Morphological changes and SALS of thermotropic polyesters during isotropic and liquid crystallization transitions

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The morphology of two thermotropic polyesters with mesogenic units and flexible spacers along their backbones during isotropic and liquid crystallization transitions was studied by means of polarizing microscopy and small angle light scattering (SALS). These transition processes were found to be composed of the initiation of the new phase at local places of the old phase matrix and growth of the new phase domains. A change of Hv scattering patterns was observed in the transition temperature ranges and is explained by models proposed in previous papers as the result of heterogeneity of the mesophase systems.

(Keywords: thermotropic polyester; nematic–isotropic transition; SALS; polarizing microscopy)

INTRODUCTION

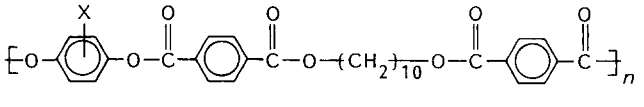
The existence of one or more mesophases above the melting point is characteristic of thermotropic liquid crystalline polymers. With increasing temperature the mesomorphic polymer samples finally become isotropic at the so-called isotropic transition temperature. At this critical temperature an equilibrium exists between the anisotropic and isotropic melts. Studies on the morphological changes during this transition and its counterpart, liquid crystallization from the isotropic melt, will undoubtedly give insight into the characteristic features and the formation of polymer liquid crystals.

Polarizing microscopy is widely used for studying the morphology of liquid crystals. The optical texture of liquid crystalline materials under a polarizing microscope is characteristic of different mesophases[1] and has been observed for many polymer liquid crystals. Although morphological features of polymer samples at temperatures near the isotropic transition have been shown in a few cases[2-4], no data from systemic studies of the morphological changes were reported. Small angle light scattering (SALS) studies may give information about the ordering of molecular packing within the polymer 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 the cholesteric mesophase[5,6]. A change of Hv scattering patterns from circular to non-circular was observed for some nematic polymer samples before the isotropic transition in a very narrow temperature range[2,7,8], but no exact explanation has been reported.

In our previous work[9,10] morphological features of a thermotropic polyester poly(chlorophenelene terephthaloxy decamethylene terephthalate), PTDT-Cl, during transitions between isotropic and anisotropic melts were studied in detail by means of polarizing microscopy and SALS. The transition processes were found to be composed of the initiation of the new phase in the old phase matrix and the growth of new phase domains, and specific two-phase textures were observed in the transition temperature ranges. The change of scattering patterns was then explained as the result of phase heterogeneity of the samples near the transition temperatures. In the present work the generality of the results obtained for PTDT-Cl is checked by using polyesters of similar structure, but different substitutions on the middle benzene rings.

EXPERIMENTAL

Two aromatic polyesters, PTDT-Br and PTDT-Me, were used in this work and their chemical structure is shown in Scheme 1. They were prepared from 1,10-decane



Scheme 1 Chemical structure of PTDT-Br (X = Br) and PTDT-Me (X = CH_3)

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bisterephthaloyl chloride and hydroquinone of the corresponding substitutions. The synthesis procedure has been described elsewhere[11]. The intrinsic viscosity in tetrachloroethane at 25°C is 0.30 and 0.52 $dl\,g^{-1}$ for PTDT-Br and PTDT-Me, respectively. Thin film specimens were prepared by solution casting. An Olympus polarizing microscope and SALS apparatus of type LS-1, both with hot stage, were used for morphological studies. The heating and cooling rates were about 2 and 4°C min^{-1}, respectively, for both methods. Thermograms were recorded by using a Perkin–Elmer DSC-4. Runs were conducted at a heating rate or cooling rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The thermograms of the two samples are given in *Figures 1* and *2*. The two endothermal peaks in the heating process are attributed to the transition from crystalline to nematic phases T_{KN} and the transition from nematic to isotropic melts T_{NI}. In the cooling process the exothermal peaks are related to liquid crystallization from isotropic melt T_{IN} and crystallization from nematic phase T_{NK}. Values for these peak temperatures are listed in *Table 1*.

