ELSEVIER

Polymer 41 (2000) 4501–4512

polymer

Semi-rigid thermotropic polyester containing a rigid, bent spirobicromane moieties—primary characterizations and the thermal behavior

L.-L. Lin, J.-L. Hong*

Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC

Received 21 June 1999; received in revised form 23 August 1999; accepted 30 August 1999

Abstract

Thermotropic copolyester TBH with inherent spirobicromane (SPI) moieties was prepared by polycondensation reaction between mixed diols of 4,4-bis(6-hydroxyhexanoyloxy)spirobicromane (BHS, 10 mol%), 1,7-heptanediol (HD, 90 mol%) and terephthaloyl bis(4-oxybenzoyl chloride) (TOBC). In addition, homopolyester TH (or TB) synthesized from TOBC and HD (or BHS) diol was prepared for comparison. With the incorporated SPI moieties, polyester TB is a nematic material, in contrast to the smectic C_2 mesophase observed for polyester TH and copolyester TBH. The rigid, spiro SPI moieties in polyester TB are supposed to interrupt the ordered packing of the mesogenic triads required for a smectic C_2 mesophase. Under diffraction scanning calorimetry (DSC) scans, copolyester TBH exhibited multiple endothermic and exothermic peaks, which are different from the much simpler thermal behavior observed for homopolyesters TH and TB. The multiple melting and crystallization transitions for copolyester TBH was due to the facile crystallization of the inherent flexible spacers and the potential registry of neighboring chains in the mesomorphic state according to the results from isothermal, non-isothermal crystallization experiments, and the X-ray diffraction study. Suggestively, the rigid, bent SPI moieties would impose a nonlinear geometry on the connected spacers and mesogenic units and consequently, influence its chain arrangement in the mesomorphic state. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic polyester; Spirobicromane; Mesophase packing

1. Introduction

There has been lots of research on the synthesis of thermotropic polyesters [1–3] with unique thermal and physical properties. Among them, the wholly aromatic thermotropic polyesters generally have high crystal-to-mesophase transitions, T_m, [4,5] and are insoluble in most organic solvents. To obtain polymers with considerably low T_ms, several chemical modifications including: (i) the introduction of bulky, or non-symmetrical substituents; (ii) the use of flexible spacer; (iii) the use of nonlinear or bent monomers; and (iv) copolymerization of different monomers [6–13] have been previously used. Here, route of copolymerization provides versatile ways to prepare new thermotropic copolyesters of low T_m through the uses of conventional monomeric diacids and diols.

Thermotropic polyester prepared from condensation reaction of flexible 1,7-heptanediol (HD, Fig. 1) and terephthaloyl bis(4-oxybenzoyl chloride) (TOBC, Fig. 1) [14] possesses low thermal transitions ($T_m = 176$ and $T_i = 253$°C) as compared to the wholly aromatic polyesters; however, its solubility in organic solvents is still limited. To resolve the solubility problem, a spiro diol, spirobicromane (SPI, with its simulated structure in Fig. 1), was used to copolymerize with HD and TOBC in our laboratory [15]. Copolyesters thus prepared have good solubility, however, liquid crystal properties were lost if the incorporated SPI content is more than 20 mol% [15]. The spiro SPI moieties would impose a nonlinear geometry on the connected mesogenic TOBC triads and retard the formation of the mesomorphic ordered structure. Example cited above case illustrates a serious destruction effect of SPI moieties if there are directly connected to the mesogenic triads. Intuitively, it would be interesting to learn what is the effect of the spiro SPI units if they are connected with flexible spacers instead of the rigid TOBC triads? With this purpose, a monomeric BHS diol (cf. Fig. 1) with its central SPI unit connected with flexible 1,6-dioxy-hexamethylene chains (cf. Fig. 1) were thus prepared and used to synthesize polyester and copolyester to formulate the influence of the SPI moieties on the mesomorphism.

Crystallization behavior of a number of thermotropic polyesters had been the research focus in the last decade.

---

* Corresponding author. Tel.: +886-7-525-2000-4065; fax: +886-7-525-4099.

E-mail address: jlhong@mail.nsysu.edu.tw (J.-L. Hong).

PII: S0032-3861(99)00668-0

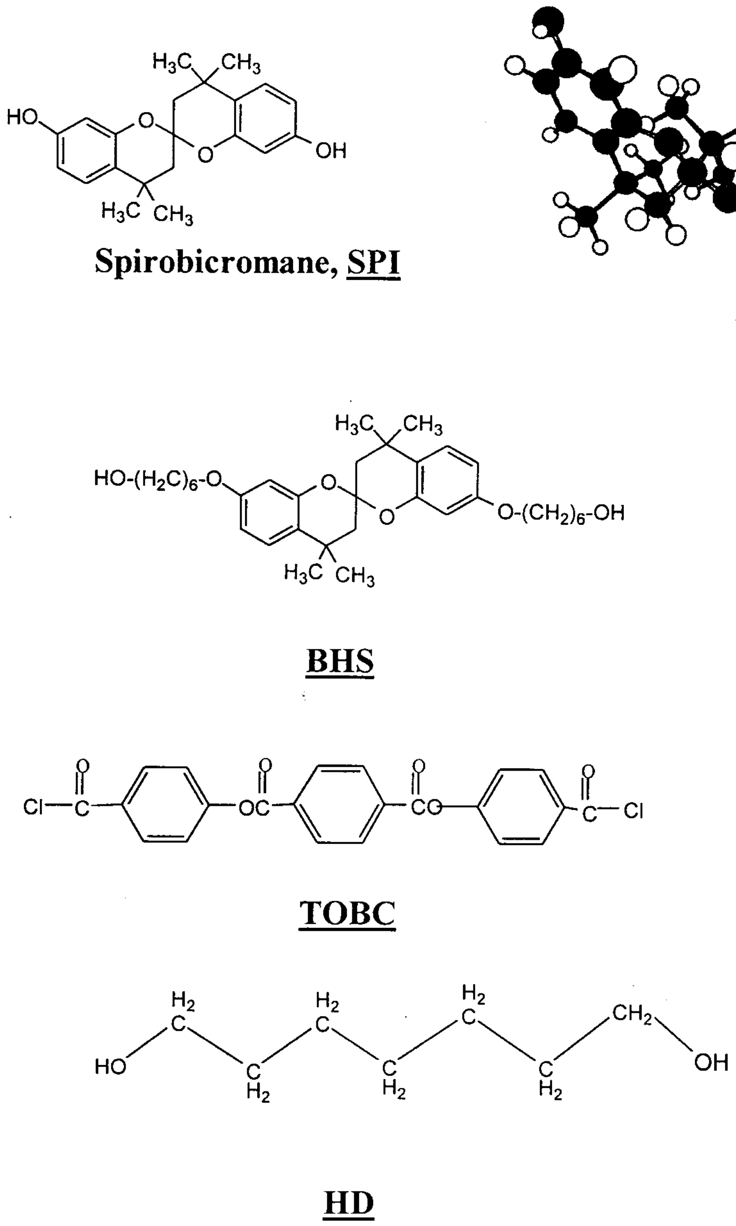
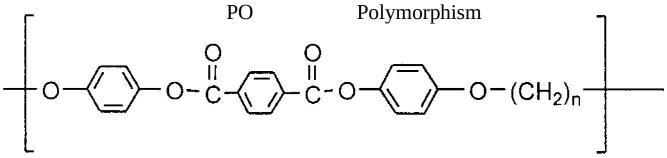
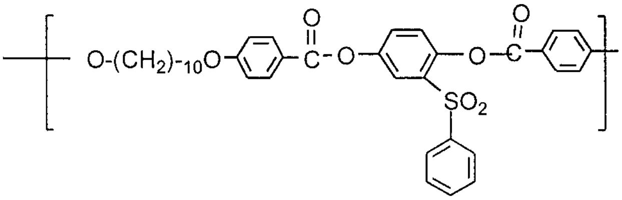
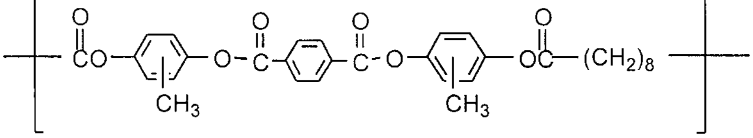
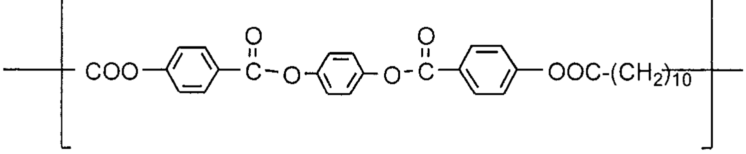
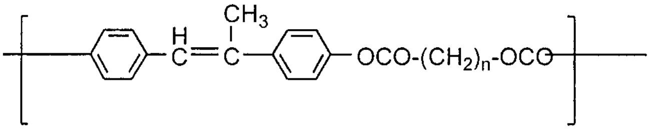


