Kinetics of Mesophase Transitions of Thermotropic Copolyesters. 2. Two Transition Processes

Stephen Z. D. Cheng,* James J. Janimak, Anqiu Zhang,† and Zhenglong Zhou†

Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325-3909.

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ABSTRACT: Kinetic studies of isothermal experiments have indicated two transition processes in low-temperature ranges for the thermotropic copolyesters: a fast process which occurs during quenching from their nematic melts and forming quenched form crystals, with hexagonal packings, and a slow process which develops gradually with increasing isothermal time as annealed form crystals with orthorhombic packings. From the study of three copolyesters which consist of different chemical compositions, the understanding of these two transition processes can be achieved. The influences of the chain structure regularity and molecular motion to the transitions are also discussed.

Introduction

Thermotropic copolyesters with rigid chain molecules frequently display an anisotropic melt. During a transition from such a melt to the solid state, they usually pass through aggregation of the rigid chain molecules.[1] From the experimental observations, the transitions take place with low enthalpy and entropy changes.[1-3] The X-ray structures of the copolymers show a high degree of axial orientation and three-dimensional order. The meridional maxima are aperiodic.[4,5] The basic structure is suggested to have rotational disorder due to conformational mobility, as exemplified by mechanical and dielectrical relaxation data.[6] The chain packing in the mesophase structure has been proposed to be based on a matching of order of monomer units between adjacent molecules.[7] The formed mesophase during the transition has been suggested as "conformationally disordered crystals (condis crystals)".[1,8,9]

The kinetic study of these mesophase transitions has shown several common features.[1] Those that are of interest here are the two transition processes during isothermal experiments observed in the low-temperature range (the isothermal temperature is lower than the exothermic peak temperature of nonisothermal experiments, see ref 1). A fast transition process has been characterized as "solidification", and it occurs during quenching from the anisotropic melt. A slow transition process follows, which is close to a normal crystallization process but with very low Avrami parameter n. These two processes have been found, in the cases of copolyesters with different compositions of p-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), to be independent of each other. Furthermore, during the development of the slow process (annealed form), the previously formed crystals of the fast process (quenched form) remain almost constant, and the heats of transition are largely unchanged.[1] We have concluded that the existence of previously formed crystals seriously hinders the development of the latter slow process.

For this series of copolyesters, it has been reported from wide-angle X-ray diffraction (WAXD) results that the quenched form shows a hexagonal packing[10] and the annealed form an orthorhombic packing.[11] On the other hand, recent WAXD experiments on another copolyester that is copolymerized with HBA, 4,4′-dihydroxybiphenyl (HBP), and p-benzenedicarboxylic acid (TPA) has indicated three different crystalline packings, namely, a quenched form, βq; an annealed form, βa; and a low-temperature form which can only be transferred with the βa form, α.[12] Again, one believes that βq is hexagonal and βa orthorhombic.[12,13]

A great effort from Blackwell et al.[10,13-16] had been made to indirectly prove the randomness of these copolyesters by X-ray analysis. Nuclear magnetic resonance (NMR) should be a direct technique to determine such random sequences in the copolyesters. Recent development in the determination of dyad sequence distribution for the HBA/HNA copolyesters via NMR method has also been reported.[17]

In this paper, the second in this series, we attempt to report our new differential scanning calorimetry (DSC) and WAXD data on the kinetic study of the mesophase transitions in three copolyesters with different chemical compositions and chain structure regularities. Our experimental results reveal that the fast and slow transition processes grow independently. Depending upon the chain structure regularities and isothermal conditions, the previously formed crystals (quenched form) may be released during the development of the annealed form. WAXD data also indicate the change of the crystal packing.

Experimental Section

Three random copolymers are used in this study. One of them is composed of HBA and HNA with molar ratio 75/25 (HBA/HNA). The molar mass of the average repeating units can be calculated to be 132.5 g/mol. This sample was kindly supplied by the Celanese Research Co. The copolymers were characterized by Celanese through their inherent viscosities in pentafluorophenol at 333 K (7.8 dL/g). The other two of the three random copolyesters were synthesized in our laboratory. They are composed of p-hydroxybenzoic acid (HBA), 4,4′-dihydroxybiphenyl (HBP), p-benzenedicarboxylic acid (TPA), and 1,3-benzenedicarboxylic acid (IPA). The molar ratios for these two samples were 60/20/15/5 and 60/20/20/0 HBA/HBP/TPA/IPA, respectively. p-Acetoxybenzoic acid was obtained by refluxing 100 g of p-hydroxybenzoic acid, 200 mL of acetic anhydride, and 0.2 g of sodium acetate for 3 h. Upon cooling, the white solid was filtered; the product was vacuum dried at 333.2 K for 24 h, and the melting point was found to be 460.2–461.2 K. 4,4′-Diacetoxybiphenyl was prepared by refluxing 50 g of 4,4′-dihydroxybiphenyl, 50 mL of acetic anhydride, and 0.1 g of sodium acetate at 403.2 K for 3 h. The resulting product was washed in distilled water at 293.2 K, filtered, and recrystallized from acetic acid. Its melting point was 436.2–437.2 K. All copolyesters were prepared in the same manner by utilizing an ester interchange technique. Solid-state polymerization under vacuum at 600 K for 4 h was applied to raise the molecular mass of the resulting copolyesters. From end group analysis via infrared spectroscopy, the copolyesters of this study can be estimated to contain about 120–150 repeating units.

