Copolyesters Based on Poly(butylene terephthalate)s Containing Cyclohexyl and Cyclopentyl Ring: Effect of Molecular Structure on Thermal and Crystallization Behavior

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Received June 8, 2007; Revised Manuscript Received July 12, 2007

ABSTRACT: In an effort to understand the role of molecular structure on the thermal properties of polyesters and copolyesters, the following polyesters were synthesized: poly(1,4-cyclohexane dimethylene terephthalate) (PCT), poly(butylene-1,4-cyclohexane dicarboxylate) (PBCD), poly(1,3-cyclopentane dimethylene terephthalate) (PCPDT), and poly(butylene-1,3-cyclopentane dicarboxylate) (PBCP). PCT and PCPDT are semicrystalline polymers with crystallization and melting temperatures higher than poly(butylene terephthalate) (PBT). However, PBCD and PBCP have lower glass transition temperature than PBT. From these homopolymers a series of poly(butylene-*co*-1,4-cyclohexane dimethylene terephthalate) (P(BT-*co*-CT)), poly(butylene terephthalate-*co*-1,4-cyclohexane dicarboxylate) (P(BT-*co*-BCD)), poly(butylene-*co*-1,3-cyclopentylene dimethylene) (P(BT-*co*-CPDT)), and poly(butylene terephthalate-*co*-1,3-cyclopentane dicarboyxlate) (P(BT-*co*-PBCP)) random copolyesters were synthesized for the first time, and their cocrystallization behavior was investigated using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The copolymers were found to be statistically random and crystallized in all compositions. The P(BT-*co*-CT) and (P(BT-*co*-CPDT) copolyesters exhibited typical eutectic behavior in melting and crystallization, which indicated isodimorphic cocrystallization behavior. On the other hand, in the case of P(BT-*co*-BCD) and P(BT-*co*-PBCP) copolymers, the melting and crystallization temperatures showed linear dependency with composition, indicating isomorphic-like crystallization behavior.

Introduction

Aliphatic aromatic polyesters are a class of thermoplastic polyesters with useful properties like high heat distortion temperature, high rigidity, good mechanical properties, toughness, excellent surface appearance, good chemical resistance, and stable electrical insulation properties.[1] Commercially successful polymers of this class are poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate)s (PEN).[2] Among these polymers, PBT is a fast-crystallizing polymer and, hence, well-suited for extrusion and injection molding applications. Properties of PBT are influenced by the degree and nature of crystallization and its spherulitic morphology.[3] However, at glass transition temperature (T_g) (∼40 °C) the mobility of the polymer chains in the amorphous region increases considerably, resulting in decrease in stiffness. Hence, PBT is not suitable for applications involving high heat.[4]

The properties of PBT can be modified in many ways to meet the requirements of specific applications. Copolymerization, blending with other polymers, and use of additives have been explored to modify the properties of PBT. It is well-known that aromatic groups impart molecular rigidity which contributes to improved properties of semicrystalline polymers. Cycloaliphatic diols also impart rigidity to the polyester chain. Polyester derived from 1,4-cyclohexane dimethanol (CHDM) and dimethylene terephthalate (DMT) has a high melting temperature (T_m) ranging from 250 to 305 °C depending on the cis/trans ratio.[5,6] The T_g, similarly, increases from 60 °C (cis) to 90 °C (trans). Cycloaliphatic diols such as CHDM have been used for the purpose of improving the performance of polyesters.[7,8] Improved impact property of copolyesters of PET/PCT has been attributed to the conformational flexibility of the cyclohexane rings and its influence on chain mobility.[9−11]

Crystallinity and crystallization are important properties of polyesters and copolyesters. In fact, properties of crystallizable polyesters are strongly dependent on the morphological structure (size, shape, perfection, volume fraction, and orientation of crystallites), which is formed by crystallization from the molten state. Okui et al.[12] have studied the crystallization behavior of poly(ethylene terephthalate-*co*-1,4-cyclohexylenedimethylene terephthalate) (P(ET/CT)) random copolyesters. The crystallization behavior in a random copolymer is largely influenced by the copolymer sequence. Zhu and Wegner[13] asserted that only sequences with a specific average length crystallize, with shorter and longer sequences being excluded from crystal. Li et al.[14,15] have studied the crystallization behavior of poly(ethylene terephthalate-*co*-isophthalate) PET/PEI random copolyesters with different molar ratios. With increasing PEI, the copolyesters become less crystallizable and even amorphous when the composition of PEI is above 20%. Thus, for crystallizable polymers, crystallization behavior is an interesting research subject to control morphological structure and understands the resultant properties.[16]

Cocrystallization behavior of random copolyesters whose component homopolymers are both crystallizable have been reported.[17−25] Cocrystallization is facilitated when main-chain conformations between the comonomer segments have some similarity. Depending on the nature of crystallization, cocrystallization is termed isodimorphic or isomorphic crystallization. In the case of isodimorphism, the copolymer crystallizes into the crystal structure of one component and changes over to the crystal structure of the other component at an intermediate composition and a melting point minimum (eutectic melting temperature) is observed in the plot of melting point vs copolymer composition.[17,18] Isodimorphic cocrystallization behavior in the entire range of copolyester compositions is exhibited by few systems like poly(butylene terephthalate-*co*-

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10.1021/ma071272q CCC: $37.00

butylene 2,6-naphthalate) (P(BT-*co*-BN)), poly(butylene 2,6-naphthalate-*co*-1,4-cyclohexane dimethylene naphthalate) (P(BN-*co*-CN)), poly(butylene terephthalate-*co*-1,4-cyclohexane dimethylene terephthalate) (P(BT-*co*-CT)),[17,18] and poly(hydroxybutyrate-*co*-hydroxyvalerate) (P(HB-*co*-HV)).[19−22] In the case isomorphic crystallization, both the monomers cocrystallize into one of the crystal structures but smoothly change over to the other crystal structure with change in composition. Furthermore, in the case of isomorphism, melting point minimum is not observed in the plot of melting temperature vs composition.