Fig. 1. Chemical structure of spirobicromane (SPI) and BHS. (the computer simulated structure for SPI (ball-and-stick model) was also included).

The multiple melting behavior of the fully aromatic copolyesters prepared from 1,4-dihydroxybenzoic acid and 2,6-dihydroxynaphtholic acid had been ascribed to a two transition processes [16–19]. In contrast, complicated results had been reported for the crystallization behavior of the semi-rigid thermotropic polyesters. Representative examples were summarized in Table 1, in which different mechanisms attributable to multiple melting endotherms observed during DSC scans were suggested [20–25]. Here, a dual crystal population [25] (or chain registry [23,24]) was used to explain the melting and crystallization behavior of the semi-rigid polyesters PM1, PM2 and HMS-*n* listed in Table 1. This hypothesis described that certain registry of neighboring chains in the nematic state can serve as potential nuclei for primary crystal and the crystals formed in the remaining portions upon secondary crystallization. In other words, any existing mesomorphic state should complicate the thermal behavior of liquid crystalline polyesters; the situation will be more complicated for copolyester cases since the sequence distribution of the comonomer units adds complexities to their thermal behavior.

In this contribution, we attempted to study the effect of SPI moieties in a semi-rigid copolyester TBH (Scheme 1, syntheses of monomeric BHS and copolyester TBH). Here, a conventional BHS (Scheme 1) diol with the incorporated spiro SPI and flexible spacer was prepared, and copolymerized with TOBC and HD diol to prepare copolyester TBH. In addition, two homopolyesters TB and TH from the

Table 1
Chemical structures of different semi-rigid polyesters and the origins for their multiple melting behaviors

Chemical structure	Symbol	Origin for multiple melting
	PO	Polymorphism
	PSQ10	Recrystallization and perfection
	PM1	Registry of neighboring chains in the nematic state
	PM2	Registry of neighboring chains in the nematic state
	HMS-*n*	Dual crystal

respective condensation reactions shown in Scheme 2 (synthesis of polyester TB and TH) were prepared for the purpose of comparison. All the polymers were characterized and compared in the aspect of their melting behavior; especially, the complicated thermal behavior of copolyester TBH was studied by the applications of isothermal, non-isothermal crystallization experiments and X-ray diffraction study.

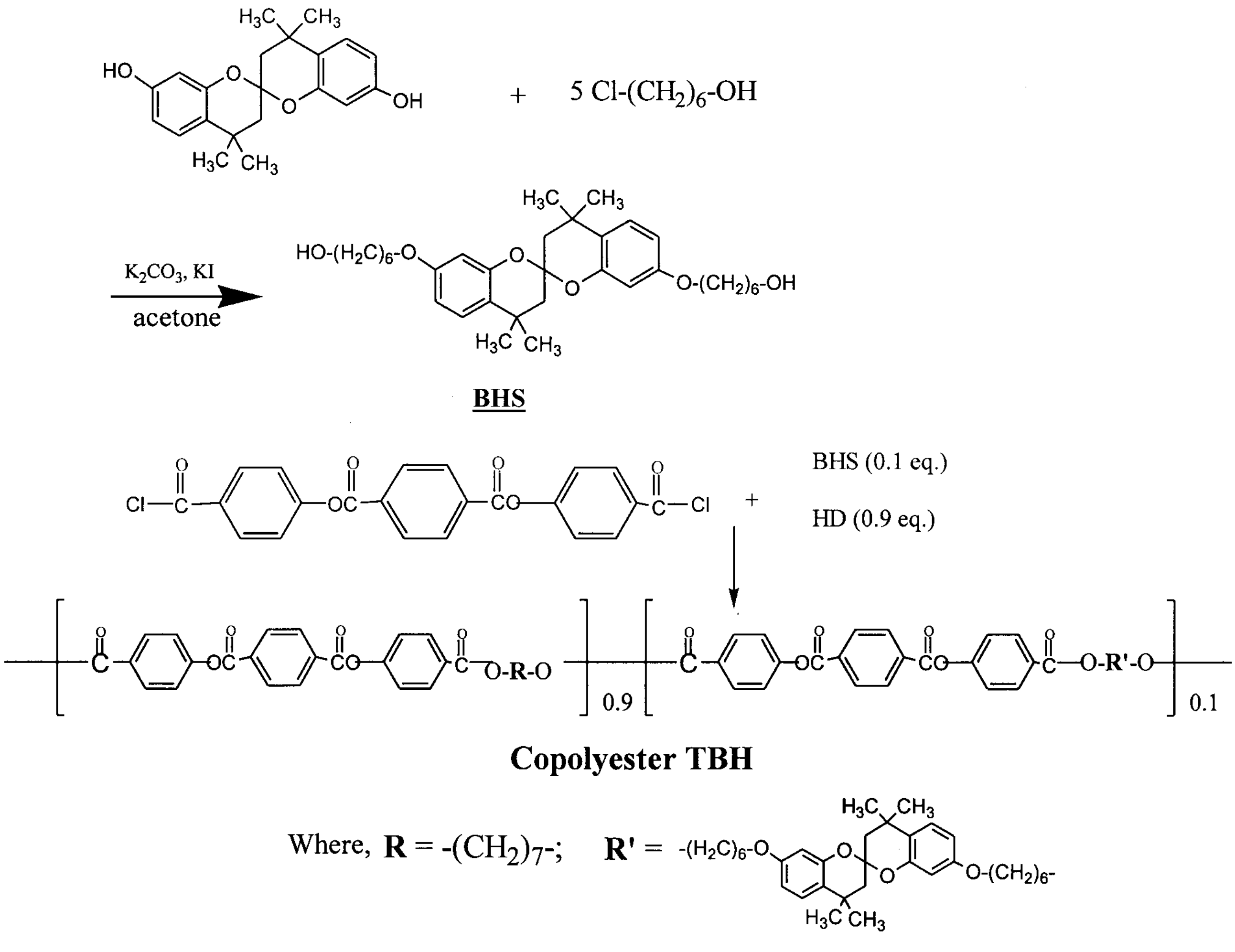
2. Experimental

2.1. Materials and instrumentation

1,7-Heptanediol (HD) and 6-chloro-1-hexanol were vacuum dried at 50°C for 12 h and stored over molecular sieve 4 Å (Linde). Pyridine was distilled after treating with KOH. 1,1,2,2-Tetrachloroethane (TCE) was pre-dried over molecular sieve 4 Å (Linde) for over 1 week before use.

Proton NMR was recorded with a VXR-300 FT-NMR 300 MHz model. Tetramethylsilane (TMS) was used as the internal standard in all cases. The texture of the liquid crystals was observed with a Nikon Optiphot-POL microscope equipped with a Linkam TMS controller and THMS 600 hot stage. X-ray diffraction pattern was obtained with a Siemens Diffraktometer D 5000 model with Ni-filtered K_α radiation.