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† Permanent address: China Textile University, Shanghai, China.

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Films were prepared by pressing samples to a 1-mm thickness at a temperature 80 K below their transition temperature. To avoid any influence of previous thermal history, each sample was used once only.

Differential scanning calorimetry (Perkin-Elmer DSC2) was connected to a newly established microlaboratory thermal analysis system on an IBM PC computer. Both temperature and heat flow scales were calibrated with high purity melting standards (naphthalene, benzoic acid, indium, lead, and tin). For the copolyesters, the samples were heated above their transition temperatures and held for 15 s. Then, the samples were quenched to a predetermined crystallization temperature, T_c, and kept for different fixed periods of time, t_c. The samples were then heated again at 10 K/min to above their transition temperatures, and the DSC heating traces were recorded. The sample weights were controlled in a range 15~20 mg. All pan weights were within a deviation of ±0.002 mg. Each experiment was repeated three times to obtain reproducibility (±1.2% for ΔH_d and ±0.1% for T_d). All thermal analyses were run under an atmosphere of dried nitrogen. A detailed description of the experimental procedures can be found in ref 1.

Wide-angle X-ray diffraction (WAXD) experiments were carried out on a Rigaku X-ray generator with a 12-kW rotating anode as a source of the incident X-ray beam. The line-focused beam is monochromatized with a graphite crystal and a pulse-height analyzer to Cu Kα radiation. A D/Max-B X-ray powder diffractometer was controlled by an IBM personal computer (PS-2). The scanning angle range (2θ) was 8–40° to determine the reflections of the samples. A temperature controller was added onto the X-ray apparatus for thermal WAXD measurements. The precision of the controller was ±0.5 K in the temperature range between room temperature and 620 K. Program heating or isothermal experiments can be performed under computer control. One complete scan of the whole 2θ range requires 2 min. The crystallinities of the copolyesters were determined by subtraction of the backgrounds which correspond to the WAXD patterns of their anisotropic states measured at high temperatures above their transition temperatures. The d-spacings were calibrated with silicon powder (325 mesh size).

For the copolyesters of 75/25 HBA/HNA, the samples were heated to above their transition temperature and held for 15 s. Then they were quenched to 505 K on the X-ray diffractometer, and WAXD measurements were carried out at fixed periods of time. For the copolyesters of 60/20/15/5 and 60/20/20/0 HBA/HBP/TPA/IPA, the samples were heated to above their transition temperatures and held for 15 s. Then they were quenched to 580 K in a Du Pont DSC cell. After crystallization for a fixed period of time, the samples were quenched to room temperature. The WAXD measurements were performed at room temperature. The reason for following this experimental procedure is that these two copolyesters exist in polymorphic forms as described in the previous section. Quenching to room temperature leads to the observation of the form which appears at lower temperatures (~<373.2 K). It is known that the form can only be transferred from the βa form (crystallized or annealed at a high temperature) but not from the βq form (quenched form).[12] Since the difference between the βq form and the α form is much clearer than that between the βq and the βa form, the WAXD measurements at room temperature show more distinguishable results. Each experiment was repeated 3 times, and the reproducibility is good to within ±0.08°, which is the maximum standard deviation for 2θ measurements.

It has also been fairly well understood that at high temperatures transesterification reactions occur in these copolyesters. In order to avoid the change of chemical structures and sequences of the copolyesters due to this reaction for the HBA/HNA copolyesters, our isothermal temperatures are below 505 K, which is quite safe for the long-time isothermal experiments. For the HBA/HBP/TPA/IPA copolyesters, we limited our isothermal temperatures to 600 K, at which our solid-state polymerization experiments were carried out.

A polarized optical microscope (POM) (Nikon Labophot-Pol) was used in conjunction with a Leitz hot stage. In order to observe birefringence patterns of the two copolyesters 60/20/15/5 and 60/20/20/0 HBA/HBP/TPA/IPA, the sample films were pressed in between two glass slides and heated under a dried nitrogen atmosphere to above their transition temperatures (620 and 690 K for these two copolyesters, respectively). The photographs were taken after the films were held for 5 s at those temperatures. The visual observations were made at 625× magnification. The polarizer underneath the condenser polarizes the light in a plane of 45° to the axis of the birefringent plate.

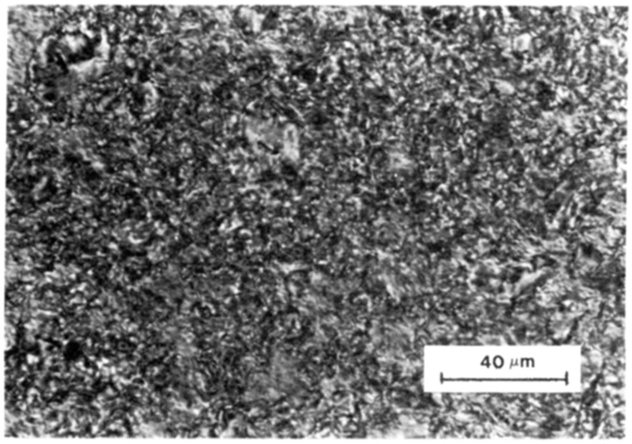

Figure 1. Nematic liquid crystal pattern of Schlieren textures with threadlike lines at 620 K under polarized optical microscopy for 60/20/15/5 HBA/HBP/TPA/IPA.