The focus of the present work is to synthesize several new polyesters and copolyesters containing cyclohexyl and cyclopentyl rings in the main chain and study the effect of molecular structure on the thermal and crystallization behavior. To that end, for the first time we synthesized polyesters based on 1,4-bis(hydroxymethyl)cyclohexane, 1,4-cyclohexane dicarboxylate, 1,3-bis(hydroxymethyl)cyclopentane (or 1,3-cyclopentane dimethanol), and 1,3-dimethylcyclopentane dicarboxylate. Furthermore, using the above monomers, random copolyesters, such as poly(butylene terephthalate-*co*-1,4-cyclohexane dimethylene terephthalate) (P(BT-*co*-CT)), poly(butylene terephthalate-*co*-1,4-cyclohexane dicarboxylate) (P(BT-*co*-BCD)), poly(butylene terephthalate-*co*-1,3-cyclopentylene dimethylene terephthalate) (P(BT-*co*-CPDT)), and poly(butylene terephthalate-*co*-1,3-cyclopentane dicarboyxlate) (P(BT-*co*-PBCP)), were also synthesized for the first time. Detailed studies showed the underlying effect of chemical structure on the thermal and crystallization behavior of these polymers.

Experimental Section

Poly(butylene terephthalate) (PBT). DMT (5 g, 0.026 mol), 1,4-butanediol (BD) (3.6 g, 0.038 mol), and titanium isopropoxide (0.1 wt %) were taken in a two-neck round-bottom flask equipped with nitrogen (N_2) inlet, air condenser, and spiral trap to collect the distillate. A 1:1.5 molar ratio of DMT to BD was used. The reaction mixture was heated at 180−210 °C for 3 h and then at 230 °C for another 3 h under a constant flow of N_2. The temperature was then raised to 250 °C, and the pressure was gradually decreased to 0.02 mbar when excess BD distilled out. Polycondensation reaction was further continued at 250 °C for 8 h. The flask was cooled under vacuum, polymer was recovered, and the yield was 5.75 g (99%). Inherent viscosity (η_{inh}) = 0.9 dL/g (phenol/1,1′,2,2′-tertrachloroethane (TCE) 60/40 w/w).

Poly(1,4-cyclohexane dimethylene terephthalate) (PCT). DMT (5.01 g, 0.026 mol), CHDM (7.06 g, 0.049 mol), and titanium isopropoxide (0.01 wt %) were taken in a tube reactor fitted with N_2 inlet, air condenser, and spiral trap to collect the methanol. The transesterification reaction was done at 190−210 °C for 1 h until methanol distillation ceased. Polycondensation was done at 270 °C for 30 min and at 290 °C under reduced pressure (0.02 mbar) for 15 min. The hot polymer was poured into cold water, filtered, and washed several times with hot water. The oligomer was dried in vacuo. The oligomer was slurried in dry toluene containing 0.01 wt % titanium isopropoxide. After stirring for 1 h, toluene was removed under vacuum. The oligomer was dried and subjected to solid-state polymerization at 220 °C for 5 h and at 250 °C for 5 h under reduced pressure (0.02 mbar). The obtained polymer had a η_{inh} = 0.66 dL/g (phenol/TCE 60/40 w/w).

Poly(1,3-cyclopentane dimethylene terephthalate) (PCPDT). DMT (2.5 g, 0.013 mol), 1,3-bis(hydroxymethyl)cyclopentane (CPDM) (1.84 g, 0.014 mol), and titanium isopropoxide (0.1 wt % with respect to DMT) were taken in a two-neck round-bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser, and spiral trap to collect distillate. The flask was heated to 160 °C under a stream of N_2 when methanol distilled out. Reaction was continued at 160−200 °C for 3 h and further at 210 °C for 4 h, and the pressure was gradually reduced over 30 min to 0.02 mbar and isothermally held for 11 h at 230 °C. The reaction flask was cooled under vacuum. Yield = 3.2 g (95%); η_{inh} = 0.8 dL/g (60/40 phenol/TCE w/w).

Poly(butylene-1,4- cyclohexane dicarboxylate) (PBCD). Dimethyl-1,4-cyclohexane dicarboxylate (3.99 g, 0.02 mol), 1,4-BD (2.7 g, 0.03 mol), and titanium isopropoxide (0.1 wt %) were charged into a two-neck round-bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser, and spiral trap to collect the distillate, methanol. The reaction mixture was heated at 200−230 °C for 8 h, and the pressure was reduced to 0.02 mbar and heated at 250 °C for 10 h. The flask was cooled under vacuum, and the polymer was recovered. Yield = 4.5 g (99%); η_{inh} = 0.6 dL/g (phenol/TCE 60/40 w/w).

Poly(butylene-1,3-cyclopentane dicarboxylate) (PBCP). *cis*-Dimethyl-1,3-cyclopentane dicarboxylate (2.63 g, 0.014 mol), BD (1.91 g. 0.02 mol), and titanium isopropoxide (0.1 wt % with respect to DMT) were taken in a two-neck round-bottom flask fitted with N_2 gas inlet, air condenser, and spiral trap. The reaction mixture was heated at 160−180 °C for 2 h when methanol distilled out. The reaction was continued at 210−230 °C for 8 h. The pressure was gradually reduced to 0.02 mbar, and reaction continued at 230 °C for 10 h. The flask was cooled under vacuum. A rubbery polymer was obtained. Yield = 1.91 g (97%); η_{inh} = 0.66 dL/g ($CHCl_3$).

Poly(butylene-*co*-1,4-cyclohexane dimethylene terephthalate) Copolyesters (P(BT-*co*-CT)). DMT, BD, CHDM, and titanium isopropoxide (0.1 wt %) were taken in a two-neck tube reactor equipped with N_2 gas inlet, short path vacuum distillation adaptor, and a spiral trap to collect the distillate. A 1:1.13 ratio of DMT to diol was used in all polymerizations. The transesterification was carried out at 180−210 °C for 1 h, followed by another of 4 h at 230−250 °C. Polycondensation reactions were performed at 250−310 °C, and the pressure was slowly reduced to 0.02 mbar over 30 min and isothermally held for 6 h. The reactor was cooled under vacuum and polymer was recovered.

Poly(butylene terephthalate-*co*-1,4-cyclohexane dicarboxylate) (P(BT-*co*-BCD)). DMT, dimethyl-1,4-cyclohexane dicarboxylate (DMCD), 1,4-BD, and titanium isopropoxide (0.01 wt %) were charged into a two-neck round-bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser, and spiral trap to collect the distillate, methanol. A 1:1.5 ratio of diester to diol was used in all polymerization reactions, and the DMT/DMCD ratio was varied (90/10, 70/30, and 50/50). The flask was heated to 200−230 °C for 8.5 h, and the pressure was reduced to 0.02 mbar and heated at 250 °C for 11 h. The flask was cooled under vacuum, and the polymer was recovered.