Polarizing micrographs of samples PTDT-Br and PTDT-Me at different temperatures in the heating process are given in *Figures 3* and *4*, respectively. Above T_{KN}, optical texture of nematic mesophase has been observed for both samples, as shown in *Figures 3*(*a*) and *4*(*a*). Specific two-phase textures were observed during the T_{NI} transition of the samples in a temperature range which was almost consistent with that covered by the T_{NI} endothermal peak of the corresponding thermograms (*Figures 1* and *2*). At the beginning of the transition the new isotropic phase appears as black threads under a polarizing microscope, and dark domains are formed at places of high thread concentration due to intersection of two or more threads or thread coiling (*Figures 3*(*b*) and *4*(*b*)). The size and darkness of these domains increase with temperature. The size of the domains shown in *Figures 3*(*b*) and *4*(*c*) is about 6–10 μm. These growing isotropic domains then contact and combine with each other. Finally, a conversion occurs from an anisotropic continuous matrix to an isotropic matrix. The micrographs show bright anisotropic domains embedded in a dark matrix (*Figures 3*(*e*) and *4*(*d*)). The size of these mesophase domains decreases with temperature rapidly and a clear Maltese cross was usually observed for these domains before their final disappearance at high temperatures in the transition range.

Polarizing micrographs for the reverse process, liquid crystallization from the isotropic melt, for the two samples are given in *Figures 5* and *6*. Two-phase textures were also observed for both samples in the T_{IN} transition temperature range, which is almost consistent with that indicated by the corresponding T_{IN} exothermal peaks from differential scanning calorimetry (d.s.c.) measurements (*Figures 1* and *2*). At an initial stage of the T_{IN} transition very small bright spots appear in the dark background, indicating the initial formation of the mesophase in the isotropic melts. These mesophase domains are almost circular in shape, and they exhibit