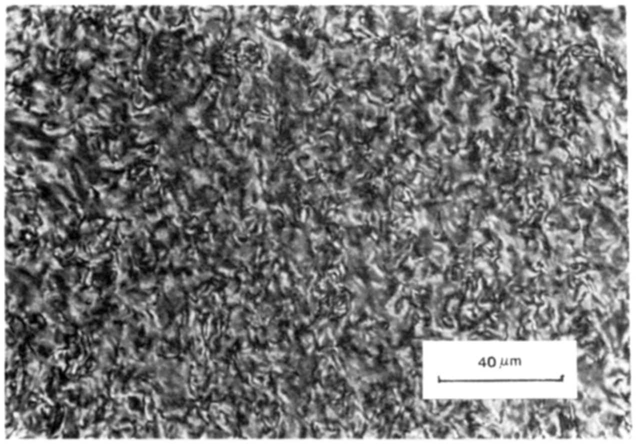

Figure 2. Nematic liquid crystal pattern of Schlieren textures with threadlike lines at 690 K under polarized optical microscopy for 60/20/20/0 HBA/HBP/TPA/IPA.

Results

Observations of POM. Figures 1 and 2 show the birefringence patterns of the two copolyesters (60/20/15/5 and 60/20/20/0 HBA/HBP/TPA/IPA) at temperatures of 620 and 690 K, respectively, which are above their transition temperatures observed from DSC measurements (see below). One can find that their patterns represent Schlieren textures with threadlike lines, which is indicative of typical nematic melts. If one slightly shifts the cover slide, the birefringence pattern changes to a lined pattern, as shown in Figure 3, indicating flow behavior for the copolyesters above their transition temperatures.

WAXD Measurements. Figure 4 shows the WAXD results for the copolyester of 75/25 HBA/HNA quenched from its nematic melt and then crystallized at 505 K. At the shortest isothermal time (about 1.5 min), we can find its quenched form with one main reflection peak at 2θ = 19.64°, one weak peak at 2θ = 26.62°, and one very weak peak at 2θ = 34.32°, indicating d-spacings of 4.52, 3.35, and 2.61 Å, respectively. The peaks corresponding to 2θ = 19.64° and 34.32° reveal the crystal planes of (100) and (110) in a hexagonal packing with a = 5.22 Å. The peak with 2θ = 26.62° corresponds to the off-equatorial spots,

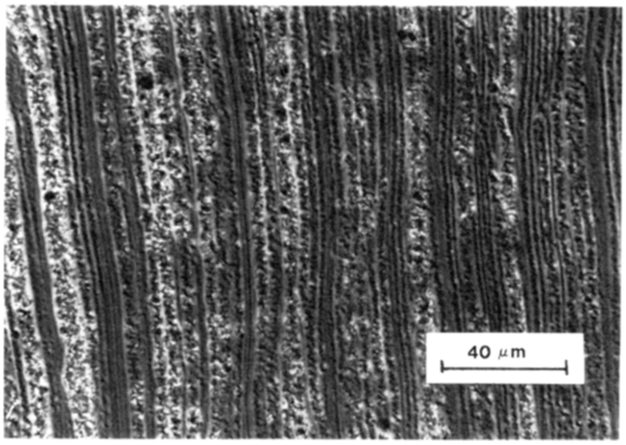

Figure 3. Nematic liquid crystal pattern after slight shift of the cover slide for Figure 2. The shift direction is parallel to the line pattern.

which shows some degree of three-dimensional order in the samples. The crystallinity at this moment is about 8~10% based on our calculation.

With increasing isothermal time, several changes in the reflection pattern can be observed. First, the intensity of the main reflection peak increases. This peak shifts to a smaller angle ($2\theta = 19.36°$ at $t_c = 10\,000$ min), and its half-peak width is surprisingly broadened in the early stage of the isothermal experiments until a separation of the peak at $2\theta = 19.88°$ (d-spacing = 4.46 Å) from the main reflection peak is clear. This separated peak has almost the same intensity as the quenched sample. Second, a new reflection peak gradually appears at $2\theta = 22.11°$ (at $t_c =$ 10 min) corresponding to a d-spacing of 4.02 Å, and it shifts to a smaller angle ($2\theta = 21.80°$ at $t_c = 10\,000$ min) and slightly increases its intensity with increasing t_c. Third, the very weak reflection peak at $2\theta = 34.32°$ does not increase its intensity but shifts to a wider angle ($2\theta =$ 34.73° at 10 000 min). The weak reflection peak at $2\theta =$ 26.62°, at the same time, increases its intensity and shifts to a wider angle ($2\theta = 27.37°$ at $t_c = 10\,000$ min). Finally, the overall crystallinity develops with increasing t_c up to about 40% at $t_c = 10\,000$ minutes (see also the results of ref 1).

On the basis of an orthorhombic packing, one can calculate the crystal planes of these results to the reflection peaks obtained at $t_c = 10\,000$ min; for example, the peaks at $2\theta = 19.36°$ and 21.80° correspond to the (110) and (200) planes with a = 8.16 Å and $b = 5.53$ Å. However, the other two peaks at $2\theta = 19.88°$ and 34.73° cannot fit such a packing. They are, in fact, supporting evidence for a hexagonal packing with $a = 5.15$ Å. This judgment can be further supported by the invariabilities of those intensities for the two reflection peaks, as shown in Figure 4. Therefore, the WAXD results at long isothermal times reveal a mixture of two crystal packings, namely, a hexagonal and an orthorhombic packing, and the existence of both packings is independent. Figure 5 shows the size changes of the unit cells with respect to isothermal time for both packings. One can find that both a and b of the orthorhombic packings expand and a of the hexagonal packing shrinks.

