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Effect of isotropization on the thermal behavior of two thermotropic copolyesters containing spirobicromane moieties

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Abstract

Two thermotropic copolyesters with inherent rigid spirobicromane (SPI) moieties were prepared to evaluate their registry effects of neighboring chains in the mesomorphic state. Due to this chain registry effect, copolyester I-19, synthesized from polycondensation of terephthaloyl bis(4-oxybenzoyl chloride) (TOBC), heptanediol (HD, 90 mol%), and SPI (10 mol%) exhibited different thermal behavior between samples cooled from the mesomorphic and the isotropic liquid states. Chain arrangements in copolyester I-19, once randomized by isotropization, can not be readily improved by a further annealing process. In contrast, crystallinity of copolyester II-19 prepared from reaction of TOBC, HD (90 mol%), and bis(6-hydroxyhexanoxy)spirobicromane, 10 mol%) (BHS) can be significantly enhanced by annealing even when previous thermal treatment in the isotropic liquid state was performed. Suggestively, the minor component (i.e. SPI or BHS) in the corresponding copolyesters plays a decisive role in their responses toward annealing. The rigid, bent SPI moieties in copolyester I-19 efficiently retarded the crystallization process. In contrast, the flexible 1,6-dioxyhexamethyl spacers introduced in the BHS moieties greatly reduce the detrimental effect of the bent SPI moieties on the crystallization behavior of copolyester II-19. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic copolyester; Thermal behavior; Isotropization

1. Introduction

Multiple melting behavior of thermotropic polyesters has been well documented [1–5]. The causes for the multiple melting transitions of the semi-rigid thermotropic polyesters are various and can be classified into polymorphism [1], recrystallization and perfection process [2], and certain registry of neighboring chains in the mesomorphic state [3–5], dependent on the chemical structures of the polyesters surveyed. Among them, the hypothesis of registry of neighboring chains in the mesomorphic state illustrates an interesting hypothesis, which suggests mesomorphic chain registry can serve as potential nuclei for primary crystals and the crystals formed in the remaining portions upon secondary crystallization. Considering that mesomorphic chain arrangements are important for the subsequent crystallization and melting process, thermal history, which is intimately related to the chain arrangement, is important for thermal behavior of liquid crystalline polyesters. Effect of thermal history on the melting behavior of thermotropic polyester systems will be the topic of this study.

Previously, we had prepared thermotropic copolyesters from the polycondensation reactions of terephthaloyl bis(4-oxybenzoyl chloride) (TOBC) (Fig. 1), spirobicromane (SPI) [6] or 4,4′-bis(6-hydoxyhexanoyloxy)spirobicromane (BHS) [7], and 1,7-heptanediol (HD), and had also investigated their thermal behavior [7,8]. Here, the use of the rigid, bent SPI as comonomer (cf. the computer simulated structure in Fig. 1) is supposed to impose a non-linear geometry on the connected mesogenic TOBC triads. The mesogenic triads neighboring to the SPI moieties in copolyester I-19 (Fig. 2) will be conceivably difficult to align either in the corresponding solid or the mesomorphic state. On the contrary, the situation will be different if SPI units were linked to flexible spacers instead of mesogenic TOBC moieties — that is, through the use of BHS monomer, the detrimental effect of SPI moieties on chain packing will be significantly reduced through the neighboring 1,6-dioxyhexane spacers. Our previous investigations [8,7] did support this comment since both copolyesters (as copolyesters I-19 and II-19 in Fig. 2) have different melting and

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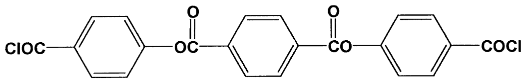
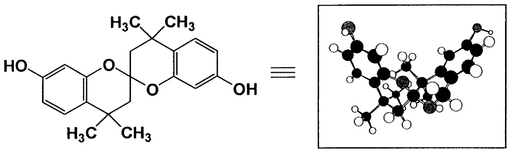
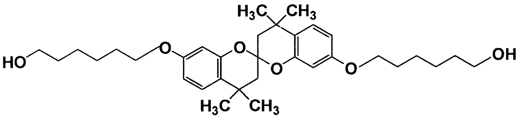


Terephthaloyl bis(oxy-4-benzoyl chloride), TOBC

HO-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$-OH
1,7-Heptanediol, HD



Spirobicromane, SPI



4,4-bis(6-hydroxyhexanoyloxy)spirobicromane, BHS

Fig. 1. Chemical structure of spirobicromane (SPI), 4,4-bis(6-hydroxyhexanoyloxy)spirobicromane (BHS), and 1,7-heptanediol (HD). (Ball-and-stick model of SPI simulated from Chem3D was also included).