Poly(butylene terephthalate-*co*-cyclopentane dimethylene terephthalate) (P(BT-*co*-CPDT)). DMT, 1,4-BD, 1,3-bis(hydroxymethyl)cyclopentane, and titanium isopropoxide (0.1 wt % with respect to DMT) were taken in a two-neck round-bottom flask equipped with magnetic stirring bar, N_2 inlet, short path vacuum distillation adaptor, spiral trap, and a vacuum control assembly. A 1:1.15 ratio of DMT to diol was used in all polymerizations, and BD/CPDM ratio was varied (90/10, 80/20, 50/50, and 20/80). The reaction was carried out at 160−220 °C for 6−8 h. The pressure was gradually reduced to 0.02 mbar over 20 min and reaction continued at 230−250 °C for 10−12 h. The flask was cooled under vacuum.

Poly(butylene terephthalate-*co*-1,3-cyclopentane dicarboyxlate) (P(BT-*co*-PBCP)). DMT, CPDE, BD, and titanium isopropoxide (0.1 wt % with respect to diester) were taken in a two-neck round-bottom flask equipped with N_2 inlet, short path vacuum distillation adaptor, and a spiral trap. A 1:1.5 ratio of diester to diol was used in all polymerization reactions, and the DMT/CPDE ratio was varied (90/10, 80/20, 70/30, and 50/50). The reaction mixture was heated at 160−220 °C for 6−8 h under a stream of N_2 gas. The pressure was gradually reduced over 1 h to 0.02 mbar, as the excess BD distilled out and reaction continued at 230−250 °C for 10−12 h. The flask was cooled under vacuum.

Characterization. Inherent viscosities were measured at 30 °C in an automated Schott Gerate AVS 24 viscometer, using an

Ubbelohde suspended level viscometer in phenol/TCE (60:40 w/w) at a polymer concentration of 0.5 wt %. The apparent molecular weight and molecular weight distributions were determined using GPC-TQ equipped with two detectors, one being UV with variable wavelength and other RI, and two 60 cm PSS SDV-gel columns: 1 × 10 m/100 Å, 1 × 10 m/linear: 10^2-10^6 Å with $CHCl_3$ as eluent for mobile phase flowing at the rate of 1 mL min^{-1}. The calibration was performed using monodispersed polystyrene standards from PSS Germany.

^1H and ^{13}C NMR spectra were obtained on a Bruker DRX 500 spectrometer at 25 ± 1 °C, operating at 500 and 125 MHz, respectively. About 12 and 100 mg of sample dissolved in 0.5 mL of solvent ($CDCl_3$)/trifluoroacteic acid (TFA-d_1) for ^1H and ^{13}C NMR spectra, respectively. The spectra were internally referenced to tetramethylsilane. For quantitative ^{13}C NMR analysis of the microstructure, the relaxation delay and spectral width was 2 μs and 250 ppm, respectively. 1000 FID's were acquired with 3K data points and Fourier-transformed.

The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10 °C/min under a nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization temperature upon cooling (T_c) from the cooling thermogram. The instrument was calibrated using standard protocol.

Olympus BM 50 polarizing optical microscope with Mettler FP85 hot stage was used to study the spherulitic morphology of the samples. The samples were completely melted in the hot stage, and isothermally held at a temperature 15 °C above the melting temperature for 2 min. The sample was then cooled to the crystallization temperature, which was about 20 °C lower than the melting temperature, and the growth of spherulitic morphology was monitored.

The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator with copper target and wide-angle powder goniometer. The generator was operated at 40 kV and 150 mA. The samples were ground into fine powder and used for the measurements. The samples were scanned from $2\theta = 5°$ to 35° at a speed of 1 deg/min. A very small amount of silicon powder was mixed with samples for calibration purpose. However, the diffractograms shown in the figures were scanned without silicon powder.

Results and Discussion

Homopolymers. The thermal behavior of the homopolyesters will be discussed first. Among the homopolyesters synthesized, PBT is extensively studied in the literature and was, therefore, taken as the standard for purposes of comparison. To enable this comparison, PBT was also synthesized in the laboratory free of additives and delustrants that can influence its thermal properties. The other polyester that has been investigated earlier is PCT. Thermal properties of PCT and P(BT-*co*-CT) were published in conference proceedings[26] earlier but are, nevertheless, included here for comparison and for the sake of completion. Figure 1 shows the structure and thermal properties of all the homopolyesters synthesized. It can be seen that these polyesters exhibit wide variation in thermal properties. The homopolyesters, viz., PBT, PCT, and PCPDT, are semicrystalline in nature and exhibit well-defined crystallization and melting points. PCPDT has been synthesized for the first time, and optical microscopy shows well-defined big-banded spherulites when crystallized from the melt. On the other hand, PBCD, as prepared, shows a melting temperature at 56 °C with heat of fusion 32 J/g. On cooling from the melt or on the second heating, PBCD does not crystallize, indicating extremely low crystallization rate compared to that of PBT, and may be treated as an amorphous polymer. The amorphous behavior arises from *e*,*e*/*a*,*e* ratio of cyclohexane dicarboxylate, which is determined from NMR to be 70/30. It is reported[27,28] that the PBCD containing *e*,*e*-1,4-cyclohexane dicarboxylate is a semicrystalline polyester with a T_m of 163 °C, T_c of 112 °C, and a T_g of 31 °C. PBCP, which has been synthesized for the first time, is an amorphous polyester with a T_g of −44 °C.

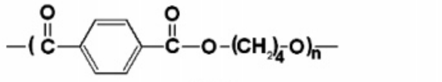
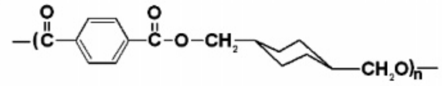
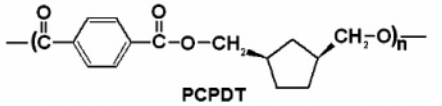
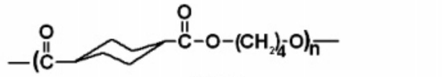
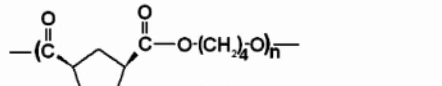
Structure	Thermal properties (°C)		
	T_g	T_c	T_m
 PBT	40	193	226
 PCT	90	246	296
 PCPDT	60	140	207
 PBCD	−10	–	56
 PBCP	−44	–	–

Figure 1. Structure and thermal properties of various homopolymers synthesized.