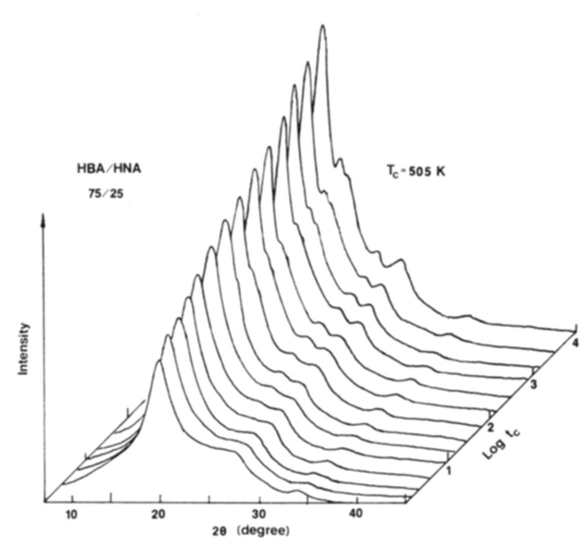

Figure 4. Set of WAXD patterns of different isothermal times for the copolyester 75/25 HBA/HNA quenched from its nematic melt and crystallized at 505 K.

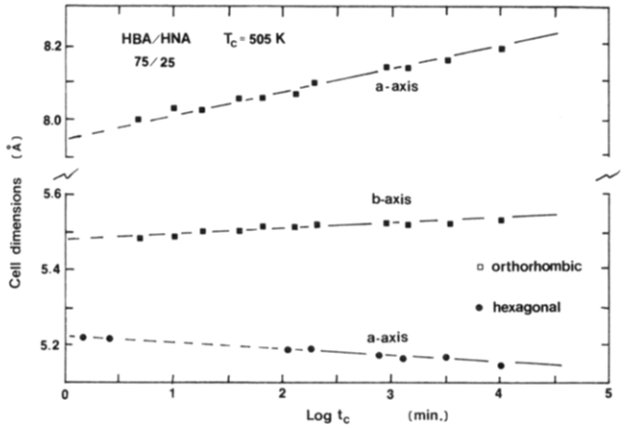

Figure 5. Size changes of the unit cells of 75/25 HBA/HNA with respect to time at $T_c = 505$ K for both crystal packings (circular symbol for hexagonal packing and square symbol for orthorhombic packing). The dashed line represents the predicted data, which cannot be determined from our experiments.

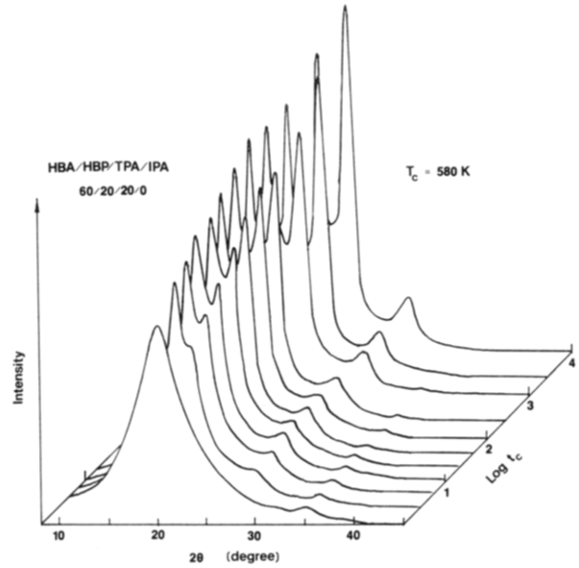

Figure 6. Set of WAXD patterns at different isothermal times for the copolyester 60/20/20/0 HBA/HBP/TPA/IPA quenched from its nematic melt and crystallized at 580 K.

In the cases of 60/20/15/5 and 60/20/20/0 HBA/HBP/TPA/IPA, one can observe that with increasing isothermal time at 580 K the α form, which is transferred from the βa form during quench, increases, indicating the growth of the βa form in the slow transition processes. Figure 6 shows the copolyester of 60/20/20/0 HBA/HBP/TPA/IPA as an example. A main reflection peak at $2\theta = 19.86°$ (d-spacing = 4.47 Å) can be observed. It corresponds to a hexagonal packing with $a = 5.16$ Å if one

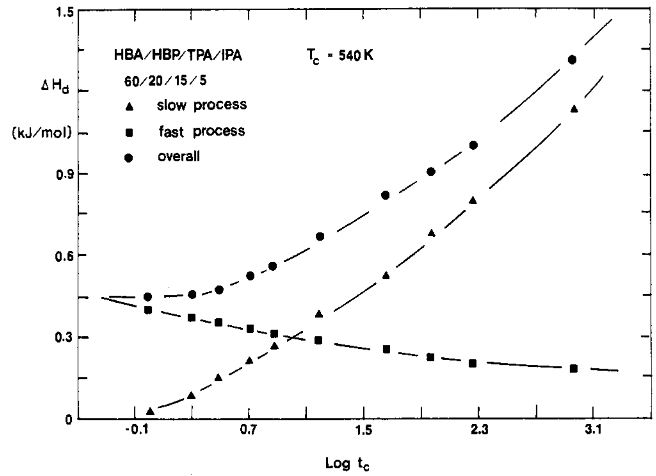

Figure 7. Relationship between ΔH_d and log t_c at T_c = 540 K in isothermal experiments for the copolyester 60/20/15/5 HBA/HBP/TPA/IPA in which solid squares represent the fast transition process and solid circles represent the overall change of ΔH_d.

