process and were attributed as the transition from crystalline to nematic phases T_{KN} and the transition from nematic to isotropic melts T_{NI} respectively. The liquid crystallization exothermal peak was detected at 188 °C (T_{IN}) during cooling the isotropic melt.

The variation of micrograph in the isotropization process is given in Figure 2. At temperatures corresponding to onset of the isotropization endothermal peak in DSC measurements the polarizing micrograph changes quickly from the typical optical texture of nematic phase (Figure 2a) to a bright background with randomly distributed black threads, and dark domains were formed at places of higher thread concentration due to intersection of two or more threads or thread coiling (Figure 2b). The size of the domains shown in Figure 2c is about 4–10 μm. The threads are isotropic, while the dark domains are not completely isotropic, but less anisotropic than the surrounding matrix. The size and darkness of the domains increase with temperature (Figure 2d) and they combine with each other to form continuous isotropic regions. Then the micrograph shows small bright domains embedded in a dark matrix (Figure 2e). The size of them decreases with temperature rapidly, and clear Maltese cross was usually observed before their final disappearance at temperatures above 200 °C.

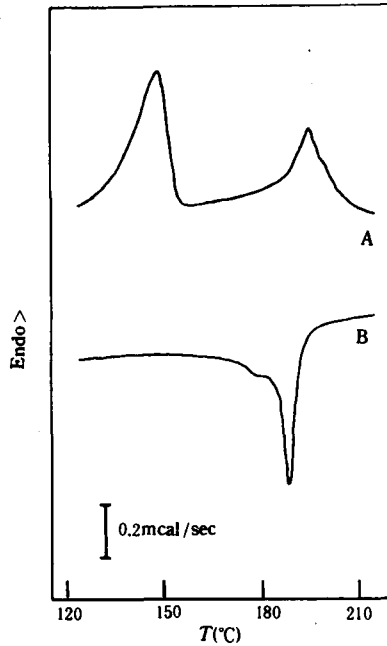


Fig. 1 Thermograms in heating (A) and cooling (B) processes

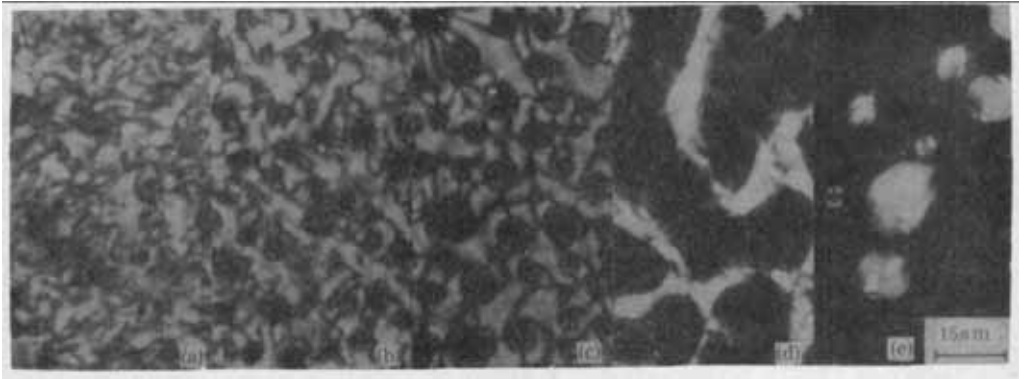


Fig. 2 Polarizing micrographs at different temperatures in a heating process:
a) 156 °C, b) 174 °C, c) 178 °C, d) 183 °C and e) 189 °C

The change of polarizing micrograph in the reverse process, the liquid crystallization from isotropic melt was also observed and is given in Figure 3. At temperatures around 188 °C very small bright spots begin to appear in the dark background, which indicates the initial formation of the mesophase in the isotropic melt. The size of the mesophase domains increases with lowering temperature and is about 5 μ m in Figure 3a. These domains are almost circular in shape, and they exhibit Maltese cross at the primary stage of their appearance. With further lowering temperature these growing domains contact with each other and combine to form larger and larger domains as shown in Figures 3b and 3c. Then the mesophase becomes predominant and form a continuous matrix with isolated dark isotropic regions of irregular

shape. In some cases a secondary initiation of mesophase in the remaining isotropic phase was observed (Figure 3d). Finally the typical optical texture of nematic mesophase is obtained (Figure 3e).