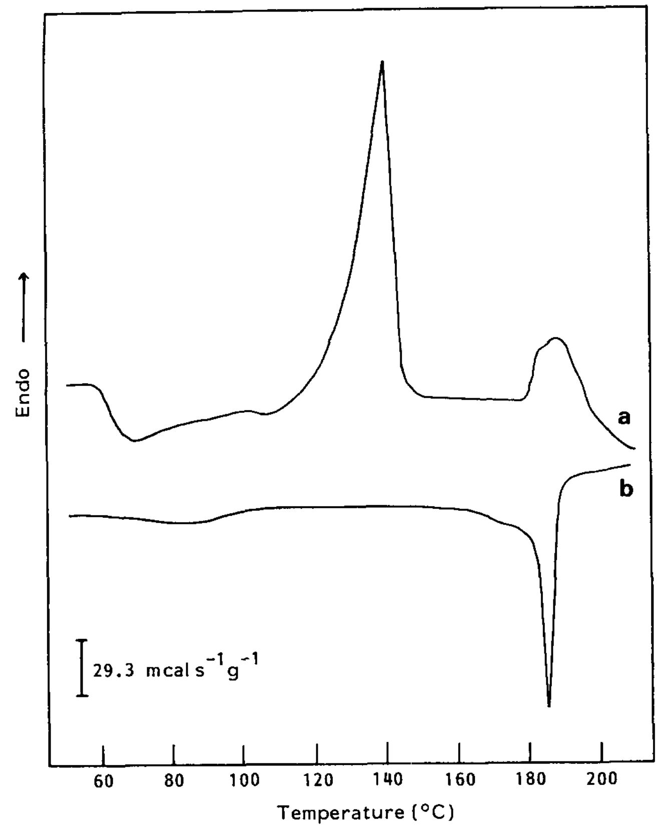

Figure 1 Thermograms of PTDT-Br in (a) heating and (b) cooling

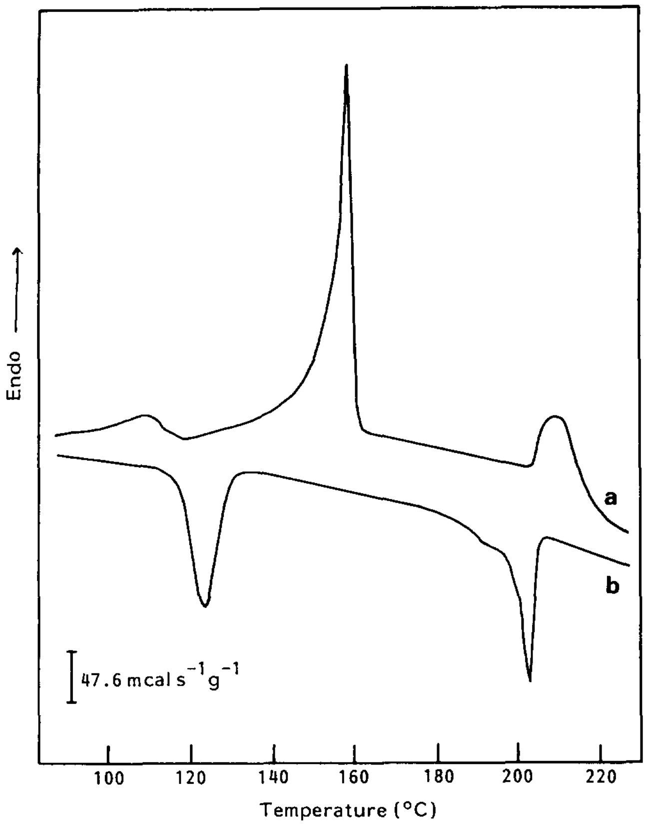

Figure 2 Thermograms of PTDT-Me in (a) heating and (b) cooling

Table 1 Transition temperatures of the polyesters

Sample	T_{KN} (°C)	T_{NI} (°C)	T_{IN} (°C)	T_{NK} (°C)
PTDT-Br	141	190	186	84
PTDT-Me	159	210	203	124

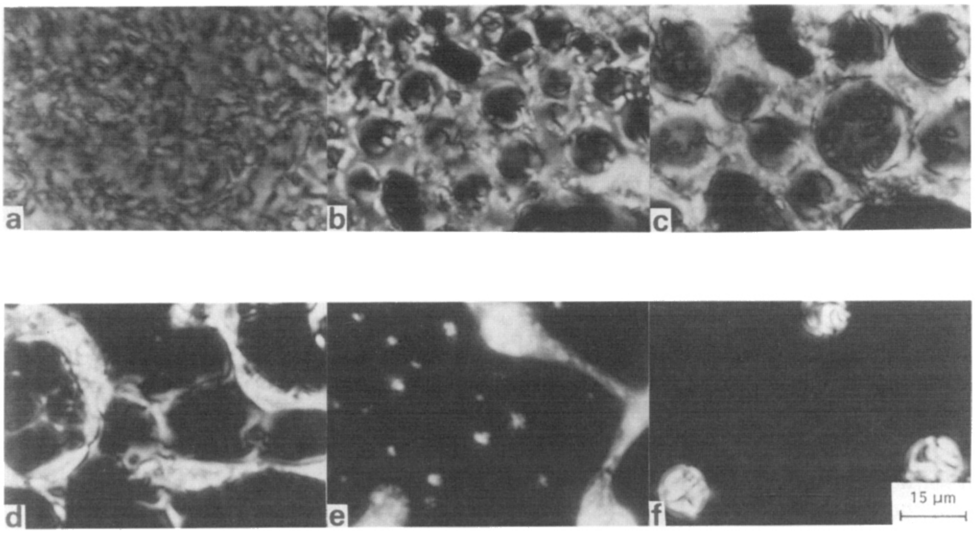

Figure 3 Polarizing micrographs of PTDT-Br at different temperatures in heating: (a) 134°C, (b) 174.5°C, (c) 177°C, (d) 181.5°C, (e) 185°C, (f) 187°C