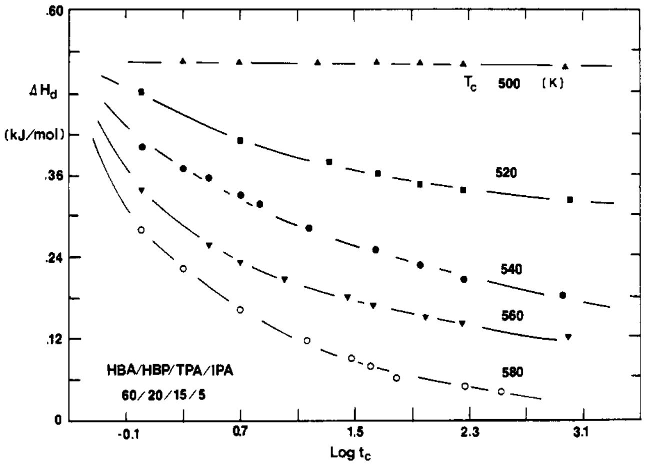

Figure 8. Relationship between ΔH_d of the fast transition process and log t_c at different isothermal temperatures for the copolyester 60/20/15/5 HBA/HBP/TPA/IPA.

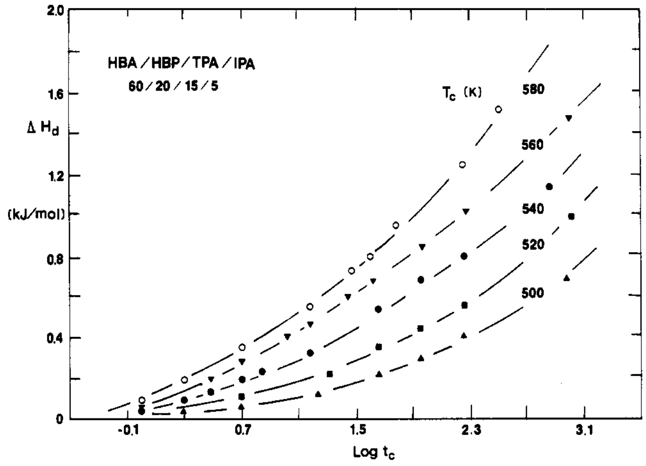

Figure 9. Relationship between ΔH_d of the slow transition process and log t_c at different isothermal temperatures for the copolyester 60/20/15/5 HBA/HBP/TPA/IPA.

assigns this peak as the (100) plane of this packing. A very weak reflection peak at 2θ = 34.77° (d-spacing = 2.58 Å) indicates the (110) plane of the hexagonal packing.

With increasing isothermal time, this main reflection peak shifts continuously to a smaller angle in a time range of 2000 min, and then it almost keeps a constant angle of 2θ = 19.29° (d-spacing = 4.60 Å) up to 10 000 min. The half-peak width becomes increasingly narrow in that time range, as shown in Figure 6. After t_c = 2.5 min, two new reflection peaks can be clearly identified at 2θ = 22.04° (d-spacing = 4.03 Å) and 2θ = 28.48° (d-spacing = 3.13 Å). The reflection peak of 2θ = 22.04° shifts continuously to a wider angle in the time range of 2000 min (2θ = 22.40°, corresponding to a d-spacing of 3.97 Å), and then, only very slight change can be observed (in the experimental error range) up to 10 000 min. On the other hand, the reflection peak of 2θ = 28.48° shifts continuously to a smaller angle in that time range (2θ = 28.19°, corresponding to a d-spacing of 3.17 Å at t_c = 2000 min) and then almost keeps to this constant value. At the same time, the reflection peak of 2θ = 34.77° gradually disappears. We believe that the reflection peaks of 2θ = 19.29° (4.60 Å), 22.40° (3.97 Å), and 28.19° (3.17 Å) belong to the α form with an orthorhombic packing.[12] The gradual changes of the reflection peaks in the time range of 2000 min indicate the coexistence of two different crystalline packings, and furthermore, the hexagonal packing gradually vanished with increasing times. Please note that the fast process releases on the same time scale for this copolyester at 580 K (see below, Figure 13). Finally the continuous increase of the reflection intensity reveals an increase in crystallinity of this copolyester.

A similar observation was obtained for the copolyester of 60/20/15/5 HBA/HBP/TPA/IPA.