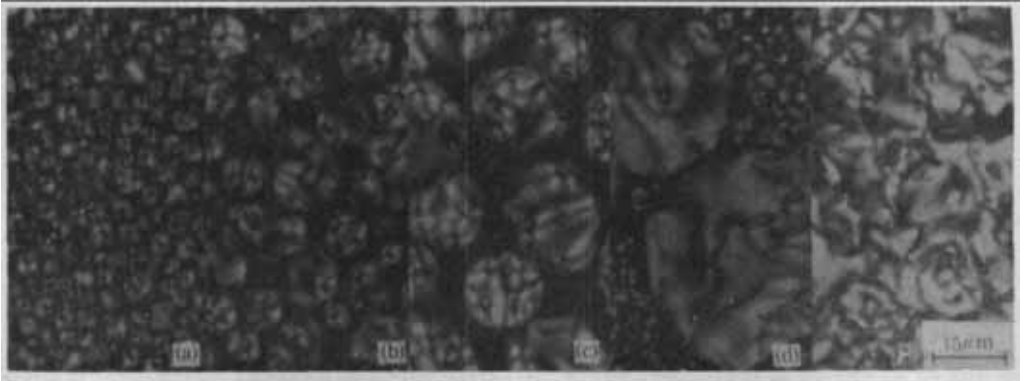


Fig. 3 Polarizing micrographs at different temperatures in a cooling process:
a) 183 °C , b) 180 °C , c) 178 °C , . d) 168 °C and e) 146 °C

Our results of microscopic study indicate that both transitions between the anisotropic and isotropic melts are composed of an initiation of new phase at local places in the old phase matrix and a growth process of the new phase domains. In this sense these transitions are similar to the fusion and crystallization of polymers. It is also clear from the micrographs that the specimens are two-phase in nature during the transitions between isotropic and anisotropic melts. The two phase temperature range is almost consistent with that of the endo- or exo-thermal peaks related to the isotropization and liquid crystallization respectively in the DSC measurements as discussed by Blumstein et al.^[3]. The appearance of isotropic dark threads at the initial stage of isotropization implies the existence of less ordered regions in the mesophase specimens. They are possibly the interfacial layers between mesophase domains resulted from kinetic causes and/or structural defects. The observed Maltese cross in mesophase domains at higher temperatures of both transitions may imply the existence of some portion of long range correlation in orientation ordering within these domains.

The SALS Hv patterns of film specimens at different temperatures are given in Figure 4. Above T_{KN} the specimens become mesomorphic and show circular symmetric Hv patterns at temperatures not close to T_{NI} (Figure 4a). With increasing temperature noncircular symmetry of the scattering pattern appears at about 180 °C (Figure 4b). In addition to a circular scattering spot, extension of scattering intensity along the $\pm 45^\circ$ azimuthal directions can be observed. At temperatures above 190 °C a clear four-leaf clover pattern was detected (Figure 4c). The Hv scattering decreases with further heating and becomes undetectable at temperatures above 200 °C. The observed change of Hv scattering patterns in a heating process near T_{NI} is similar to that reported in the literature^[6,7]. An almost reversible change of scattering pattern was detected in this work during cooling the specimens from the isotropic melt state and is shown in Figure 4, too.

The circular symmetric Hv scattering patterns of this polymer at temperatures above T_{KN} are consistent with the patterns of other nematic liquid crystals and may imply, according to Stein and Wilson^[9], the existence of the so-called random correlation