PCT has higher T_g, T_c, and T_m compared to PBT. PCPDT, on the other hand, shows a higher T_g than PBT but has lower T_c and T_m. The crystallization rate as measured by crystallization half-time shows that PBT and PCT crystallize very rapidly. Detailed crystallization kinetics data are not presented here, but isothermal crystallization studies made on these samples reveal that the crystallization half-time at maximum crystallization rate temperature is of the order of 20 s for PCT. For PBT only, the high-temperature region could be studied, as the crystallization rate is too fast to allow samples to be quenched into an amorphous state. The PCPDT, on the other hand, has lower crystallization rate compared to PBT and PCT. Crystallization half-time of PCPDT is 6 min at 130 °C, which is the maximum crystallization rate temperature. PBCD and PBCP are rubbery at room temperature as their T_g values are −10 and −44 °C, respectively.

These results indicate that the thermal properties are highly structure sensitive. The PCPDT and PCT are structurally more rigid than PBT with higher T_g than PBT. On the other hand, PBCD and PBCP are more flexible than PBT and therefore rubbery at room temperature. The crystallization behavior of the polyesters depends on the molecular structure. The faster crystallization behavior of PBT and PCT compared to PCPDT may be attributed to their structures, i.e., planar structure of PBT and PCT vis-à-vis the nonplanar structure of PCPDT on account of the cyclopentyl group. This inhibits the easy packing of the chains in the lattice leading to slower crystallization rates. Similarly, PBCD and PBCP molecules are very flexible and nonplanar; hence, they do not easily pack into a lattice for crystallization.

Copolyesters. Figure 2 shows the structure of various copolyesters prepared from the homopolyesters. All the copolyesters are prepared by the standard melt condensation procedure, and hence, a representative procedure for one of the copolyes-

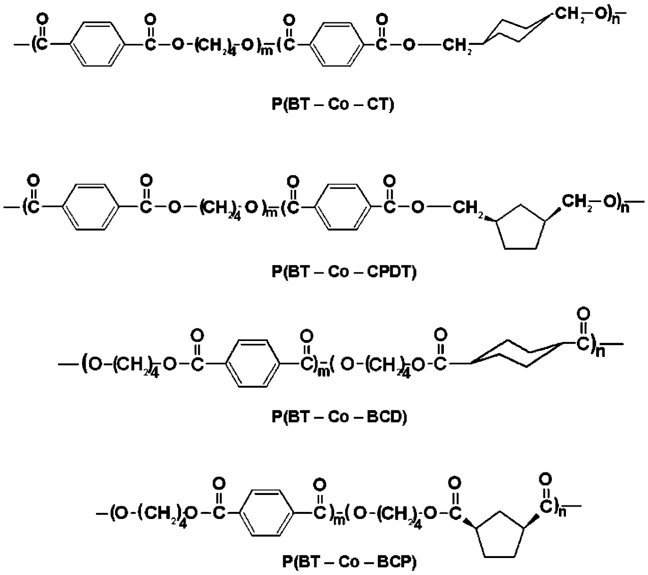

P(BT – Co – CT)
P(BT – Co – CPDT)
P(BT – Co – BCD)
P(BT – Co – BCP)

Figure 2. Structures of copolyesters synthesized.

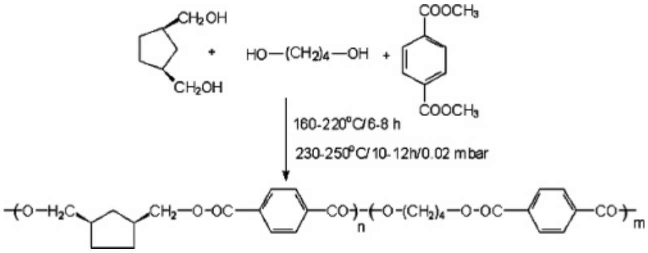


Figure 3. Synthesis of poly(butylene terephthalate-*co*-cyclopentylene dimethylene terephthalate).

ters, viz., poly(butylene terephthalate-*co*-cyclopentylene dimethylene terephthalate) (P(BT-*co*-CPDT)), will be discussed in detail.

Copolyesters of DMT and 1,4-BD containing CPDM were synthesized by melt condensation using titanium isopropoxide catalyst. The reaction scheme is depicted in Figure 3. A series of copolyesters were synthesized by changing the molar ratio of BD/CPDM (90/10, 80/20, 50/50, and 20/80). The copolyesters containing more than 50% CPDM, $PBT_{45}CPDT_{55}$, and $PBT_{15}CPDT_{85}$ were found to be soluble in chloroform, while the other two compositions were insoluble. The inherent viscosities were in the range 0.5−1.03 dL/g. The apparent M_n and M_w of $PBT_{45}CPDT_{55}$ were found to be 88 940 and 1 85 500 with a polydispersity of 2.08. A typical ^{1}H NMR spectra of poly(BT-*co*-CPDT) copolyester with indication of the notation used in NMR assignments is shown in Figure 4, where CPDT is a cyclopentylene dimethylene terephthalate unit and BT is a butylene terephthalate unit. Signal assignment was accomplished by comparison of spectra obtained for different copolymer compositions. Chemical shifts of all peaks appearing in such spectra, together with their respective assignments, are given in Table 1.