DSC Measurements. The temperature range of this isothermal-kinetic study was in between 500–580 K for 60/20/15/5 HBA/HBP/TPA/IPA and 520–600 K for 60/20/20/0 HBA/HBP/TPA-IPA, respectively. For comparison, a temperature range of 480–505 K for 75/25 HBA/HNA was used.[1]

An an example, Figure 7 shows for 60/20/15/5 HBA/HBP/TPA/IPA at T_c = 540 K the relationship between heats of transition (ΔH_d) and logarithmic time (t_c). The observed results indicate that there are two transition processes. The fast process forms crystals during quenching from the nematic melt, and its heat of transition (solid squares) decreases with increasing time. On the other hand, a slow process gradually builds up, and its heat of transition (solid triangles) increases with time. The overall heat of transition (solid circles) can be seen to be contributed by the compensation of those two processes. Figure 8 shows the heats of transition for the fast process decrease with increasing time at different temperatures for 60/20/15/5 HBA/HBP/TPA/IPA. At T_c = 500 K, very little change in the heat of transition can be observed in the time region studied. With increasing temperature, the decrease in the heat of transition accelerates. A parallel increase in the heat of transition for the slow process of this copolyester at different temperatures is shown in Figure 9, revealing that this transition accelerates with increasing temperature. Figure 10 represents the relationship between transition temperature (T_d) and time. The transition temperature of the fast process is independent of the crystallization temperature and remains constant (602 K) in the early stages of time. The transition temperature of the slow process increases linearly with respect to logarithmic time in the same stage. The slope of such a linear increase is independent of temperature. With increasing temperature and time, the transition temperature of the fast process decreases, and simultaneously, the transition temperature of the slow process increases steeply while changing their increasing slopes by a factor of about 2~3. The observed time of such changes becomes shorter with increasing temperature. At the

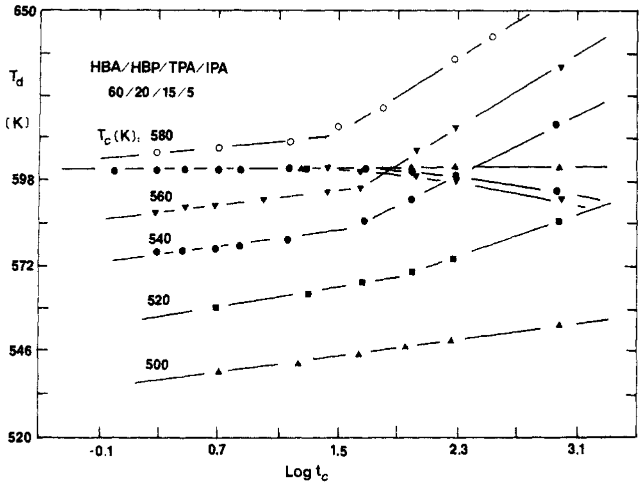

Figure 10. Relationship between T_d and log t_c at T_c = 500, 520, 540, 560, and 580 K for the copolyester 60/20/15/5 HBA/HBP/TPA/IPA. The horizontal line of T_d at 602 K with respect to log t_c represents the transition temperature of the fast process at T_c = 500 K. With increasing T_c, this line deviates toward lower transition temperatures initiated at a particular t_c. Correspondingly, their heats of transitions decrease as shown in Figure 8.

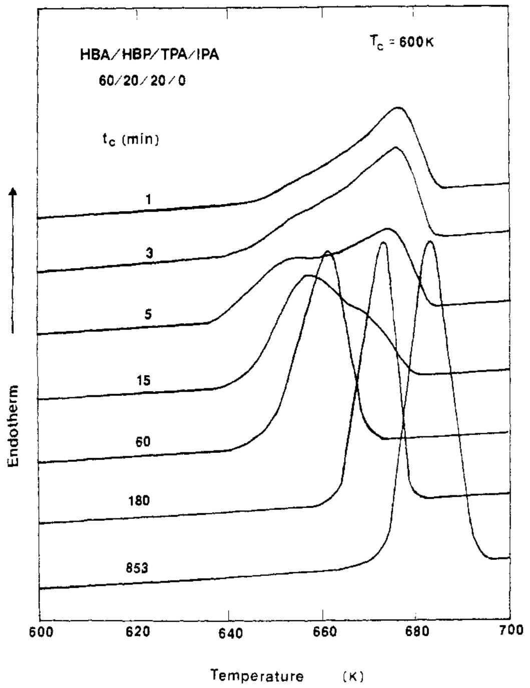

Figure 11. Set of DSC heating traces at T_c = 600 K in different isothermal time periods for the copolyester 60/20/20/0 HBA/HBP/TPA/IPA.

lowest temperature of 500 K, one cannot see such a change in the time period studied.

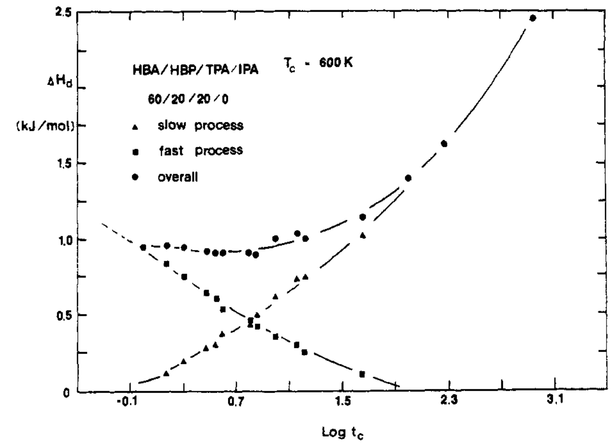

Figure 12. Relationship between ΔH_d and log t_c at T_c = 600 K in isothermal experiments for the copolyester 60/20/20/0 HBA/HBP/TPA/IPA, in which solid squares represent the fast transition process, solid triangles represent the slow transition process, and solid circles represent the overall changes of ΔH_d.