Thermal transition temperatures were detected with a Perkin–Elmer DSC 7 model. The carrier gas was nitrogen



Scheme 1.

at a flow rate of ca 10 ml/min. Calibration of the calorimeter was conducted for each heating rate using an indium standard. Different thermal treatments were specifically performed on copolyester TBH. Before each treatment, the samples were heated to the mesomorphic state (210°C), and kept at that temperature for 3 min; it has been observed that reproducible results were obtained by changing the time at 210°C from 3 to 20 min.

In the annealing experiments, samples after non-isothermally crystallized at a cooling rate of 20°C/min were heated in the DSC from room temperature to the chosen annealing temperature (T_a, ranging from 100 to 150°C), and kept at that temperature for different times (t_a). The samples were then cooled at a rate of 20°C/min to room temperature before re-heating to yield the DSC thermograms.

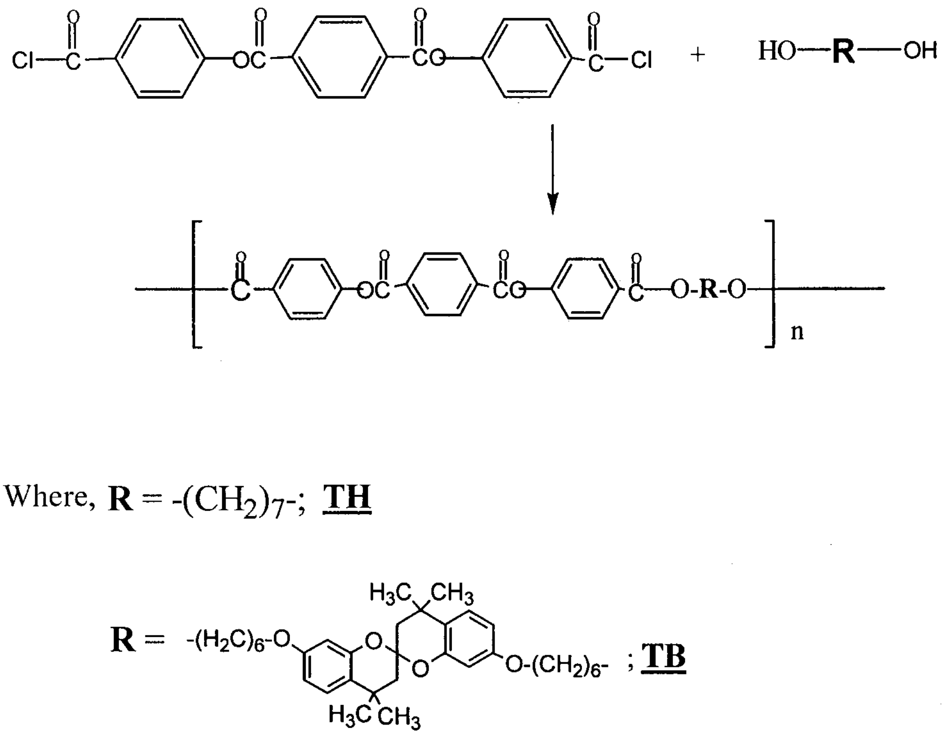
The isothermal crystallization samples were quenched from 210°C to the crystallization temperature (T_c, ranging from 100 to 165°C) and kept there for different time periods (t_c). The samples were then cooled to room temperature and re-heated to obtain the DSC traces. In some cases, re-heating was performed right after the isothermal crystallization process, and the immediate rescan of the DSC traces recorded.

The non-isothermal crystallization samples were cooled from the mesomorphic state (210°C) at different rates (5, 10 and 20°C/min) before re-heating to obtain the DSC thermograms.

2.2. Synthesis

Synthesis of TOBC had been described previously [26]. Copolyester TBH was obtained by condensations of TOBC with 1/9 molar ratio of BHS and HD (Scheme 1). BHS (or HD) monomer was primarily synthesized to react with TOBC to yield polyester TB (or TH) (Scheme 2).

Synthesis of 4,4-bis(6-hydroxyhexanoyloxy)spirobicromane (BHS) monomer. Mixtures of spirobicromane (SPI, 20 mmol), K_2CO_3 (36 mmol) and KI (~1 wt%) in 30 ml of acetone were heated to reflux before the addition of 6-chloro-1-hexanol (100 mmol) in 10 ml of acetone. The reaction was continued for 48 h. The resulting solution was then subjected to a two phase (H_2O/diethyl ether) extraction process. The ether layer was then vacuum dried to obtain the final product, BHS. ^1H NMR(300 MHz, $CDCl_3$): δ 7.19 (d, 2H, aromatic 5-Hs in SPI), 6.52 (q, 2H, aromatic 3-Hs in



Scheme 2.

SPI), 6.19 (d, 2H, aromatic 2-Hs in SPI), 3.84 (t, 4H, –Ar–O–CH_2–), 3.61 (t, 4H, HO–CH_2–), 2.01 (q, 4H, –CH_2– in SPI), 1.52 (m, 28H, –O–CH_2–$(CH_2)_4$–CH_2–O– and –CH_3).

Syntheses of polyester TH, TB and copolyester TBH. Syntheses of all polymers followed the same procedures. Under nitrogen atmosphere, solution of diol monomer (10 mmol of BHS (or mixture of BHS/HD of 1–9 mmol)) in 5 ml of TCE was slowly added to a solution of TOBC (10 mmol), pyridine (catalytic amounts) in 15 ml of TCE. Reaction was continued at 60°C for 24 h. The crude product was precipitated from methanol, and washed with 5% aqueous HCl, 5% aqueous $NaHCO_3$, 5% aqueous HCl solution, and distilled water. Final polymers were obtained after filtration and dried under vacuum. Representative ^1H NMR of polyester TB (300 MHz, $CDCl_3$) is shown below: δ 8.35 (s, 4H, terephthalate of Triad), 8.15 (d, 4H, 2,6-*p*-oxybenzoyl of Triad), 7.33 (d, 4H, 3,5-*p*-oxybenzoyl of Triad), 7.20 (d, 2H, aromatic 5-Hs in SPI), 6.53 (d, 2H, aromatic 4-Hs in SPI), 6.22 (s, 2H, aromatic 2-Hs in SPI), 4.33 (t, 4H, –CO–O–CH_2–), 3.66 (t, 4H, –O–CH_2–), 2.01 (q, 4H, –CH_2– in SPI), 1.52 (m, 28H, –O–CH_2–$(CH_2)_4$–CH_2–O– and –CH_3). Inherent viscosity was measured at a concentration of 0.5 g/dl, using a Ubbelohde viscometer at 30°C. η_{inh} (in TCE + CF_3CO_2H (1 wt%)) of TH = 0.31 dl/g, η_{inh} (in TCE) of TB = 0.18 dl/g and η_{inh} (in TCE) of TBH = 0.30 dl/g.

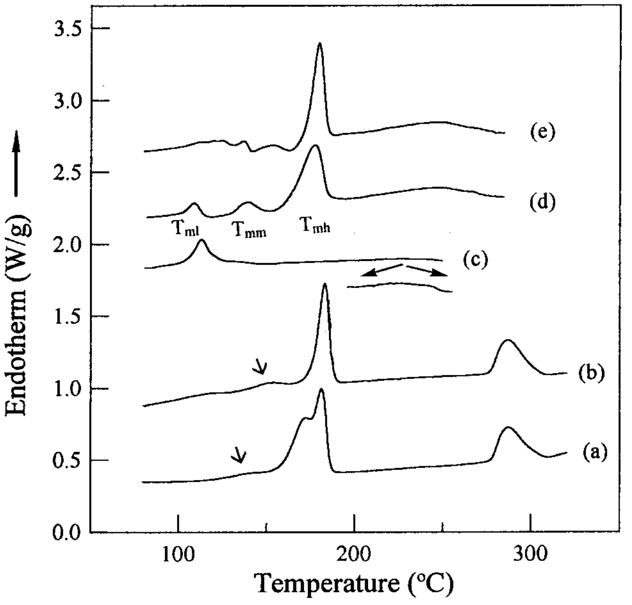


Fig. 2. DSC thermograms of: (a) the as-synthesized polyester TH; (b) second scan of polyester TH after cooling from 210°C; (c) the as-synthesized polyester TB; (d) the as-synthesized copolyester TBH; and (e) second scan of copolyester TBH after cooling from 210°C (heating rate = 20°C/min).