crystallization behavior. The multiple melting and crystallization transitions observed for both copolyesters can be interpreted based on the comonomer sequence distribution and the chain registry effect in the mesomorphic state according to our previous study [7,8]. It is conceivable that mesomophic chain arrangement will be randomized by isotropization, and melting and crystallization behavior for a thermotropic polyester with and without previous heating in the isotopic liquid state will be different. A thermotropic polyster with low isotropization temperature (T_i) is required in this study since possible transesterification or decomposition reaction in the isotropic liquid state would obscure the investigation. Copolyesters I-19 and II-19 fulfill this requirement due to their low T_is. Therefore, both copolyester samples cooled from their mesomorphic and isotropic liquid states were compared in this study to evaluate the effect of thermal history on registry of neighboring chains in the mesophase. The chain registry effect on the resulting melting and crystallization behavior can be thus evaluated and compared in terms of chemical structures through the use of two copolyesters in this study. The distinct responses to thermal treatments were systematically evaluated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) study.

2. Experimental

Syntheses and characterizations of copolyesters I-19 [6,8] and II-19 [7] were detailed previously. Inherent viscosities measured at a concentration of 0.5 g/dl in TCE (1,1,2,2-tetrachlorethane, at 30°C) are 0.31 dl/g for copolyester I-19 and 0.30 dl/g for copolyester II-19. Origins of the multiple melting and crystallization behavior in copolyester I-19 and II-19 were also discussed in the respective manuscripts [8,7].

Thermal transitions were detected with a Perkin-Elmer

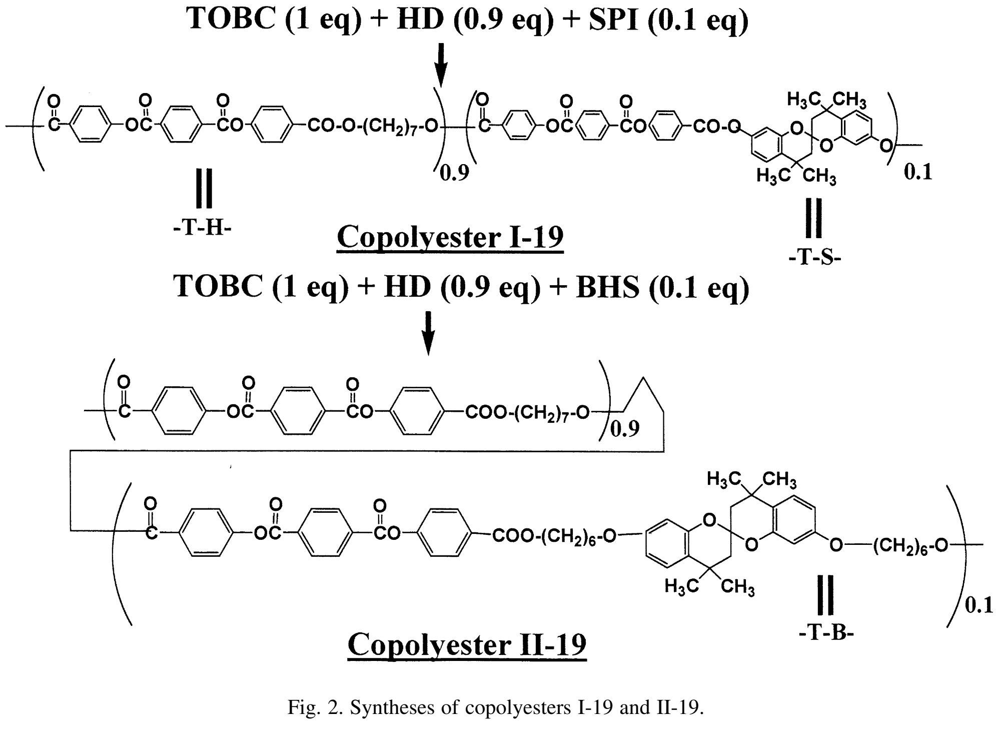


Fig. 2. Syntheses of copolyesters I-19 and II-19.

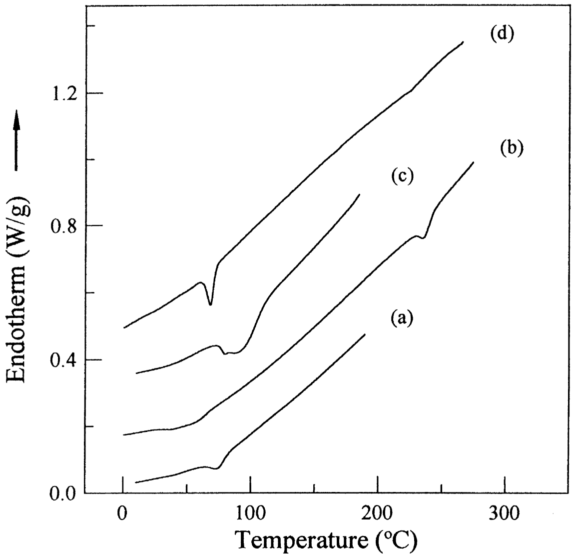


Fig. 3. DSC cooling thermograms of the copolyester I-19 after heating to (a) 210°C for 3 min and (b) 310°C, and the copolyester II-19 after heating to (c) 210°C for 3 min, and (d) 290°C. (cooling rate = 20°C/min).