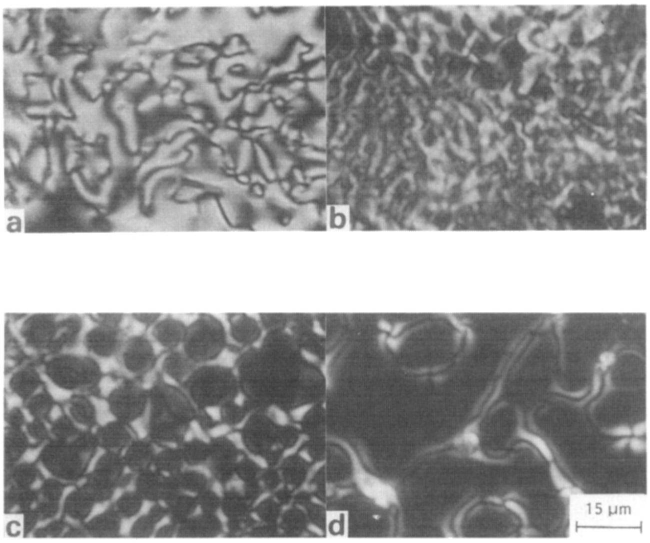

Figure 4 Polarizing micrographs of PTDT-Me at different temperatures in heating: (a) 174°C, (b) 194°C, (c) 195°C, (d) 198°C

Maltese crosses at a certain stage of growing. The size of the domains shown in *Figures 5*(*a*) and *6*(*a*) is ≈2–3 μm. With decreasing temperature the domains come into contact with each other and combine to form larger and larger domains. Then the mesophase becomes predominant and forms a continuous matrix with isolated dark isotropic regions of irregular shape. Finally, the optical texture of nematic phase is obtained (*Figures 5f* and *6d*).

These results of microscopic studies are similar to those reported previously for the polyester sample with chlorosubstitution[9,10]. This may indicate that the transitions between the anisotropic and isotropic melts of thermotropic polyesters with mesogenic units and flexible spacers along their backbones are composed of an initiation of the new phase at local places of 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 conventional polymers. The appearance of isotropic dark threads at the initial stage of isotropic transition may imply the existence of less

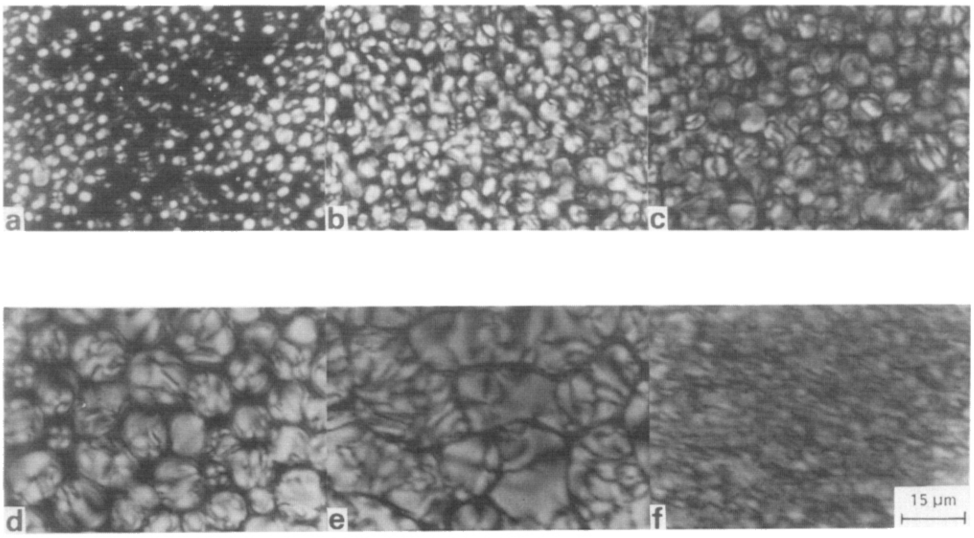

Figure 5 Polarizing micrographs of PTDT-Br at different temperatures in cooling: (a) 182.5°C, (b) 179°C, (c) 176.5°C, (d) 174°C, (e) 162°C, (f) 95°C