3. Results and discussion

BHS diol, synthesized from spirobicromane (SPI) and 6-chloro-1-hexanol (CH, Scheme 1), was used as monomer for the preparation of polyester TB and copolyester TBH. Here, excess CH was used to avoid the potential polycondensation reaction between SPI and CH. Thermotropic

Table 2
Data adapted from DSC scans of polyesters TH, TB and copolyester TBH

Sample	T_{ml} (°C)[a]	T_{mm} (°C)[a]	T_{mh} (°C)[a]	T_i (°C)[a]	$\Delta S_i \times 10^2$ (J/g K)
TH[b]			182 (28.9)	289 (14.0)	2.64
TB[c]			113 (6.9)	230 (1.7)	0.33
TBH[d]	109 (3.3)	139 (3.1)	177 (20.3)	24 (7.6)	1.46

[a] The corresponding melting enthalpies in J/g are given in parentheses.
[b] Data were adapted from Fig. 2a.
[c] Data were adapted from Fig. 2c.
[d] Data were adapted from Fig. 2d.

copolyester, TBH and polyesters TH and TB were synthesized according to the procedures described in Schemes 1 and 2, respectively. Suggestively, copolyester TBH should have a random chain distribution in considering the equal reactivity of the aliphatic –OH groups in BHS and HD toward TOBC. The resulting polyester TH is insoluble in common organic solvents; in contrast, with the inherent SPI moieties, polyester TB and copolyester TBH can be easily dissolved in the chlorinated solvents (i.e. $CHCl_3$, CH_2Cl_2 and TCE).

3.1. Primary characterization of polyester TH, TB and copolyester TBH

DSC traces of homopolyesters TB and TH in Fig. 2 have different features. The as-synthesized TH (Fig. 2a) exhibited a broad tiny endotherm (indicated by arrow) right before the double melting ($T_m \sim 180$°C) and the isotropization ($T_i \sim 290$°C) transitions. Second rescan of the as-synthesized TH polymer (Fig. 2b) after cooling from the mesomorphic state (210°C) transformed the double melting peaks into one tiny (~150°C) and one major endotherms at slightly higher position (~176°C) than the first run, but for T_i transition, it remained intact. Suggestively, different crystalline structures induced by the TCE solvent used in the synthesis stage can be altered by thermal treatment. Here, the peak temperature of T_i transition is higher than the reported value ($T_i = 253$°C); [14] however, this difference may be due to the method of detection (by visual observation in the previous report [14]) or molecular weight difference. In contrast to the intense peaks observed for TH, polyester TB exhibited a single melting transition at 113°C followed by a broad, tiny isotopization transition (as the magnified features shown in Fig. 2c) in the ranges of 210–246°C. The SPI-containing BHS moieties in TB are assumed to reduce the thermal transition temperatures (T_m and T_i) as compared with those for TH polymer. DSC traces of the as-synthesized copolyester TBH in Fig. 2d consists of two small (as T_{ml} and T_{mm}, respectively) and one large melting (as T_{mh}) peaks ahead of the broad T_i transition that ranged from 225 to 260°C. Here, small exothermic heats were involved between the three melting transitions. Second scan of copolyester TBH sample after cooling from the mesomorphic state (Fig. 2e) exhibited different features, in which the presence of the multiple exotherms suggests the progress of the facile re-crystallization process. Comparatively, the highest melting endotherm (T_{mh}) appeared at approximately the same position with the melting transition of TH polyester (cf. Fig. 2b); therefore, it may correspond to the melting process of the –(TOBC–HD)– segments. Origin of these multiple endotherms and exotherms is discussed later in this paper but before that, primary comparison between these three samples can be made.

Enthalpy (ΔH_m and ΔH_i) and the calculated entropy during isotropization (ΔS_i) of the as-synthesized samples were summarized in Table 2. Polyester TH possesses the highest ΔH_m ($= 28.9$ J/g), incorporation of 10 mol% of BHS moieties resulted in the slight decrease of the total ΔH_m ($= 26.7$ J/g) for copolyester TBH. Polyester TB, with a whole –(BHS–TOBC)– unit, has the lowest ΔH_m ($= 6.9$ J/g) among all three samples. A similar order is also operated for ΔH_i, that is, polyester TH has the highest ΔH_i, then is copolyester TBH and polyester TB possesses the lowest ΔH_i value. The incorporation of the BHS units seems to reduce the chain stability in the mesophase, an effect can be also seen based on the respective ΔS_i values. Based on the previous study of Dewar and Griffin on different nematic esters, [27] entropy involved during isotropization is determined by both isotropic temperature and enthalpy change, which can be illustrated by $\Delta S_i = \Delta H_i / T_i$. Since isotropic liquid state is completely randomized, polyester TH gains more entropy in passing from the mesomorphic to isotropic liquid states as compared to polyester TB and copolyester TBH. The small ΔS_i value for polyester TB suggests its mesophase is relatively unstable, a point will be further disclosed by X-ray study.

Under polarizing light, polyesters TB exhibited texture of scattered birefringent droplets (Fig. 3a). The corresponding X-ray diffraction pattern in its mesomorphic state showed no low-angle peak and therefore, a nematic mesophase is assigned for copolyester TB. This less-ordered nematic mesophase contributes to the small ΔS_i value for TB sample. For polyester TH, the broken fan texture (Fig. 3b) may suggest the presence of a smectic mesophase. In contrast, copolyester TBH exhibited lots of unidentified, small birefringent domains distributed over the whole specimen (Fig. 3c). The much smaller domain sizes in copolyester