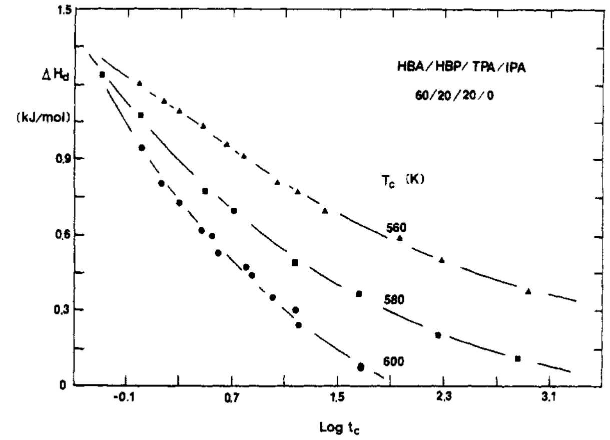

Figure 13. Relationship between ΔH_d of the fast transition process and log t_c at different isothermal temperatures for the copolyester 60/20/20/0 HBA/HBP/TPA/IPA.

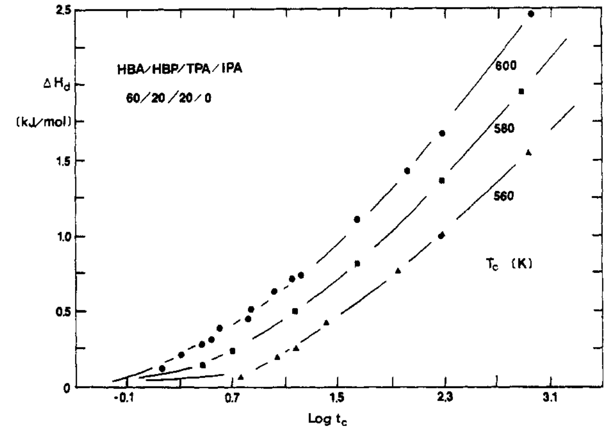

Figure 14. Relationship between ΔH_d of the slow transition process and log t_c at different isothermal temperatures for the copolyester 60/20/20/0 HBA/HBP/TPA/IPA.

For the copolyester of 60/20/20/0 HBA/HBP/TPA/IPA, similar observations can be found. Figure 11 shows a set of DSC melting traces for this copolyester after isothermal experiments (T_c = 600 K) at different lengths of time. One can find that at a short time period (1 min) only one transition peak is seen, which corresponds to the fast transition process. With increasing time, this peak is continuously shifted to low temperatures, and its heat of transition correspondingly is reduced. At the same time, another transition peak grows initially as a shoulder at the low-temperature side of the previous peak (3 min), but its development is indicated by the increase in the transition temperature to the higher temperature side and in its heat of transition. After about 1 h, the transition peak of the slow process becomes dominant. Quantitative changes of these heats of fusions with respect to time at T_c = 600 K are shown in Figure 12, as an example. The overall change of the heat of transition in this figure exhibits a minimum at about 8 min. Figures 13 and 14 show behavior similar to that in Figures 8 and 9. The heat of transition of the fast process decreases with increasing time, and this decrease is dependent upon crystallization temperature. The opposite tendencies can be observed for the slow process in this copolyester. Again, the relationship between transition temperatures and logarithmic time for this copolyester shows a behavior similar to the case of 60/20/15/5 HBA/HBP/TPA/IPA) in Figure 10.

Discussion

In order to understand the kinetics of these two transition processes from their nematic melts (Figures 1–3), one has to answer the questions arising from the experimental observations:

(1) We have found that growth of the quenched and annealed forms is totally independent from each other (Figures 7–14, see also Figures 2a,b and 3a,b in ref 1). What is the origin of the independent growth of these two transition processes?

(2) The quenched form (fast process) generally has a higher transition temperature, and the annealed form (slow process) initially has a lower one (Figures 10 and 11, see also Figures 2c and 3c in ref 1). However, a general understanding is that the quenched crystals are less ordered compared with the annealed crystals. What is the explanation for such an apparent controversy?

(3) The amount of the quenched form in the case of 75/25 HBA/HNA remains almost invariant (Figure 2a,b in ref 1), and those in the cases of 60/20/15/5 HBA/HBP/TPA/IPA (Figures 7–9) and 60/20/20 HBA/HBP/TPA (Figures 12–14) gradually decrease in our isothermal experiments. What is the reason causing the release of the quenched form?

As we have discussed in our previous paper, it has been expected that transition of rigid copolyesters occurs, which is basically different from crystallization of flexible linear macromolecules, via aggregation from an anisotropic molten (nematic here) state where chains are already extended, more or less parallel, free of entanglements, and in proper sequence for crystallization. Since the fast transition process occurs so rapidly, it has been recognized to be a solidification process, which is defined as a heat-transfer (conduction) controlled transition.[1] One may expect that the aggregation occurs in relatively ordered domains containing many chain conformations. From X-ray analysis, it is documented as a hexagonal packing.[10] On the other hand, the slow transition process produces an annealed form. During the transition, molecular motion can possibly form crystals with matching counits, and it leads to a more closely packed system of orthorhombic packing.[11] Our X-ray results have proven these two packings (Figures 4–6).

Regarding the first question, one generally expects that the earlier grown crystals should act as nuclei for further crystal growth in order to decrease the free energy barrier brought by primary nucleation.[18] In our case, nevertheless, the crystals formed during the fast process are less ordered than those formed during the slow transition process. It is evident that the less ordered hexagonal form cannot act as nuclei to stimulate the growth of the more ordered orthorhombic form. The explanation of the independent growth for these two crystal forms is thus quite straightforward.