The composition of the copolyesters could be determined from the areas of the glycolic proton resonances in the ^{1}H NMR spectra. The signal at 4.4 ppm appearing as a singlet in the ^{1}H NMR spectra of the copolyester $PBT_{46}CPDT_{54}$ is due to PBT, and the doublet at 4.3, 4.26 ppm is assigned to PCPDT. The microstructure of the copolyesters was analyzed using ^{13}C NMR spectroscopy. The quaternary aromatic carbon resonances appeared to be sensitive to dyad sequence effects. The ^{13}C NMR spectra of the copolyester $PBT_{45}CPDT_{55}$ are shown in Figure 5, and the peak assignments are given in Table 1. Figure 6 shows the ^{1}H NMR spectra of PBT, PBT45PCPDT55, and PCPDT samples and the ^{13}C NMR spectra of P(BT-*co*-CPDT) copolymers. The quaternary carbon of the terephthalate (labeled as d) is split into four—BB (133.81), CPCP (133.94), CPB (133.98), and BCP (133.81)—and is shown in Figure 6B**.** The four different dyads possible in the copolymer repeat units are depicted in Figure 7. According to Yamadera and Murano,[29] if four kinds of signals due to homolinks and heterolinks are observed in the NMR spectrum of the copolymer, then the average sequence length and the degree of randomness of the copolymer can be determined. The molar fractions of the butylene (B) unit and cyclopentylene (C) units were obtained from integration of the peaks. Molar fractions of butylene terephthalate (P_B) and cyclopentylene dimethylene terephthalate (P_{CP}) units were obtained from the relative intensities of the four kinds of signals in the NMR spectrum using eq 1.

$$P_B = \frac{f_{BCP} + f_{CPB}}{2} + f_{BB} \qquad P_{CP} = \frac{f_{BCP} + f_{CPB}}{2} + f_{CPCP} \tag{1}$$

where f_{BB}, f_{CPCP}, f_{BCP}, and f_{CPB} correspond to the proportion of the integrated intensities of BB, CPCP, BCP, and CPB to the total intensity of the butylene moieties, respectively.

If one could inspect the units along the copolymer chain from one end to the other, the probability (P_{TCD} or P_{CDT}) of finding T (or CD) unit next to a CD (or T) unit would be

$$P_{BCP} = \frac{f_{BCP} + f_{CPB}}{2PB} \qquad P_{CPB} = \frac{f_{BCP} + f_{CPB}}{2P_{CP}} \tag{2}$$

The number-average sequence length of a butylene terephthalate (BT) unit and cyclopentylene dimethylene (CPDT) unit are given by

$$L_{nB} = \frac{2P_B}{f_{BCP} + f_{CPB}} \qquad L_{nCP} = \frac{2P_{CP}}{f_{BCP} + f_{CPB}} \tag{3}$$

The degree of randomness (B) is defined by eq 4

$$B = P_{BCP} + P_{CPB} \tag{4}$$

For random copolyesters B is unity. A value of B equal to zero indicates a mixture of homopolymers, while a value of 2 indicates an alternating distribution.[29] Table 2 shows the average sequence length and degree of randomness. The dyad distribution was also calculated on the basis of the Bernoullian statistical model.[30] A similar analysis is made for the other copolymers, viz., P(BT-*co*-BCD), P(BT-*co*-PBCP), and P(BT-*co*-CT). All the copolymers investigated are completely random in nature. It is observed that the experimentally determined average sequence lengths are in all cases in accordance with that predicted one on the basis of ideal copolycondensation statistics with degree of randomness close to unity.[29−33]

Thermal Behavior of the Copolymers. Thermal behavior of the copolyesters is studied by differential scanning calorimetry. The copolyesters are grouped into two on the basis of their thermal behavior. P(BT-*co*-CT) and P(BT-*co*-CPDT) are grouped together as they exhibit similar thermal behavior and will be discussed first. It may be noted that as-polymerized samples have varying thermal history, and hence, thermal properties obtained during the first heating cannot be compared. Therefore, all the samples were initially melted well above their melting points and cooled to RT at 10 °C/min. Thereafter, the samples were heated at 10 °C/min to obtain the thermal properties.

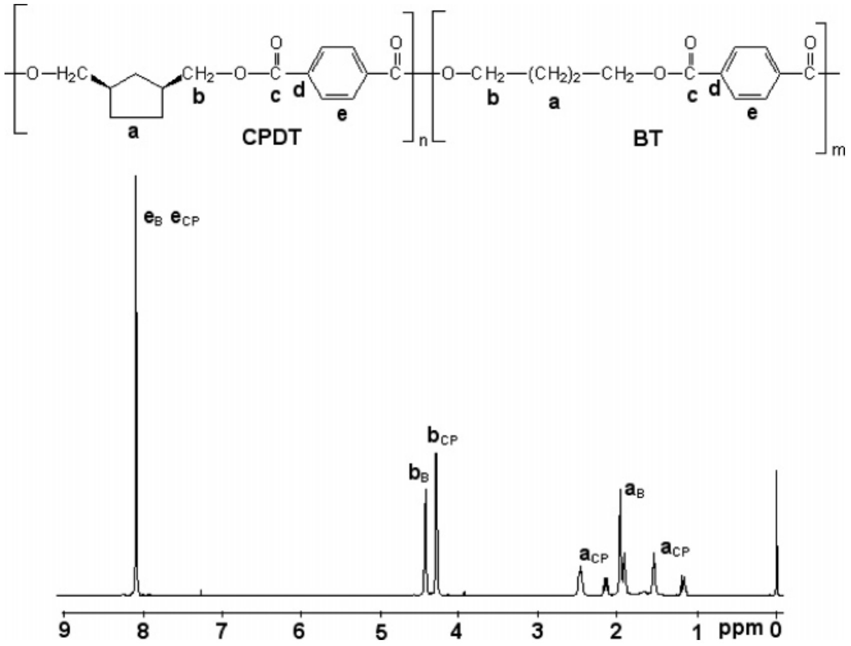


Figure 4. Typical ^{1}H NMR spectrum of poly(BT-*co*-CPDT) copolyester with its peak assignment.

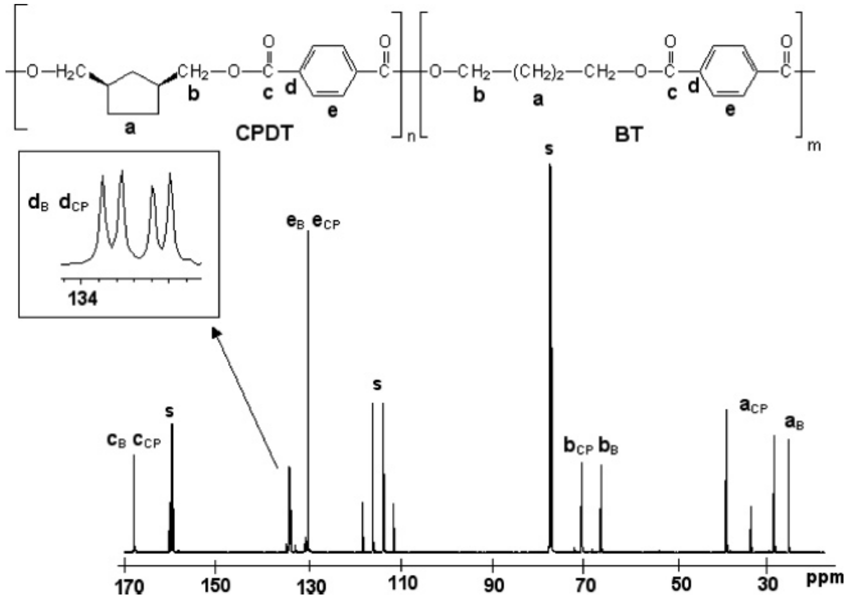


Figure 5. ^{13}C NMR spectrum of copolymer $PBT_{45}CPDT_{55}$.