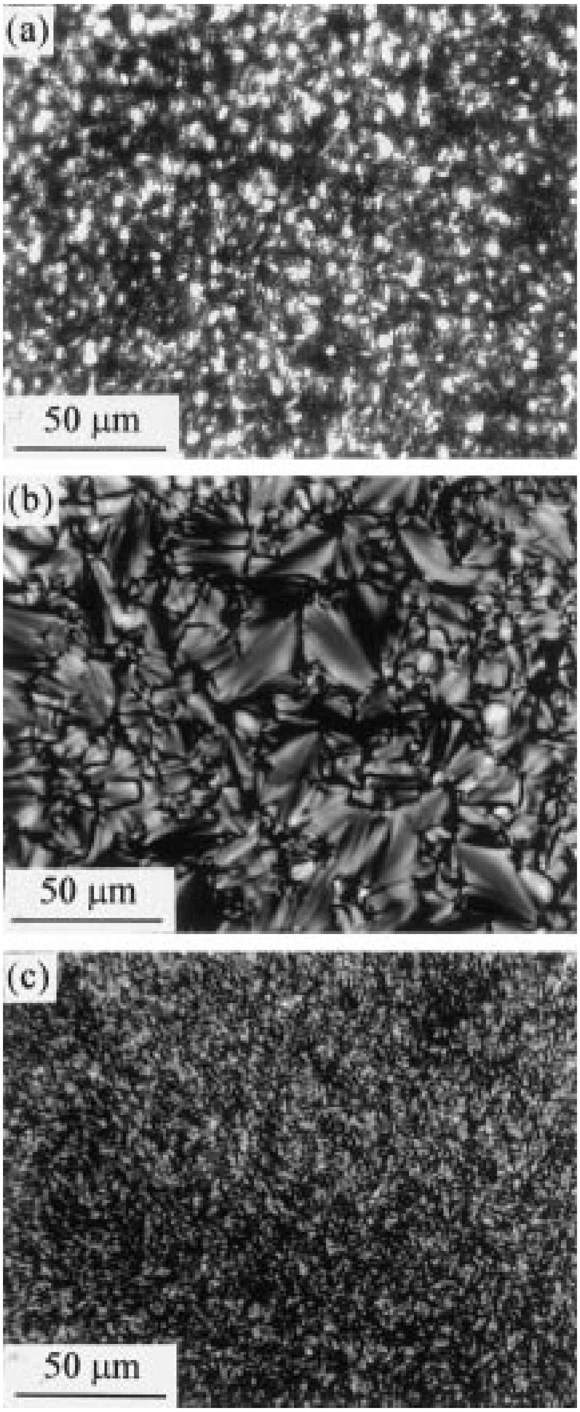


Fig. 3. POM photographs of: (a) polyester TB at 140°C; (b) polyester TH at 220°C; and (c) copolyester TBH at 200°C.

TBH as compared with polyester TH may reflect the relative mesomorphic order in both samples.

Molecular arrangement of the polyesters at various temperatures can be evaluated by the temperature-programming WAXD study. First, we examined the diffraction patterns of the polyester TH shown in Fig. 4a. At room temperature, TH possesses 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 23.5°. All the diffraction peaks remained intact at $T = 100$ and 140°C; however, two diffraction peaks at $2\theta = 3.6$ ($= 24.51$ Å) and 7.2° ($= 12.25$ Å) were visualized after heating TH to the mesomorphic state (i.e. from 180 to 280°C). The length of the repeating –(TOBC–HD)– unit evaluated from Chem3D is 29.12 Å (as shown in the bottom of Fig. 4); therefore, a smectic C structure with a tilt angle of 50° can be temporarily assigned for polyester TH at this moment. However, Ellis et al. [28] had previously suggested a smectic C_2 mesophase for polyester TH [28] based on the correlated results between *d*-spacing from X-ray diffraction study and the calculated length of repeat unit. The smectic C_2 (or C_p) mesophase [29,30] illustrates a new type of chain arrangement in which the mesogenic units in each layer are tilted to the layer normal but with their tilt direction is opposite to each other between neighboring layers. It is important to note that the mesognic groups in the polymer chains of even-membered are approximately parallel to the chain axis, while in odd-membered polyesters the mesogenic groups are tilted by certain angles to the chain axis, their tilt directions being opposite between the mesogenic groups that are next to each other along the polymer chains. Such situation was understood by picturing the methylenic units in the polymer chains that are all-*trans* conformation [29]. Reasonably, we may assign that polyester TH possesses a smectic C_2 structure since it contains an odd-number methylenic chains. Copolyester TBH in the mesomorphic state (i.e. from 180 to 230°C) exhibited a similar low-angle diffraction peak at $2\theta = 3.6°$ (Fig. 4b), which suggests a smectic C_2 mesophase for TBH; however, the absence of the second-order diffraction at $2\theta = 7.2°$ and the broad diffraction pattern for the peak at $2\theta = 3.6°$ suggest a less-ordered mesophase for copolyester TBH as compared with TH polyester. This fact plus the nematic mesophase observed for polyester TB all indicates that incorporation of BHS moieties considerably interrupts the ordered chain packing in the mesomorphic state.

As cited above, polyester TH possesses a layered smectic mesophase; in contrast to the less-ordered nematic mesophase for polyester TB. Previous study on polyesters prepared from TOBC and different aliphatic diols [14] (or other systems [31]) indicates that the conformations of the polymer chains and the placement of the mesogenic units will be increasingly more ordered for polymers with longer aliphatic spacer. With this regard, polyester TB with a longer spacer length (disregard the central SPI unit, a total C12 chain was placed in between the two mesogenic TOBCs) than the polyester TH has should possess a more stable mesophase; nevertheless, a less-ordered nematic mesophase was formed for TB. The role of SPI-containing BHS units in polyester TB is therefore important. As suggested in Fig. 1, SPI unit possesses a rigid, bent structure with its terminal –OH situated in a nonlinear position, which should impose certain restrictions on the neighboring chains even if they are flexible spacers. Suggestively, SPI

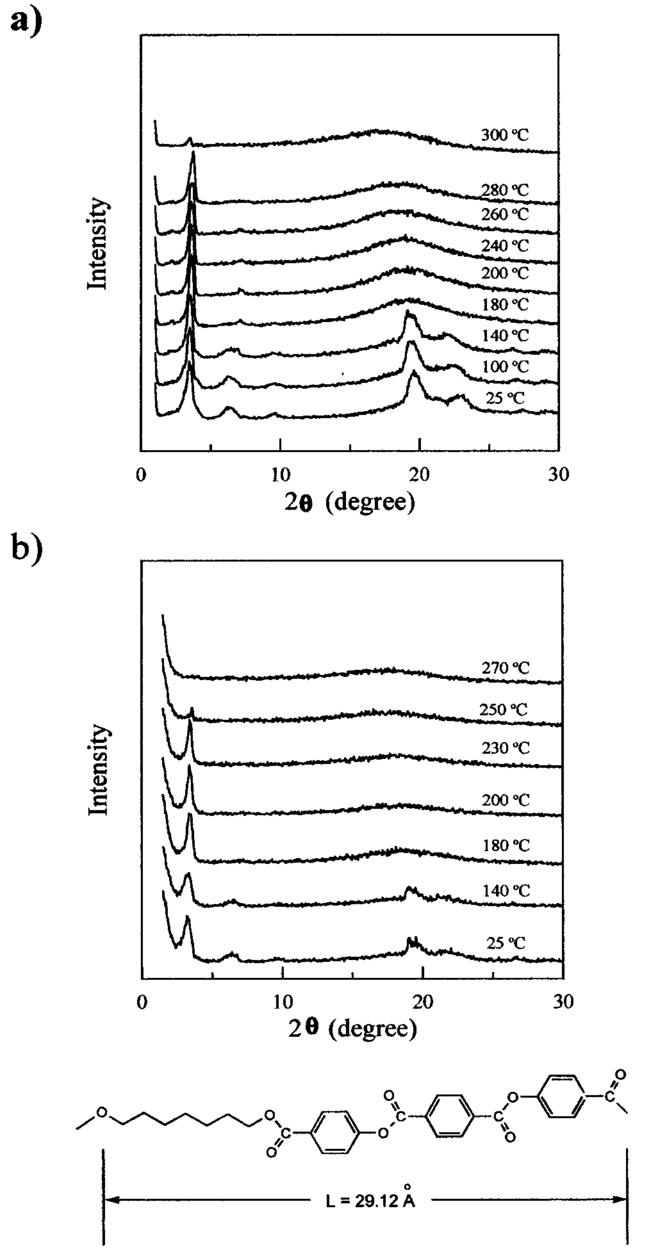


Fig. 4. X-ray diffraction patterns of: (a) polyester TH; and (b) copolyester TBH at various temperatures.