DSC-7 model. The carrier gas was nitrogen at a flow rate of ca. 10 ml/min, and sample pans were always filled with approximately 6 mg of polymer sample. Calibration of the calorimeter was conducted for each heating rate using indium and lead standards. The as-synthesized samples were primarily heated to either the mesomorphic or the isotropic liquid state before cooled (cooling rate = 20°C/min) to subject to further thermal treatment. For preparation of the isotropically-randomized sample, immediate cooling from the corresponding isotropic liquid state was necessary to minimize potential transesterification or decomposition. Heating and cooling for different thermal treatments were performed at the same rate, 20°C/min. For the annealing experiment, samples were heated to the annealing temperature for 2 h and cooled (cooling rate = 20°C/min) to room temperature before re-heating to generate the DSC thermogram.

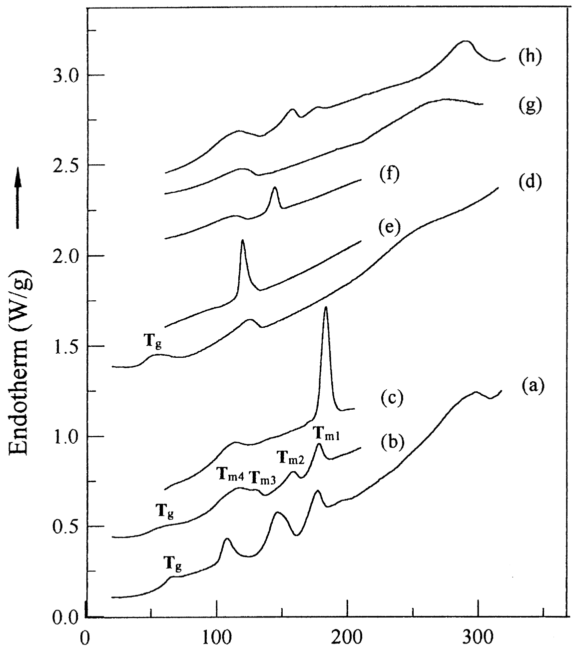


Fig. 4. DSC thermgorams of (a) the as-synthesized I-19, and the as-synthesized I-19 after (b) heating at 210°C for 3 min, (c) heating at 210°C for 3 min and annealing at 165°C for 2 h, (d) heating to 310°C, (e) heating to 310°C and annealing at 100°C for 2 h, (f) heating to 310°C and annealing at 120°C for 2 h, (g) heated to 310°C and annealed at 140°C for 2 h, and (h) heating to 310°C and solvent-treatment (the samples after each thermal treatment were cooled at a rate of 20°C/min to room temperature before re-scan to yield the thermograms).

WAXD experiments were carried out with a Siements Diffraktometer D 5000 model (Cu K_α Ni-filtered radiation). The system was evacuated to a pressure of 10^{-5} torr before heating to a high temperature. Samples were firstly heated to their mesomorphic states (210°C) to make homogeneous films before cooling to room temperature for thermal treatments.

3. Results and discussion

The as-synthesized copolyesters I-19 and II-19 were primarily heated to different states before being cooled to examine their crystallization behavior. Copolyester I-19 cooled from 210°C (mesomorphic state, Fig. 3a) has its crystallization exotherm located at a higher temperature (74°C) than that (57°C) for the sample cooled from 310°C (the isotropic liquid state, Fig. 3b). In addition, the exothermic heat involved is higher for the one cooled from 210°C (4.9 vs. 2.7 J/g). A similar trend was observed for copolyester II-19 — that is, the sample cooled from 210°C (the mesomorphic state; Fig. 3c) exhibited a larger crystallization exotherm located at higher temperatures than that obtained from the sample cooled from 290°C (the isotropic liquid state; Fig. 3d). Here, the multiple exotherms for copolyester II-19 cooled from 210°C indicate the prevalence of a complicated crystallization process during cooling; in contrast, a sharp crystallization peak was observed for the sample cooled from 290°C. A primary comparison between two copolyesters can be made; either for the samples cooled from the mesomorphic or the isotropic liquid state, copolyester II-19 has more heat involved during crystallization as compared to copolyester I-19.