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts (*δ*, ppm) of PBT, PCPDT, and Poly(BT-*co*-CPDT) Copolyesters

^{1}H Chemical Shifts

	^BH_a	^BH_b	^BH_e	$^{CP}H_a$	$^{CP}H_b$	$^{CP}H_e$
PBT	2.02	4.5	8.12			
PCPDT				1.0−1.9, 2.1, 2.5	4.30, 4.26	8.07
$PBT_{45}CPDT_{55}$	1.96	4.4	8.07	1.0−1.8, 2.0−2.6	4.30, 4.26	8.07

^{13}C Chemical Shifts

	^BC_b	^BC_c	^BC_d	^BC_e	$^{CP}C_b$	$^{CP}C_c$	$^{CP}C_d$	$^{CP}C_e$
PBT	65.9	167.6	133.7	129.8				
PCPDT					68.86	165.66	133.98	129.41
$PBT_{45}CPDT_{55}$	66.0	167.8	133.9	129.89	70.2	167.7	133.78	129.89

Melting and glass transition temperatures of the copolyesters are shown in Figure 8a,b. The T_g of the P(BT-*co*-CT) and P(BT-*co*-CPDT) copolyesters increased with increasing CT and CPDT mole fractions; from 40 °C for pure PBT to 60 °C for homoPCPDT. In the case of P(BT-*co*-CT) copolyesters T_g changes linearly from 40 °C for PBT to 90 °C for PCT.

P(BT-*co*-CT) and P(BT-*co*-CPDT) copolyesters, in all composition ranges, showed melting endotherm on heating and crystallization exotherm on cooling. The P(BT-*co*-CPDT) copolyester at intermediate composition, $PBT_{45}CPDT_{55}$, did not crystallize from the melt on cooling at 10 °C/min. However, on annealing above the T_g, the sample showed a very weak

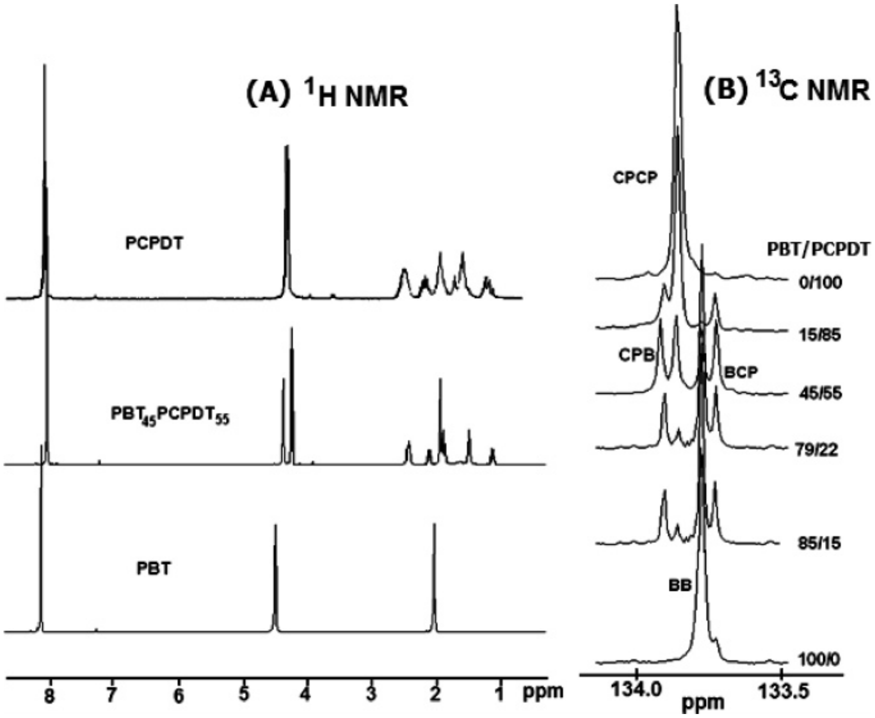


Figure 6. (A) ^{1}H NMR spectra of PBT, $PBT_{45}PCPDT_{55}$, and PCPDT. (B) Expanded ^{13}C NMR spectra of PBT, PCPDT, and poly(BT-*co*-CPDT) copolyesters in the range 133.5−134.5 ppm.

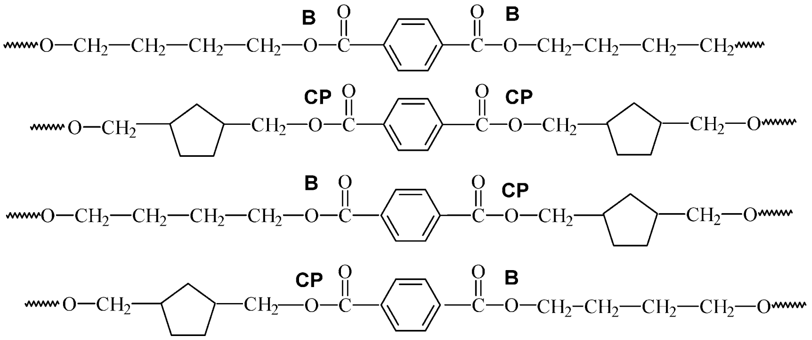


Figure 7. Possible dyad sequences for the quaternary carbon in the poly(BT-*co*-CPDT) copolyester.