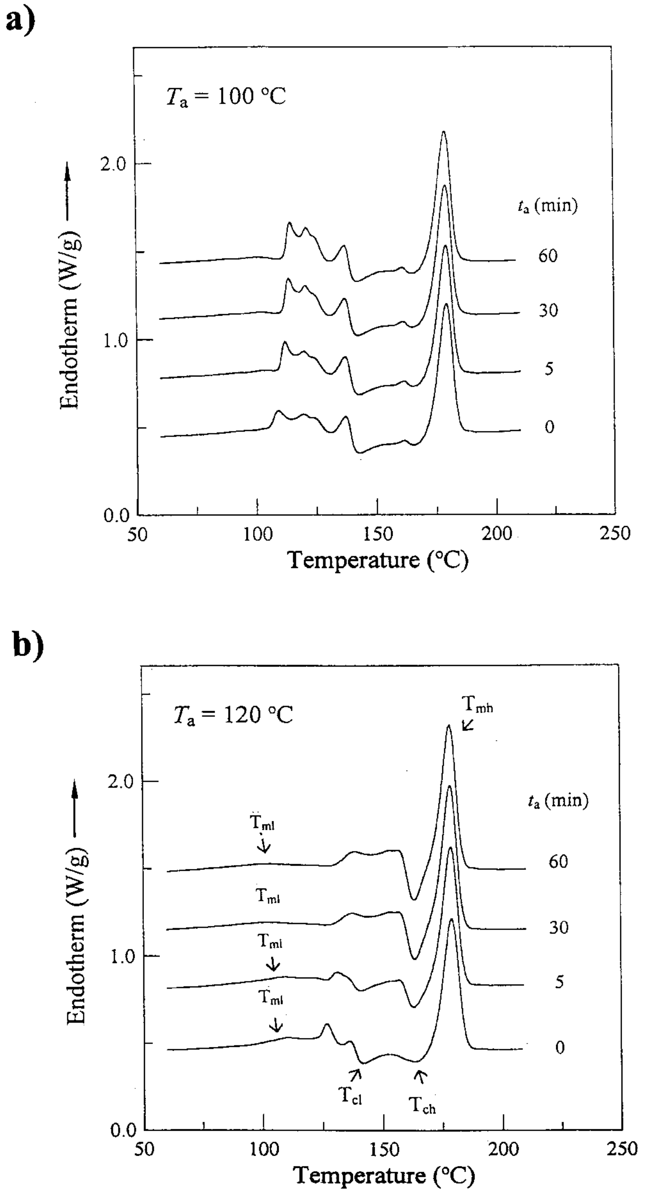


Fig. 5. DSC thermograms of copolyester TBH after annealing at (a) 100°C and (b) 120°C for various time (heating rate = 20°C/min).

moieties in polyester TB forced the neighboring dioxyhexamethylene chains and the connected TOBC triads to adopt a nonlinear arrangement, which consequently failed to form a layered smectic C_2 structure. Presence of a major –(TOBC–HD)– segment may be responsible for its smectic C_2 phase shown for copolyester TBH. The comonomer sequence and its distribution along the polymer chain contributed to the multiple melting behavior of copolyester TBH, and is studied below.

3.2. Multiple melting behavior of copolyester TBH

Copolyester TBH samples annealed at different temperatures (T_as) were subjected to DSC scans to reveal the origins of the multiple melting behavior for copolyester TBH. Selected samples annealed at different temperatures ranged from 100 to 165°C (Figs. 5 and 6) all resulted in one particularly intense melting endotherm appeared at slightly higher position than the annealing temperature (T_a). In case of $T_a = 100°C$, the corresponding DSC thermograms showed complicated multiple endotherms and exotherms (Fig. 5a). With increasing annealing time, the low-temperature endotherms showed slight variations but for the high-temperature exotherms and endothems, remained intact. Samples annealed at 120°C exhibited major variations on the transitions in the temperature ranges of 125–170°C, in which the low-temperature crystallization (T_{cl}) peak disappeared at $t_a = 30$ min (Fig. 5b) and the high-temperature

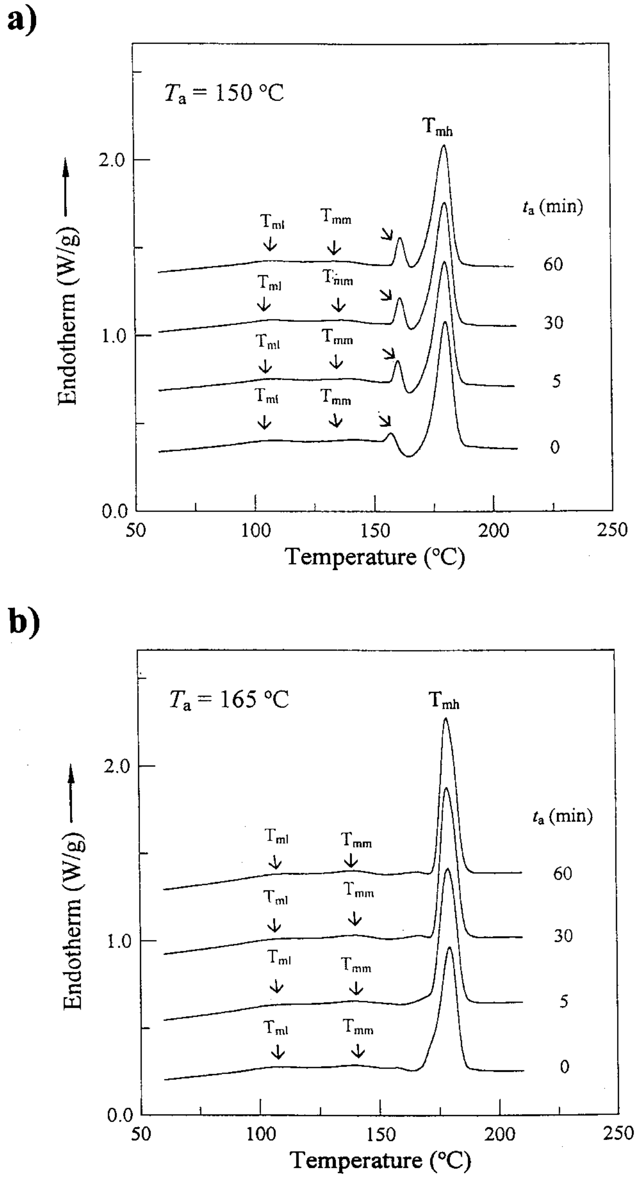


Fig. 6. DSC thermograms of copolyester TBH after annealing at (a) 150°C and (b) 165°C for various time (heating rate = 20°C/min).

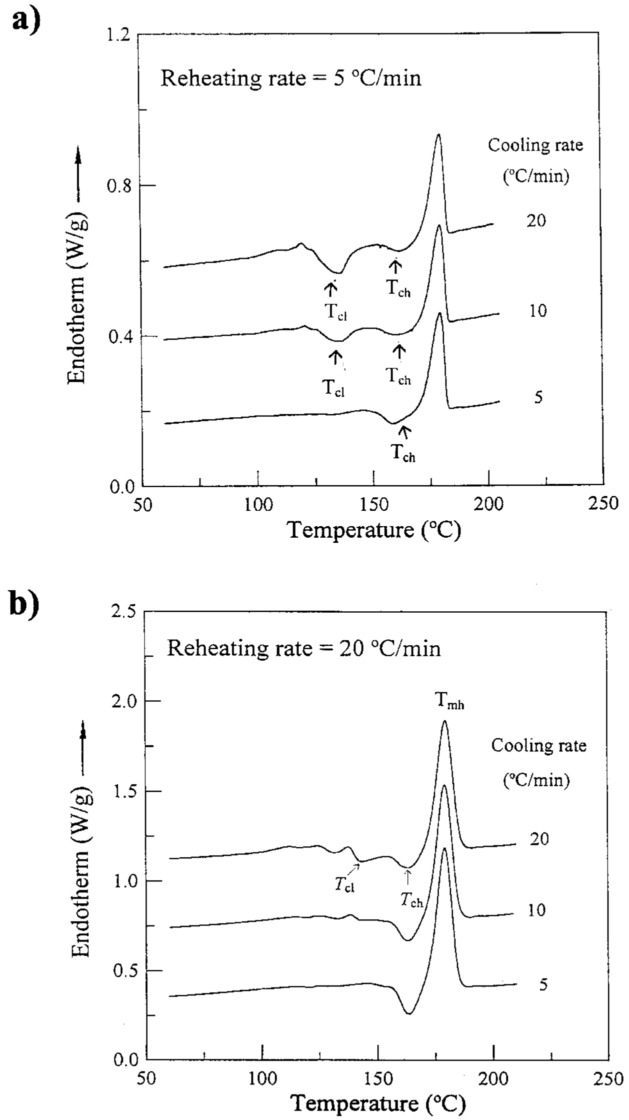


Fig. 7. Non-isothermal crystallization DSC scans of copolyester TBH at a re-heating rate of (a) 5 and (b) 20°C/min after cooling from 210°C at different rates.