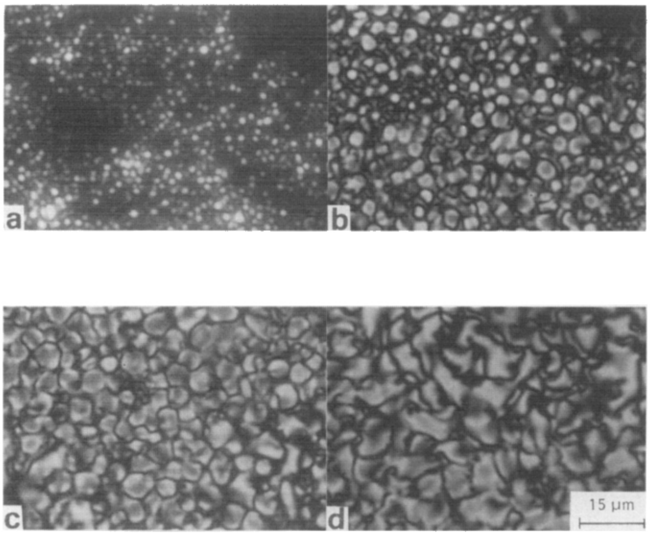

Figure 6 Polarizing micrographs of PTDT-Me at different temperatures in cooling: (a) 194°C, (b) 188°C, (c) 182.5°C and (d) 164°C

ordered regions in the mesophase specimens. They are possibly the interfacial layers between mesophase regions resulting from kinetic causes and/or structural defects. The observed Maltese cross of mesophase domains at higher temperatures of both T_{NI} and T_{IN} transitions implies the existence of some kind of long range correlation in orientation ordering within these domains.

Figures 7 and *8* are the SALS Hv patterns of the two polyesters at different temperatures during T_{NI} and T_{IN} transitions. Above T_{KN} the specimens become mesophasic and show circular symmetric Hv patterns at temperatures not close to their T_{NI} temperatures (*Figures 7a* and *8a*). With increasing temperature non-circular symmetry of the scattering patterns was detected. In addition to a circular scattering spot, extension of scattering intensity along the ±45° azimuthal directions can be observed, as shown in *Figures 7*(*b*) and *8*(*b*). The intensity of the circular scattering spot decreases with a further increase in temperature, and the non-circular symmetric scattering pattern becomes predominant (*Figures 7c*, *7d* and *8c*). In some cases scattering patterns of a clear four-leaf clover type were observed before the final disappearance of the Hv scatterings. An almost reversible change of scattering patterns was detected (*Figures 7* and *8*) during cooling of the specimens from the isotropic melt state. The only difference is that in the very initial stage of liquid crystallization non-circular symmetric Hv scattering patterns with extensions of intensity along 0° and 90° azimuthal directions were observed (*Figures 7h* and *8f*).

The circular symmetric Hv scattering patterns of these polymers at temperatures above T_{KN} are consistent with the patterns of other nematic liquid crystals and may imply, according to Stein and Wilson[12], the existence of the so-called random correlation of orientation fluctuation between the polarizability axes of volume elements in the mesophase. The appearance of non-circular symmetry in scattering patterns cannot be explained as the result of a transition from nematic to cholesteric mesophases, because transitions between