Table 2. Composition, Average Sequence Lengths, and Randomness of Poly(BT-*co*-CPDT) Copolyesters

	feed composition (mol %)		copolymer composition[b] (mol %)		av sequence length		deg of randomness
copolyester[a]	X_B	X_{CP}	X_B	X_{CP}	L_{nB}	L_{nC}	B
PBT	100	0	100	0			
$PBT_{85}CPDT_{15}$	87	12	85	15	5.7	1.2	0.96
$PBT_{78}CPDT_{22}$	80	20	78	22	4.1	1.3	0.99
$PBT_{45}CPDT_{55}$	50	50	46	54	1.9	2.2	0.97
$PBT_{15}CPDT_{85}$	20	80	20	80	1.2	5.9	0.98
PCPDT	0	100	0	100			

[a] Calculated from ^{1}H NMR. [b] Calculated from ^{13}C NMR

melting endotherm. The presence of clear crystallization and melting peaks indicates cocrystallization behavior of these copolyesters over the entire range of composition. Only a few systems are known to exhibit such a behavior.[13,15] The melting and crystallization temperatures of the copolyesters showed eutectic behavior. The typical eutectic behavior indicated that the cocrystallizaion was isodimorphic in nature, and monomer units of one type were included in the crystal lattice of the other type. The eutectic composition of the P(BT-*co*-CT) system is $PBT_{74}CT_{26}$, while in the case of P(BT-*co*-CPDT) copolyesters it is $PBT_{45}CPDT_{55}$. It is interesting to note that the T_g plays a role in controlling the crystallization as CT and CPDT fractions have higher T_g than BT fraction; furthermore, CT has higher T_g than CPDT and controls the crystallization when its fraction increases above 26%.

P(BT-*co*-BCD) and P(BT-*co*-PBCP) exhibit similar thermal behavior and are different from that of P(BT-*co*-CT) and P(BT-*co*-CPDT) copolyesters. The poly(BT-*co*-BCD) copolyesters could be crystallized over the composition range studied and showed melting endotherm on heating. The crystallization and melting temperatures are shown in Figure 8c,d. The melting and glass transition temperatures show a linear relationship with composition and do not show an eutectic behavior. Although in this study, BCD, which is a poorly crystallizing polymer, having composition above 50%, was not studied, the T_g and T_m linearly extrapolate to its 100% composition values. In the case

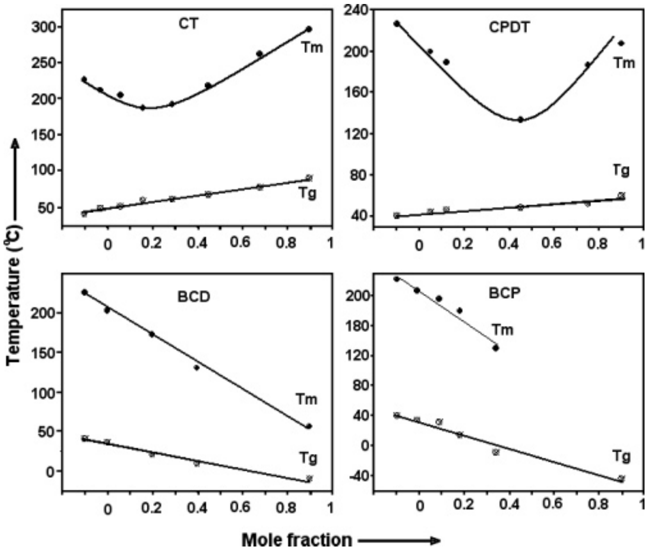


Figure 8. Dependence of glass transition and melting temperatures on copolymer composition.

of PBCP, which is an amorphous polymer, studies were not made above 50% composition. But in the composition range studied, which is up to 50%, T_g and T_m decrease with increasing composition. The presence of clear melting point indicates cocrystallization behavior of the copolyesters over the full range of composition. Absence of eutectic composition indicates that the cocrystallizaion is isomorphic in nature, and monomer units of one type are included in the crystal lattice of the other type. A similar isomorphic crystallization behavior has been reported by Jeong et al.[13] in the case of poly(hexamethylene 2,6-naphthlate-*co*-1,4-cyclohexylene dimethylene 2,6-naphthalate).

The crystallization behavior of the copolyesters was further probed by WAXS at room temperature. Figure 9 shows the diffractograms of the all the copolyesters. As-obtained samples showed diffraction pattern typical of semicrystalline polymers. The diffraction patterns of the samples having compositions close to the 50:50 composition, in the case of P(BT-*co*-CT) and P(BT-*co*-CPDT) copolyesters, are not well resolved. Hence, all the samples were annealed below their melting temperature for 2 h. After annealing, the diffraction peaks were well resolved, and Fakirov and co-workers[34] attributed it to the crystallization-induced sequential reordering in copolyesters during annealing. From the peak position the *d*-spacings were calculated using Bragg equation and plotted in Figure 10 for all the copolyesters studied. It is known that the comonomer concentration in crystal lattice is strongly dependent on the copolymer composition in bulk and crystallization conditions.[17,33] The extent of cocrystallization can be qualitatively measured by the change of the lattice *d*-spacing in the WAXS pattern.[15,33] Figure 9a shows the diffraction pattern of P(BT-*co*-CT). The crystal structure of PBT[35−37] and PCT[38] are reported to be triclinic. PBT shows strong peaks at diffraction angles 16.02°, 17.25°, 23.28°, and 25.16°. These peaks are indexed as $0\bar{1}1$, 010, 100, and $1\bar{1}1$ planes of triclinic. PCT shows peaks at 15.63°, 16.63°, 23.41°, and 25.6°. These peaks are assigned to the 011, 010, 100, and 111 planes. The variation of *d*-spacing with composition as seen in Figure 10a shows a break in the region around 30% PCT (Figure 9). The diffraction patterns of copolyesters rich in PBT (74%−100% BT) component only show patterns similar to PBT, indicating that the copolyesters crystallized in the PBT lattice. When the mole fraction of PCT increases (37%−100% CT), the coployesters crystallized in the PCT lattice. This observation