crystallization (T_{ch}) peak gradually enlarged with t_a. Prolonged annealing (from $t_a = 0$–60 min) has no effect on the high-temperature melting endotherm (T_{mh}). Here, a tiny melting endotherm (T_{ml}) was observed at samples annealed at all time. Further increase of T_a to 150 (Fig. 6a) and 165°C (Fig. 6b) yielded DSC thermograms with simpler features as compared with those in Fig. 5. In case of $T_a = 150$°C, the melting endotherms (as indicated by arrows) before T_{mh} shifted slightly and the following exotherms gradually disappeared with t_a. Here, the two tiny endotherms in the low-temperature ranges were assigned as T_{mm} and T_{ml} since they appear at the same positions as the peaks shown in Fig. 2d. These two transitions are attributed to the imperfect crystals formed during cooling from the annealing temperature and related to certain chain segments as is discussed later in this paper. Sample after annealing at 165°C for various time (Fig. 6b) basically possessed the major high-temperature T_{mh} with peak temperature and intensity remained almost constant with t_a. Formation of only one T_{mh} transition suggests that the complicated multiple transitions shown in Fig. 5 is due to physical reason rather than chemical heterogeneity originated from the synthesis step. Here, we also observed the tiny T_{ml} and T_{mm} transitions appeared at the same positions with those in Fig. 6a. Their origins will be suggested later.

The selected DSC thermograms, at a constant re-heating rate of 5 and 20°C/min of copolyester TBH samples that have been non-isothermally crystallized were shown in Fig. 7a and b, respectively. With a constant re-heating rate, the low-melting endotherms and exotherm (i.e. T_{cl}) became significant as a higher rate of 20°C/min was used

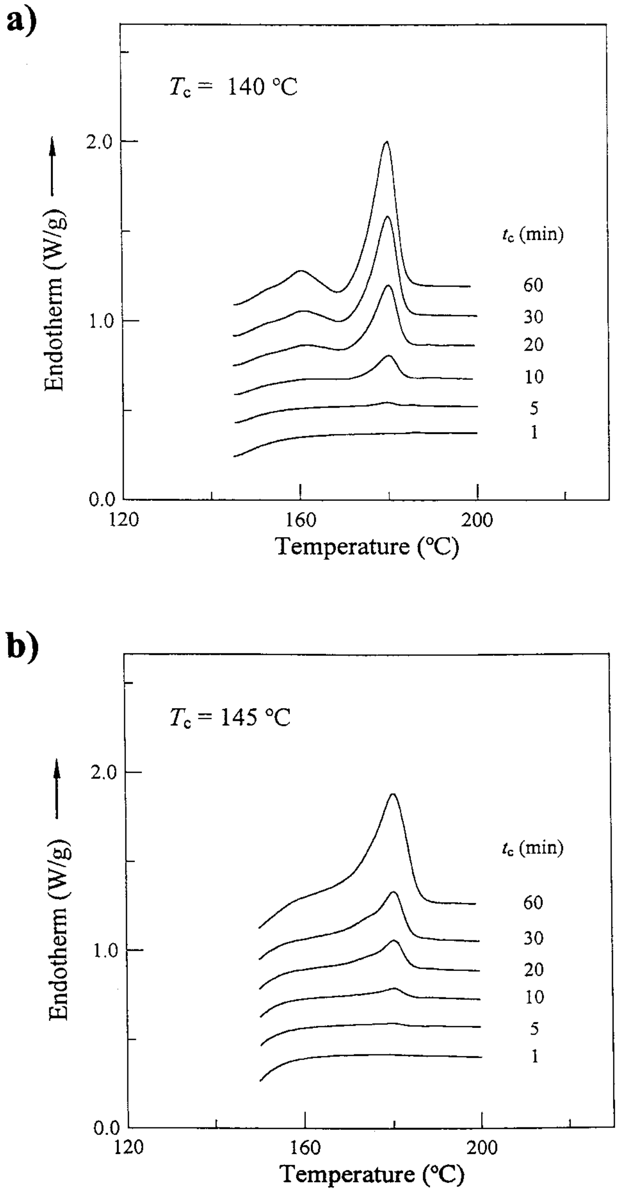


Fig. 8. Immediate rescans of copolyester TBH after crystallization at (a) 140 and (b) 145°C for various time (heating rate = 20°C/min).

to cool the sample from 210°C. With a low cooling rate (i.e. 5°C/min), only the high-temperature T_{ch} transition was resulted. It is suggested that a slow cooling rate allow polymer chain to crystallize more sufficiently. The large effect of cooling rate on the resulting thermal behavior indicates the facile crystallization process during non-isothermal scans, a result probably related to the high content of flexible spacer in copolyester TBH. Under different non-isothermal crystallization conditions, the high-temperature T_{mh} remained at the same position. The constant T_{mh} transition with various heating rates suggests that reorganization process is not a major process operated between T_{mh} and the low-temperature transitions.

Isothermal immediate rescan experiments can help to clarify the relationship between T_{mh} and other low-temperature transitions. The immediate rescan after crystallization at 140°C (Fig. 8a) showed that T_{mh} transition started to appear at $t_c = 5$ min, which is ahead of the emergence of the low-temperature endotherm at $t_c = 20$ min. The constant peak temperatures of both transitions through the whole process indicate that T_{mh} is not generated from the reorganization of any low-melting crystal. In contrast to the case of $T_c = 140°C$, the immediate rescan of copolyester TBH after crystallization at 145°C (Fig. 8b) yielded only one single T_{mh} transition, which increased its intensity with t_c. Final enthalpy (= 13.2 J/g) of T_{mh} at $t_c = 60$ min is less than that obtained at $T_c = 140°C$ (= 16.6 J/g); therefore, crystals representing the high-temperature T_{mh} were partially in a molten state at 145°C.

X-ray diffraction patterns of copolyester TBH after annealing at different temperatures for 1 h were summarized in Fig. 9. In cases of T_as = 80 and 100°C, the diffraction patterns in the wide-angle region consist of a broad peak ranging from 15 to 28°. After annealing at higher T_as of 120–165°C, the diffraction patterns became sharper as compared with the low T_a cases. The absence of any newly formed diffraction peak after annealing process excludes the possibility, that different crystal structures is the cause for the multiple melting behavior of copolyester TBH.

The possibility of a major reorganization process between T_{mh} and low-temperature endothems can be excluded from non-isothermal crystallization and annealing experiments. X-ray study excludes the possibility of different crystal structure. Therefore, the complicated thermal behavior of copolyester TBH may be attributed to dual crystal (or registry of neighboring chain in the mesophase) previously ascribed to several semi-rigid thermotropic polyesters [23–25]. It is to say, due to the slow evolution of the mesomorphic melt towards its thermodynamic equilibrium, a certain registry of neighboring chains persists in the melt. This persistent registry can be regarded as potential nuclei for primary crystallization, and further crystallization from the mesomorphic state is related to the low thermal transitions.