To answer the second question, it is well-known that, for a crystal form, less ordered crystals in that form show lower transition temperatures and more ordered crystals in that form, higher transition temperatures. It is due to the metastability of the crystals caused by kinetic effects such as crystal size, crystal defects, etc.[19] Nevertheless, in our case, we have two different crystal forms. Besides those kinetic effects, which certainly affect the transition temperatures here, we can explain such phenomenon from a thermodynamic point of view. A first-order transition temperature is determined by a thermodynamic relationship of $\Delta H/\Delta S$, where ΔH and ΔS are the changes of enthalpy and entropy during the transition, respectively. In our three copolyesters, we consider that for the rigid chain molecules, and the changes of entropy between the quenched forms and their nematic melts are small. In particular, a hexagonal packing indicates a cylindrical symmetry which involves many chain conformations within this form, and molecular motions are largely kept (see below).[8,20] On the other hand, the changes of entropy between the annealed form of crystals and their nematic melts are relatively large due to a more closed orthorhombic packing with a more ordered chain structure. For both cases, the changes of enthalpy are not big (the low changes of enthalpy during the transitions). Therefore, we can conclude that the higher transition temperature for the quenched form is mainly due to the small degree of entropy between two states. A number of examples have shown high transition temperatures, which are caused by the small changes of entropy, for example, in the case of polytetrafluoroethylene (PTFE).[21] According to Wunderlich's classification,[8,20] they are in the state of conformationally disordered (condis) crystals.

We thus have a correct sequence for the mesophase transitions in these copolyesters; namely, the transition goes from the crystals of more ordered form (orthorhombic) to the crystals with the less ordered form (hexagonal), and then the nematic melts. Also, if the annealed form is perfect enough to affect the change of enthalpy (kinetic effects), we may push its transition temperature to be above the transition temperature of the quenched form, as in the case studied here (Figures 10 and 11 and Figure 3c in ref 1).[1]

Turning to the third question, it is now commonly accepted that crystals with a hexagonal packing in the copolyesters leave relatively large volumes unoccupied in the unit cell and therefore, keep dynamic, rotational motion with respect to the chain directions and even translational motion along the chain directions, as in the case of extended chain crystallization of polyethylene at elevated pressure.[8] In the copolyesters studied here, with increasing chain structure regularity, namely, from naphthalene to *m*-phenylene (even only 5% molar fraction) to *p*-phenylene, the dimension of the hexagonal packing does not change very much (for example, $a = 5.22$ Å for 75/25 HBA/HNA and $a = 5.16$ Å for 60/20/20/0 HBA/HBP/TPA/IPA). Therefore, an increase of translational motion along the chain directions is expected. The observed release of the quenched form in the cases of 60/20/15/5 and 60/20/20/0 should be attributed to such a motion. A reasonable, but still hypothetic, explanation can be suggested: during the isothermal experiments, the chain molecules have enough time to rearrange themeselves to a more energetically favorable registration to form a more closed orthorhombic packing, and some chain molecules have to be pulled out from their original hexagonal registration. Therefore, it leads to the release of the quenched form and a combination of the growth of the annealed form, which has been demonstrated by Figures 8, 9, 13, and 14. In the case of 75/25 HBA/HNA, there is little release which can be observed at these isothermal temperatures, indicating that such translational motion is not a major effect in the formation of the annealed form during the isothermal experiments. The existence of such a quenched form, therefore, further hampers the growth of the annealed form in this case.[1] On the other hand, Figure 10 indicates that in the case of 60/20/15/5 HBA/HBP/TPA/IPA such hampering effects can only be observed in the earlier stages of the isothermal experiments. To a certain extent, the release of the quenched forms of crystals can no longer influence the development of the annealed form (the break points of the slopes $\mathrm{d}T_\mathrm{d}/\mathrm{d}(\log t_\mathrm{c})$ in Figure 10). Finally, it is not surprising to see that such molecular motion is temperature dependent (Figures 8 and 13). The releases of the quenched forms in both copolyesters (60/20/15/5 and 60/20/20/0) accelerate with increasing temperature. Of special interest is that the molecular motion is also dependent upon the chain structure regularity. The copolyester of 60/20/15/5 HBA/HBP/TPA/IPA shows a slower release of the quenched form compared with the copolyester of 60/20/20/0 (Figures 8 and 13), and note that the difference between these two copolyesters is only 5% mole fraction of IPA with meta positions of the phenylene groups. However, a direct experimental observation is still needed to prove such a hypothetical explanation.

Conclusions

(1) In the copolyesters studied here, two transition processes can be identified: the fast process with hexagonal packing and the slow process with orthorhombic packing.

(2) The quenched form develops rapidly (fast process) and can be classified as "condis crystals". These forms commonly have higher transition temperatures since the changes of entropy between their nematic melts and condis crystals are small, and molecular motion in these forms is usually relatively large.

(3) The release of these forms during isothermal experiments is dependent upon temperature and chain structure regularity of the copolyesters, which is a documentation of translational motion along the chain direction.[1]

(4) The kinetic relationship between two transition processes shows that not only are they independent of each other but also that the quenched form hampers further growth of the annealed form. The development of the annealed form is the driving force which releases the quenched form during isothermal experiments.

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Registry No. (HBA)(HNA) (copolymer), 81843-52-9; (HBP)(HBA)(TPA)(IPA) (copolymer), 60088-52-0; (HBP)-(HBA)(TPA) (copolymer), 31072-56-7.

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