The heating cycle was further performed for both samples. The as-synthesized copolyester I-19 exhibited a T_g at ~58°C before the complicated multiple melting transitions (T_ms, 100–200°C) and the isotropization transition (T_i) centered at ~288°C (Fig. 4a). If the as-synthesized copolyester I-19 was thermally treated at 210°C for 3 min, the corresponding DSC scan after cooling (Fig. 4b) would result in a different thermogram from the as-synthesized one. Firstly, the T_g was observed at a lower position (~49°C) as compared with the as-synthesized one. Also,

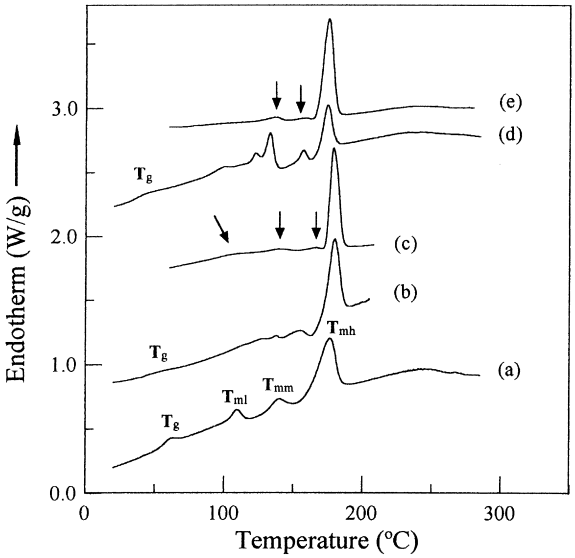


Fig. 5. DSC thermgorams of (a) the as-synthesized II-19, and the as-synthesized II-19 after (b) heating at 210°C for 3 min, (c) heating at 210°C for 3 min and annealing at 165°C for 2 h, (d) heating to 290°C, and (e) heating to 290°C and annealing at 165°C for 2 h (the samples after each thermal treatment were cooled at a rate of 20°C/min to room temperature before re-scan to yield the thermograms).

four melting transitions (labeled as T_{m1}, T_{m2}, T_{m3} and T_{m4}) were clearly visualized, which are closely related to the registry effect of neighboring chains in the mesomorphic state according to our previous study [8]. Basically, T_{m4} and T_{m1} transitions were assumed to be the melting of the primary crystals close to the –T–S– and in the pure –T–H– domains, respectively, and T_{m2} and T_{m3} transitions to be the melting of less perfect, secondary crystals close and less close to the pure crystals responsible for the T_{m1} transition. The corresponding sample can be thermally annealed at 165°C to yield a DSC thermogram (Fig. 4c) with one low- and one high-temperature T_{m4} and T_{m1} transitions. To randomize the ordered mesomorphic chain packing, copolyester I-19 was heated to 310°C before the immediate cooling to room temperature for re-scan. The corresponding DSC thermogram (Fig. 4d) exhibited a low T_g (~43°C) and broad low-temperature melting and T_i transitions. Careful inspection indicates the T_g transition, in this case, is broader and larger in magnitude as compared with the ones in Fig. 4a and b. The T_i transition, in this case, apparently locates at a lower position than that in the as-synthesized sample (Fig. 4a). Copolyester I-19 after thermally-treatment at 310°C (referred to as isotropically-randomized I-19) was further annealed at three temperatures (T_as = 100, 120 and 140°C) for 2 h and the results of the re-scans were given in Fig. 4e, f and g, respectively. Samples annealed at 100°C (Fig. 4e) showed a sharp T_m located at a temperature slightly higher than T_a; comparatively, annealing at 120°C (Fig. 4f) resulted in a broad endotherm at ~105°C along with a small, sharp endotherm at ~143°C. Here, the low-temperature endotherm at 105°C was caused by the imperfect crystal formed during cooling from 120°C. Further increase of T_a to 140°C yielded a thermogram (Fig. 4g) similar to the one for the isotropically-randomized sample (Fig. 4d). Crystals representing the melting endotherm at ~143°C in Fig. 4f are therefore situated in the molten state during annealing at 140°C. Comparison between Fig. 4c and e-g suggests that copolyester I-19 without previous treatment in the isotropic liquid state has enhanced response to annealing, in contrast to the isotropically-randomized one, in which little changes were made by annealing.

Suggestively, the different responses toward annealing between samples with and without treatment in the isotropic liquid state may be due to the possible transesterification (or decomposition) reaction during heating at the isotropic liquid state (i.e. 310°C). The possibility of major transesterification (or decomposition) reactions at 310°C can be excluded by further experiment — that is, copolyester I-19 after heating at 310°C was re-dissolved in 1,1,2,2-tetrachloroethane to erase the previous thermal history. The resulting sample after precipitation and drying can be further scanned in DSC and compared to the as-synthesized sample. The multiple melting transitions for the solvent-treated sample were again observed (Fig. 4h) — however, with less intensities than those in the as-synthesized one (Fig. 4a). The reduced intensities in Fig. 4h may be attributed to minor decomposition during the short-time stay of the sample at 310°C. The solvent-treated sample has its T_i transition with enhanced intensity and located at higher temperature than those in Fig. 4d and g, indicating that transesterification (or decomposition) should not be the main cause responsible for the obvious difference between samples with and without isotropization process. Here, T_i transition relates to the mesomorphic stability (in other words, it influences the extent of chain registry in the mesophase) and will be discussed later in the paper.