The role of BHS moieties in copolyester TBH can be commented in two aspects, i.e. its possible sequence distribution and its influence on the neighboring chains. Copolyester TBH was prepared by polycondensation of TOBC with mixed diols of BHS and HD. Monomeric BHS and HD diols, with the same aliphatic –OH terminals, would react with TOBC equally, and therefore, copolyester TBH would have its BHS and HD units randomly distributed along the polymer chains. As cited above, the rigid, bent SPI in BHS units may impose a nonlinear geometry to the neighboring 1,6-dioxy-hexamethylene chains and so, the connected TOBC mesogens. The nonlinear geometry may persist for several repeat units; however, dependent on the cooling and heating rates, rearrangement of the nonlinear chains to a more perfectly aligned geometry is highly possible due to the facile motion of the flexible

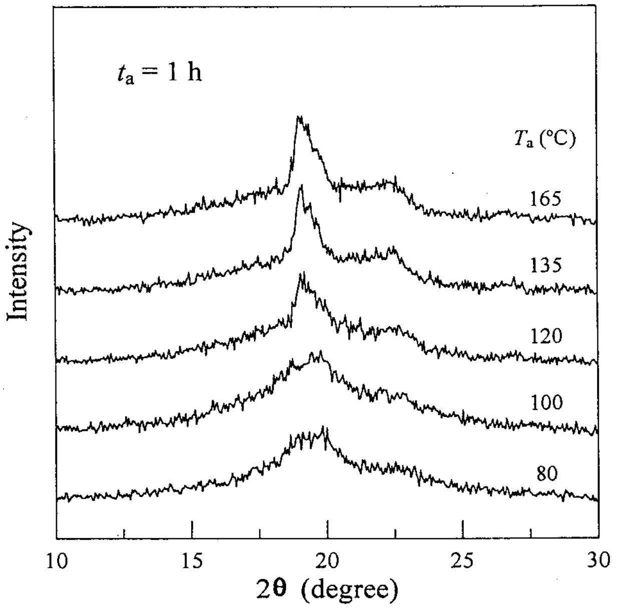


Fig. 9. X-ray diffraction patterns at the wide-angle region after annealing at different temperatures for 1 h.

1,6-dioxy-hexamethylene chain. The motion of the flexible 1,6-dioxy-hexamethylene chain also influence the rearrangement of the nearby –(TOBC–HD)– chains. Variations of the observed exotherms in different non-isothermally crystallized samples demonstrate this facile recrystallization process for copolyester TBH.

In considering the influence of the comonomer in copolyester TBH, we suggest that pure –(TOBC–HD)– segment has different thermal behavior from pure –(TOBC–BHS)– segment. Cooling from the ordered semectic C_2 state, the persistent registry of neighboring chains resulted in the formation of primary crystals, responsible for the high-melting T_{mh} and low-temperature T_{ml}. The primary crystals responsible for T_{mh} transition may be thicker, higher melting, and reside in the pure –(TOBC–HD)– domain. The fact that peak temperature of T_{mh} is close to the melting temperature of polyester TH (compare Fig. 2e with b) partially support this proposal. On the other hand, crystals of the nonlinear –(TOBC–BHS)– chains are imperfect, and melt to give low-temperature T_{ml} transition. The assignment that the melting of –(TOBC–BHS)– chain caused T_{ml} transition is disputable; however, the fact that the peak temperature of T_{ml} is close to the melting temperature of polyester TB (compare Fig. 2d with c) may support this proposal. Also, samples annealed at different T_as (= 120, 150 and 165°C, cf. Figs. 5b, 6a and b) exhibited a T_{m1} transition, a character typical of primary crystal. Melting of the secondary crystals of different origins and the facile rearrangement of the flexible chains caused the multiple endotherms and exotherms in between T_{m1} and T_{mh}. In few DSC thermograms, a melting T_{mm} transition located in the vicinity of 140°C was detected. This T_{mm} transition may be due to the secondary crystals of the –(TOBC–HD)– chains; however, evidence for this assignment is scarce at present time.

4. Conclusion

Polyester TB prepared from condensation reaction between TOBC and BHS (a SPI-containing monomer) is a nematic material, in contrast to the ordered smectic C_2 mesophase observed for polyester TH and copolyester TBH. The nonlinear chain geometry imposed by the nonlinear BHS moieties in polyester TB formed a less-ordered nematic mesophase as compared to polyester TH and copolyester TBH, in which most of the chains consist of the linear –(TOBC–HD)– segments.

DSC thermograms of copolyester TBH exhibited multiple endotherms and exotherms, which can be transformed into low-temperature T_{ml}, T_{mm} and a major high-temperature melting T_{mh} by different thermal treatments. Registry of neighboring chains in the mesomorphic state and distribution of comonomer units in copolyester TBH caused the complicated thermal behavior under DSC scans; however, high contents of flexible spacer in copolyester TBH caused transformations between crystals of different origins a facile process during thermal treatments.

Acknowledgements

We appreciate the financial support from National Science Council, N.O.C., under contract no. NSC 88-2216-E-110-005.

References

[1] Jin JI, Ober AC, Lenz RW. Br Polym J 1980;12:132.
[2] Economy JJ. Macromol Sci Chem 1984;121:1705.
[3] Varshney SK. Rev Macromol Chem Phys C 1986;26:551.
[4] Strzelecki L, Luyen DV. Eur Polym J 1980;16:299.
[5] Griffin AC, Johnson JE, editors. Liquid crystals and ordered fluids, 4. New York: Plenum Press, 1984.
[6] Krigbaum WR, Hakemi H, Kotek R. Macromolecules 1985;18:965.
[7] Jin JI, Choi EJ, Jo BW. Macromolecules 1987;20:934.
[8] Majnusz J, Catala JM, Lenz RW. Eur Polym J 1983;19:1043.
[9] Ober C, Jin JI, Lenz RW. Polym J 1982;14:9.
[10] Nieri P, Pamiredy C, Wu CN. Macromolecules 1992;25:1796.
[11] Jin JI, Chang JH, Jo BW. Polymer 1992;33:1537.
[12] Navarro F, Serrano JL. J Polym Sci; Polym Chem Ed 1992;30:1789.
[13] Cai R, Samulski ET. Macromolecules 1994;27:135.
[14] Ober C, Jin J-I, Lenz RW. Polym J 1982;14:9.
[15] Lin LL, Hong JL. Polymer 2000;41:2419.
[16] Cheng SZD. Macromolecules 1988;21:2475.
[17] Cheng SZD, Janimak JJ, Zhang A, Zhou Z. Macromolecules 1989;22:4240.
[18] Butzbach GD, Wendorff JH, Zimmermann HJ. Polymer 1986;27:1337.

[19] Ghanem AM, Dickson LC, Porter RS, Zachariades AE. J Polym Sci; Polym Phys Ed 1990;28:1891.
[20] Antoun S, Lenz RW, Jin J-I. J Polym Sci; Polym Chem Ed 1981;19:1901.
[21] Han CD, Chang S, Kim SS. Macromolecules 1994;27:7699.
[22] Marsano E, Salati U, Valenti B. Polymer 1993;34:1232.
[23] Carpaneto L, Marsano E, Valenti B, Zanardi G. Polymer 1992;33:3865.
[24] Carpaneto L, Marsano E, Salati U, Bvalenti B. Polymer 1993;34:3464.
[25] Cheng Y-Y, Cebe P, Capel M, Schreuder-Gibson H, Bluhm A, Yeomans W. J Polym Sci; Polym Phys Ed 1995;33:2331.
[26] Bilibin AY, Ten’kovstev AV, Piraner ON, Skorokhodov SS. Polym Sci USSR 1984;26:2882.
[27] Dewar MJ, Griffin AC. J Am Chem Soc 1975;97:6662.
[28] Ellis G, Lorente J, Marco C, Gomez MA, Fatou JG. Spectrochim Acta 1991;47A:1353.
[29] Helmut RB, Cladis PE, Pleiner H. Macromolecules 1992;25:7233.
[30] Watanabe J, Hayashi M. Macromolecules 1989;22:4083.
[31] Young WR, Haller I, Aviram A. Mol Cryst Liq Cryst 1971;13:357.