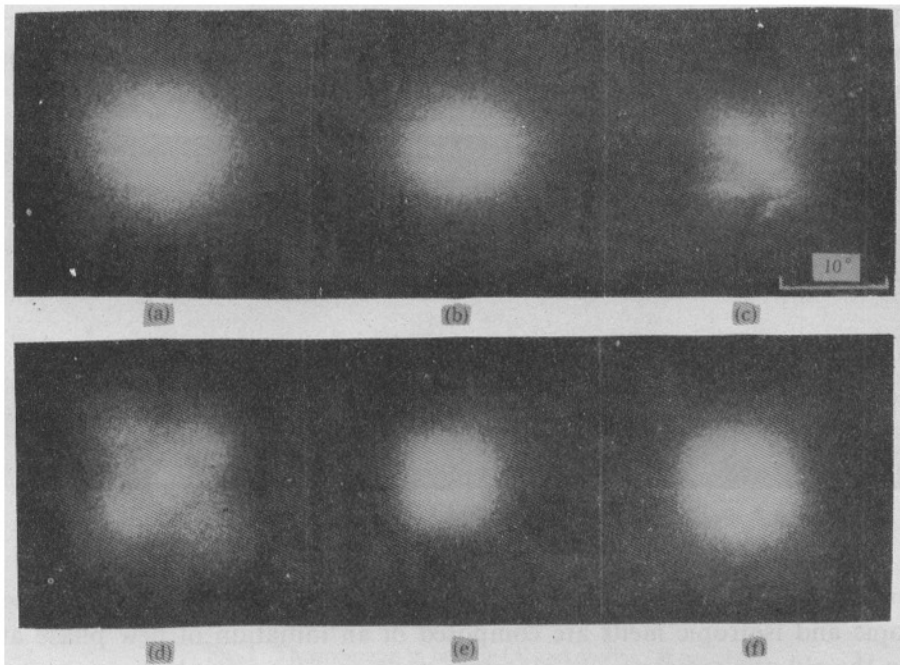


Fig. 4 Hv scattering patterns at different temperatures in heating processes [(a) 155°C, (b) 180°C and (c) 191°C] and cooling [(d) 194°C, (e) 186°C and (f) 178°C]

of orientation fluctuation between the polarizability axes of volume elements in the mesophase. The change of Hv scattering patterns with temperature can not be explained as the results of a transition from nematic to cholesteric mesophases, because transitions between these two mesophases have never been observed for any liquid crystalline materials, and the polyester molecule does not contain asymmetric centers, which are accepted as characteristic structure features for molecules being able to form the cholesteric mesophase.

We suppose that the observed change of scattering patterns around the T_{NI} or T_{IN} transitions is related with the two-phase morphology of the specimens in the transition temperature ranges. According to SALS theory^[10] the amplitude of Hv scattered ray can be expressed as:

$$E_s = K \int (\mathbf{M} \cdot \mathbf{O}) \cos k(\mathbf{r} \cdot \mathbf{S}) d\mathbf{r} \quad (1)$$

Where \mathbf{M} is the dipole moment induced by the incident electric field in the volume element at vector distance \mathbf{r} from the origin of the coordinates. \mathbf{O} is a unit vector lying in the direction of the electric vector of light transmitted by the analyzer $k = 2\pi/\lambda$, and $\mathbf{S} = \mathbf{S}_1 - \mathbf{S}_0$, where \mathbf{S}_0 and \mathbf{S}_1 are unit vectors in the directions of incident beam and scattering beam respectively. The integration is over the scattering volume V of the specimen. For a system with a nematic mesophase domain of volume V_d embedded in an isotropic matrix equation (1) has the form:

$$E_s = K \int_c (\mathbf{M}_i \cdot \mathbf{O}) \cos k(\mathbf{r} \cdot \mathbf{S}) d\mathbf{r} + K \int_{V_d} [(\mathbf{M}_n - \mathbf{M}_i) \cdot \mathbf{O}] \cos k(\mathbf{r} \cdot \mathbf{S}) d\mathbf{r} \quad (2)$$

where M_n and M_i are the induced dipole moments in the volume elements of the nematic phase and the isotropic phase respectively. The first term is the Hv scattering of an isotropic specimen and equals zero. The calculation of the second term needs information about the internal structure of the domain. For anisotropic domains distributed in isotropic matrix, as shown in Figure 2e and Figure 3a, the scattering theory^[10] will give the typical four-leaf clover Hv pattern, if the distribution of polarizability in these domains is considered to be similar to that in spherulites according to the appearance of Maltese cross in both cases.

At lower temperatures within the transition temperature ranges the specimens can be approached by a model composed of isotropic domains randomly distributed in an anisotropic matrix. In this case equation (1) can be written as:

$$E_s = K \int_v (M_n \cdot \mathbf{O}) \cos k(\mathbf{r} \cdot \mathbf{S}) d\mathbf{r} + K \int_{v_d} [(M_i - M_n) \cdot \mathbf{O}] \cos k(\mathbf{r} \cdot \mathbf{S}) d\mathbf{r} \quad (3)$$

The first term in equation (3) is the scattering of a homogeneous nematic specimen and will result in a circular symmetric Hv scattering pattern. The second term can be considered as the scattering of a specially anisotropic particle. The scattering of anisotropic particles with different shape and internal structure have been developed^[10-16]. In all the cases Hv scattering patterns of four-leaf clover type were obtained. So it is expected that the appearance of this second term may result in the uncircular symmetry of the scattering pattern being a superposition of a circular symmetric pattern and a four-leaf clover one. This is evidenced by patterns observed at corresponding temperature ranges (Figures 4b and 4e).

These results may indicate that the change of Hv scattering patterns near T_{NI} and T_{IN} is not related to the change in ordering of a homogeneous mesophase, but the change in heterogeneity of the mesophase system during the transitions.

Keywords:

Thermotropic polyester, nematic-isotropic transition, SALS, polarizing microscopy.

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