Comparatively, the as-synthesized II-19 exhibited a T_g at ~55°C before the two minor (T_{ml} and T_{mm}) and one major (as T_{mh}) melting endotherms, and the tiny, broad T_i (190–280°C; Fig. 5a). The origins of the T_{mh}, T_{ml}, and T_{mm} transitions are also related to the registry effect between neighboring chains in the mesomorphic state [7]. The T_{mh} and T_{ml} transitions are due to melting of primary crystals residing in the pure –T–H– and the –T–B– domains, respectively. Melting of secondary crystals close to the pure –T–H– domain gave rise to the T_{mm} transition. Without isotropization, the as-synthesized II-19 after heating at 210°C for 3 min has a complicated DSC thermogram consisting of a low T_g (~44°C), multiple exotherms and endotherms before the major melting transition (~180°C; Fig. 5b). Subsequent treatment by annealing at 165°C for 2 h yielded a simple thermogram with one major high-temperature T_{mh} peak along with three minor low-temperature transitions (indicated by arrows). These low-temperature transitions are probably due to the melting of imperfect crystals formed during cooling from the annealing temperature [7]. Formation of the major T_{mh} transition (Fig. 5c) for

Table 1
Data adapted from DSC scans of copolyesters I-19 and II-19

Sample	$T_g{}^a(\Delta C_p{}^b)$	$T_i{}^a(\Delta H_i{}^c)$	$\Delta S_i \times 100$ (J/(g K))
Copolyester I-19 cooled from 210°C[d]	49(0.04)	288(14.0)	2.50
Copolyester I-19 cooled from 310°C[e]	43(0.12)	255(9.8)	1.86
Copolyester II-19 cooled from 210°C[d]	44(0.03)	248(7.5)	1.44
Copolyester II-19 cooled from 290°C[f]	37(0.08)	238(6.0)	1.17

[a] in°C.
[b] in J/(g K).
[c] in (J/g).
[d] Data were adapted from a separate run, which is not included in the text.
[e] Data were adapted from Fig. 4d.
[f] Data were adapted from Fig. 5d.

the annealed sample suggests the effectiveness of the annealing process for the copolyester II-19 pre-treated at 210°C. For the isotropically-randomized II-19, the corresponding thermogram in Fig. 5d showed the continuous lowering of T_g (~37°C) and the prevalence of multiple melting and recrystallization transitions in the low-temperature regions right before the major T_{mh} transition. The larger supercooling caused by cooling copolyester I-19 from the isotropic liquid state resulted in the more intense endotherms and exotherms in Fig. 5d as compared to those in the sample without isotropization (cf. Fig. 5b). Annealing of this isotropically-randomized sample at 165°C for 2 h resulted in a thermogram (Fig. 5e) resembling that in the sample without isotropization (cf. Fig. 5c), suggesting that no major decomposition (or transesterification) occurred while heating copolyester II-19 at 290°C. Again, those small endotherms indicated by the arrows correspond to the melting of imperfect crystals formed during cooling from 165°C. At this point, it seems that annealing exerts a similar effect on copolyester II-19 samples with or without pre-treatment in the isotropic liquid states; however, the X-ray study given in the later discussion provides a different view.

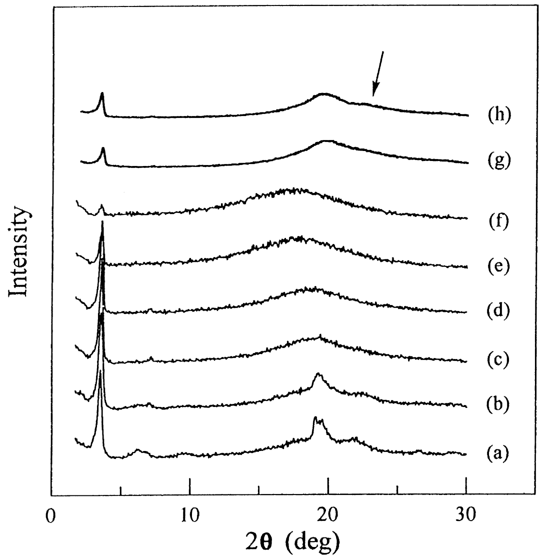


Fig. 6. X-ray diffraction patterns of copolyester I-19 samples after heating at 210°C for 3 min and kept at (a) 25, (b) 140, (c) 180, (d) 210, (e) 260 and (f) 280°C, (g) after heating to 310°C and cooling to 25°C, and (h) after heating to 310°C, annealed at 120°C for 2 h and cooling to 25°C.