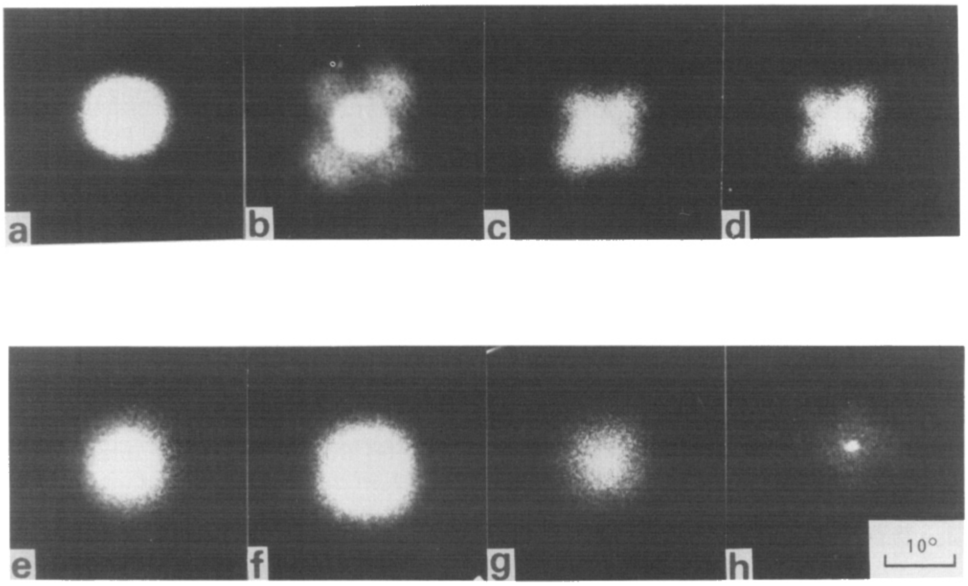

Figure 7 Hv scattering patterns of PTDT-Br at different temperatures in heating: (a) 163°C, (b) 179°C, (c) 183°C, (d) 186°C; and cooling: (e) room temperature, (f) 180°C, (g) 190°C, (h) 191°C

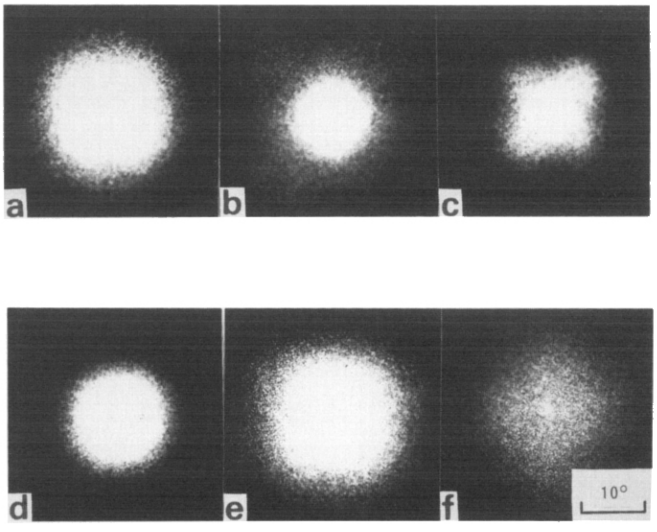

Figure 8 Hv scattering patterns of PTDT-Me at different temperatures in heating: (a) 166°C, (b) 199°C, (c) 201°C; and cooling: (d) room temperature, (e) 203°C, (f) 207°C

these two mesophases have never been observed for any liquid crystalline materials, and the polyester molecule does not contain asymmetric centres, which are accepted as characteristic structural features for molecules able to form the cholesteric mesophase.

It has been proposed in previous work[9,10] that the change of Hv scattering patterns during the T_{NI} and T_{IN} transitions can be explained, if the specific two-phase morphology of specimens is taken into account. According to this explanation, the specimens at lower and higher temperatures within the transition temperature ranges can be approached with models composed of isotropic domains embedded in an anisotropic matrix, and the opposite, anisotropic domains in an isotropic matrix, respectively. The Hv scattering of the first model is a superposition of a circular symmetric pattern and a four-leaf clover type pattern; the second model gives a four-leaf clover scattering pattern. The change in Hv scattering patterns expected from these models is also shown fairly well by the experimental results for the two polyesters used in this work.

CONCLUSIONS

The transitions between anisotropic and isotropic melts of thermotropic polyesters with mesogenic units and flexible spacers along their backbones are composed of an initiation of the new phase at local places of 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 conventional polymers. The change of Hv scattering patterns during T_{NI} and T_{IN} transitions is the result of the two-phase morphology of the specimens, but not the result of the change in ordering of a homogeneous mesophase.

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