Selected data adapted from the DSC heating runs were summarized in Table 1. In regard to T_g, both copolyesters have their T_g lowered by isotropization; in addition, we observed that heat capacity (ΔC_p) for the isotropically-randomized sample is comparatively higher than that for the sample cooled from its mesomorphic state. It seems that chain crystallization of both copolyesters during their subsequent cooling cycle was retarded by isotropization, and this will cause a sample of more amorphous nature as compared to a sample without isotropization. A comment can be made on the T_i transitions, although they are broad in shape for both cases. The enthalpy (ΔH_i) and entropy ($\Delta Si = \Delta Hi/Ti$) involved in the T_i transition during the heating cycle were also included in Table 1. Since the isotropic liquid state is completely randomized, the entropy gained from the mesomorphic to the isotropic liquid states can be used to estimate the relative stability of the mesophase involved in each sample. From the data listed in Table 1, the isotropically-randomized copolyesters I-19 and II-19 all have a less stable mesophase as compared with their corresponding samples cooled from the mesophase. The small ΔS_i value for copolyester II-19 suggests that its mesomorphic state is relatively less stable than copolyester I-19, a result correlated to the more flexible nature of copolyester II-19, as we will discuss later. The corresponding mesomorphic order thus determined from the previous thermal treatment will thereby influence its chain registry effect in the mesomorphic state and also, the melting and crystallization behavior under subsequent DSC scans.

X-ray diffraction study was performed on both copolyesters to evaluate the effect of isotropization. Copolyesters I-19 and II-19 samples after cooling from 210°C were subjected to X-ray study at different temperatures. At 25 and 140°C, copolyester I-19 basically exhibited three low-angle diffraction peaks at $2\theta = 3.45$, 6.20 and 9.65° and two broad wide-angle peaks at $2\theta = 19.6$ and 23.15° (Fig. 6a and b). After heating to the mesomorphic state (i.e. 180 to 280°C, Fig. 6c–f), the two low-angle peaks at $2\theta = 3.6$ (= 24.51 Å) and 7.2° (= 12.25 Å) are still visible, and the peak in the wide-angle region becomes broad. The length of the repeated –H–T– unit calculated from Chem3D is 29.12 Å; therefore, a smectic C structure with a tilt angle of 40° can be assigned for copolyester I-19. Homopolyester prepared from TOBC and HD was previously assigned by Ellis et al. [9] to have a smectic C_2 mesophase, which is a new type of chain arrangement with the mesogenic units in each layer tilted to the layer as normal but with the tilt directions opposite to each other

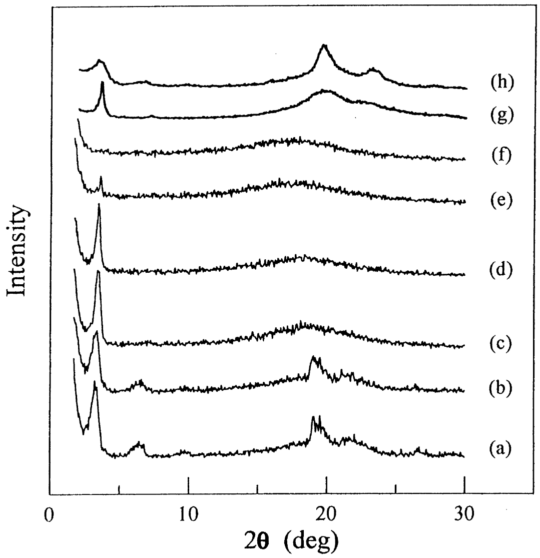


Fig. 7. X-ray diffraction patterns of copolyester II-19 samples after heating at 210°C for 3 min and kept at (a) 25, (b) 140, (c) 180, (d) 230, (e) 250, and (f) 270°C, (g) after heating to 290°C and cooling to 25°C, and (h) after heating to 290°C, annealing at 165°C for 2 h and cooling to 25°C.

Table 2
Crystallinity calculated from X-ray diffraction

Sample	Crystallinity (%)
Copolyester I-19 after cooling from 210°C[a]	32
Copolyester I-19 after cooling from 310°C[b]	22
Copolyester I-19 after cooling from 310°C and annealing at 120°C for 2 h[c]	24
Copolyester II-19 after cooling from 210°C[d]	32
Copolyester II-19 after cooling from 290°C[e]	30
Copolyester I-19 after cooling from 290°C and annealing at 165°C for 2 h[f]	41

[a] Crystallinity was calculated from X-ray pattern in Fig. 6a.
[b] Crystallinity was calculated from X-ray pattern in Fig. 6g.
[c] Crystallinity was calculated from X-ray pattern in Fig. 6h.
[d] Crystallinity was calculated from X-ray pattern in Fig. 7a.
[e] Crystallinity was calculated from X-ray pattern in Fig. 7g.
[f] Crystallinity was calculated from X-ray pattern in Fig. 7h.

between neighboring layers [10,11]. The assignment by Ellis was based on a wide-angle X-ray diffraction study on an un-oriented sample and therefore, is a speculation rather than a conclusive result. To have a clear identification of the smectic C_2 mesophase, an X-ray pin-hole study on an oriented fiber sample is required; however, an oriented fiber sample is difficult to obtain due to the high viscosity of copolyester I-19 in its smectic mesophase. At this point, we can only assign a smectic C mesophase for copolyester I-19. Here, X-ray diffraction study for the isotropically-randomized copolyester I-19 was taken at room temperature and given in Fig. 6g. Separate POM study suggests that the isotropically-randomized sample exhibits a similar broken fan texture at room temperature, indicating that the macroscopically mesomorphic structure can be safely frozen by cooling. Comparison between Fig. 6a and g clearly demonstrates the difference between samples cooled from the mesomorphic and the isotropic liquid states. The smaller low-angle and the broader wide-angle diffraction peaks in Fig. 6g suggest the existence of a less perfect mesomorphic structure in the frozen isotropically-randomized sample as compared with the sample cooled from 210°C (cf. Fig. 6a). Difference in the X-ray diffraction patterns was also reflected in the corresponding DSC thermograms, where the existence of T_{m1}, T_{m2}, T_{m3} and T_{m4} transitions for copolyester I-19 cooled from 210°C (cf. Fig. 4b) is distinct from the only low-temperature endotherm observed for the isotropically-randomized sample (cf. Fig. 4d). Subsequent annealing of the isotropically-randomized sample at 120°C for 2 h (Fig. 6h) only slightly changed its diffraction pattern. Coherent DSC thermograms of Fig. 4b and f did suggest that annealing induces formation of one tiny, extra endotherm at 143°C, which corresponds to the intensified diffraction shoulder shown in Fig. 6h (indicated by the arrow).

Copolyester II-19 exhibited similar low-angle diffraction peaks (Fig. 7c–e) to copolyester I-19 in its mesomorphic state; therefore, the same smectic C mesophase was tempararily assigned for copolyester II-19 too. The smaller low-angle peak in Fig. 7g refers to a less ordered structure in the isotropically-randomized copolyester II-19 as compared with sample only pretreated at 210°C, where a sharp low-angle diffraction peak was observed (Fig. 7a). Accordingly, isotropization actually randomizes the ordered packing of the crystalline chain segments in copolyester II-19, a result can not be clearly demonstrated by the corresponding DSC thermograms (Fig. 5b and d). Further annealing of the isotropically-randomized sample at 165°C for 2 h (Fig. 7h) resulted in the sharper wide-angle peaks; however, the broad low-angle peak indicates the average orientation in the annealed sample is still low. The enhanced crystallinity as evidenced by the enhanced peak shape in the wide-angle region was reflected in the disappearance of multiple endotherms and exotherms in the low-temperature region of the corresponding DSC thermograms (compare Fig. 5d and e).

Crystallinity of copolyester I-19 and II-19 after different thermal treatments can be calculated from the wide-angle peaks, and was summarized in Table 2. For copolyester I-19, isotropization caused the reduction of crystallinity from 32 to 22%, and further annealing of the isotropically-randomized sample did not improve its crystallinity much. On the contrary, isotropization on copolyester II-19 only affected its crystallinity a little (from 32 to 30%), and continued annealing on the isotropically-randomized sample improved its crystallinity from 30 to 41%. Here, we should noticed that isotropization actually randomized the chain orientation of copolyester II-19 since the corresponding X-ray peaks in the low-angle regions of Fig. 7a and g turned out to be different. It is then suggested that the isotropically-randomized copolyester II-19 mainly consists of a large number of imperfect, small crystals with their orientation orders conceivably lower than those in the sample without previous treatment in the isotropic liquid state. These small crystals with various orientations can be rearranged to a more ordered state by an annealing process, and resulted in enhanced crystallinity as evidenced by the X-ray and DSC results.

The premise that previous thermal history determines the melting behavior should be considered before we mention the registry effect of neighboring chains in the mesophase. On cooling from the isotropic liquid state, the sample would pass through the ordered mesomorphic state, whose chain packing would determine its crystallization behavior before the set-in of the glassy state to freeze the corresponding structure. The frozen structure would therefore determine its following recrystallization and melting behavior during the next heating cycle; that is to say, the extent of registry between neighboring chains in the mesomorphic state would be governed by the capability of the randomized chains to resume their mesomorphic packing during cooling from the isotropic liquid state. Reasonably, the ease of the isotropically-randomized chains to resume their ordered mesomorphic packing should be strongly influenced by their arrangement geometry, which is intimately related to the chemical structure of the corresponding polymer.

Both copolyesters I-19 and II-19 contain the same major ingredient (90 mol% of the –T–H– units) but different minor components (chain units of –T–S– for copolyester I-19 and –T–B– for copolyester II-19, cf. Fig. 2). To understand the effect of the minor component, the geometry difference between SPI and BHS moieties should be commented on first. As viewed from the simulated structure in Fig. 1, the central spiro carbon in SPI imposes a twisted geometrical arrangement on the two connected cyclic aromatic rings. The two hydroxyl terminals in SPI are therefore situated in a bent geometry, and will force this nonlinear arrangement into the neighboring groups once they are incorporated in the polymer chain. The SPI moieties would therefore keep the neighboring aromatic TOBC triads from packing into a parallel manner as required in an ordered mesomorphic or crystalline structure. Conceivably, this effect is long-distance since one bent unit, once generated, would take several neighboring –T–H– chain segments to readjust before an ordered smectic layers of considerable dimensions can be reached. The situation is different for copolyester II-19 since all its rigid SPI moieties are linked to flexible 1,6-dioxyhexanyl (–D–) units. With the connected –D– spacers, the detrimental effect of the SPI units in BHS would be conceivably reduced; that is to say that the mesogenic TOBC triads in copolyester II-19 are all separated from the SPI moieties by the flexible –D– units and have the opportunity to pack in a relatively parallel fashion through the adjustment of the connected –D– spacers. Our previous experimental results can further support the above point. Homopolyester prepared from TOBC and SPI is amorphous in nature without any thermal transitions before decomposition [6]. On the contrary, homopolyester from polymerization of TOBC and BHS is a nematic material [7], indicating that its inherent aromatic triads can achieve an oriented structure with one-dimensional order despite the inherent SPI moieties.

The difference between the minor components in copolyesters I-19 and II-19 exerts certain effects on their thermal behavior. Copolyester II-19 samples cooled from either its mesomorphic or isotropic liquid states tended to crystallize earlier as compared with copolyester I-19 samples with the same treatments (cf. Fig. 3). This result simply reflects the ease of the flexible BHS in copolyester II-19 to undergo crystallization, which is considered to be more difficult for copolyester I-19, during cooling from the elevated temperatures. The minor composition, although of limited amount, also affects the glassy state. With the same thermal treatments, T_gs of copolyester II-19 samples are always 5–6°C lower than those for copolyester I-19 samples.

By understanding the role of the minor components and the registry effect in the mesomorphic state, the thermal behavior of the copolyesters I-19 and II-19 can be understood. Copolyester samples after cooling from either the mesomorphic or the isotropic liquid state tend to develop its crystalline and amorphous structures during the subsequent crystallization exotherm and glass transition temperature. It is then suggested that both copolyesters at room temperature contain both the glassy smectic (no dark amorphous glassy region was detected under polarized light [6,7]) and the crystalline phases. According to the ease of the transformations of the multiple endotherms and exotherms upon annealing, we may propose that variations on the melting transitions mainly occurred in either the crystalline phase or the smectic glassy region near the crystalline domain. Therefore, the crystalline phase determined from the previous mesomorphic order is crucial for the thermal behavior observed during DSC scans. Previous studies on the registry of neighboring chains in the mesophase [3–5] were all concentrated on polyesters with a nematic mesophase, which is relatively more unstable than the smectic C mesophase as observed in copolyesters I-19 and II-19. It is conceivable that a smectic C mesophase is difficult to attain since it required a tilted layered structure; therefore, the chain arrangements in a form of smectic C structure would be difficult to retain once they are randomized by isotropization. This comment holds for both copolyesters and this difficulty to resume the original mesomorphic state is reflected in the reduced intensity of the X-ray diffraction peak at $2\theta = 3.6°$ for the isotropically-randomized copolyesters I-19 and II-19. This is to say that both samples after cooling from their isotropic liquid states mainly consist of a large number of small crystals with less ordered structures than their corresponding samples without pre-treatment in the isotropic liquid states. Nevertheless, due to the difference in the chemical structures of the minor components, both chain structures randomized by isotropization have different responses under subsequent thermal treatments. As discussed above, the SPI moieties, despite their limited amounts, in copolyester I-19 can efficiently retard the crystallization process of chain segments nearby or far away; therefore, annealing did not induce formation of any high-temperature transitions (cf. Fig. 3e–g). In contrast, the flexible BHS moieties in copolyester II-19 are not so detrimental to the crystallization process as the rigid SPI moieties in copolyester I-19. Therefore, the chain segment in the small crystals of the isotropically-randomized copolyester II-19 can undergo multiple melting and recrystallization processes under DSC scan. This ease of chain rearrangement resulted in the great enhancement of crystallinity by annealing of the isotropically-randomized copolyester II-19.

4. Conclusion

The chain segments in both copolyesters I-19 and II-19 can be randomized by an isotropization process. With bent SPI moieties, it is difficult for the isotropically-randomized copolyester I-19 to undergo recrystallization to enhance its crystalline structure. On the contrary, the chain segments in the isotropically-randomized copolyester II-19 can undergo multiple melting and recrystallization processes to improve its crystallinity. This difference was reflected in their responses to annealing processes and is basically due to the difference in the chemical structures of the minor components.

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