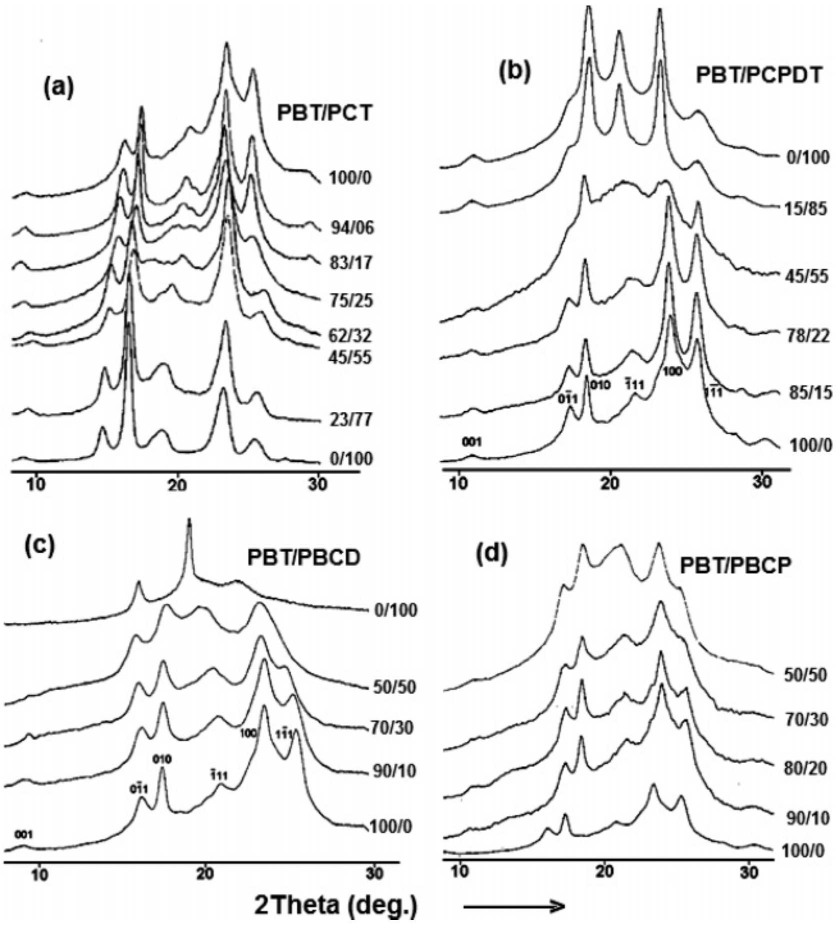


Figure 9. X-ray diffractograms of the various copolyesters at room temperature.

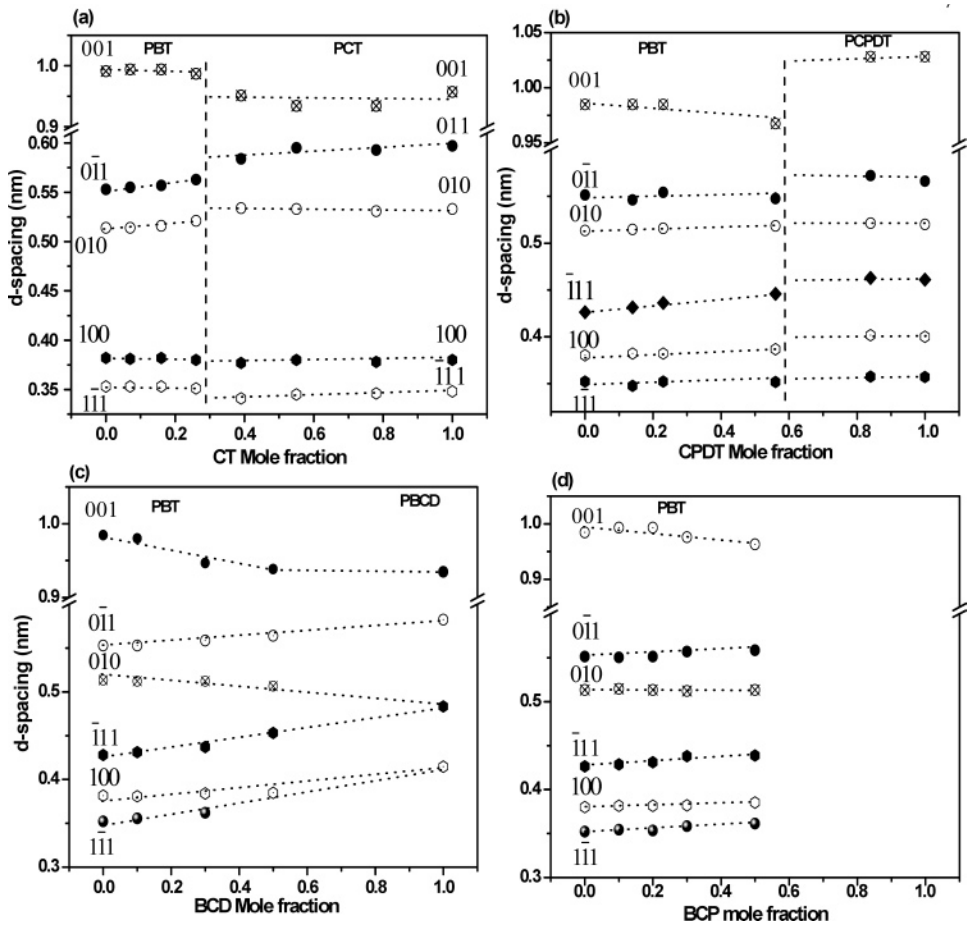


Figure 10. *d*-spacings of the reflections as a function of copolymer composition for various copolyesters

is consistent with the melting temperature data discussed in the preceding section. Change in the lattice also occurs close to the eutectic composition. This shows the ability of PCT to control the crystallization even when it is present in a minor proportion. This could arise due to the higher rigidity of PCT when compared to PBT.

The room temperature structures of the polyester PCPDT and the copolyesters P(BT-*co*-CPDT) were analyzed by WAXS. The diffraction patterns of the annealed samples are shown in Figure 9b. The diffractogram of PCPDT (Figure 9b) was distinctly different from that of PBT, indicating that PCPDT crystallizes into a different lattice. The data from the powder diffractogram were too limiting to determine the crystal structure of PCPDT. Nevertheless, from the diffractograms useful information would be extracted. From the WAXD pattern it was noted that from 45% to 100% BT content PBT-type crystal structure developed, whereas below 45% BT content PCPDT type crystal structure developed. The division of WAXS patterns depending on the composition is in agreement with the isodimorphic crystallization behavior of the P(BT-*co*-CPDT) system. As a consequence of comonomer inclusion, the *d*-spacings of both crystal structures changed with the comonomer content. Figure 10b shows the variation of *d*-spacing with composition, and it shows a break in the region around 55% PCPDT content. It is worth pointing out that in the case of poly(BT-*co*-CT) the break occurred at a lower PCT content (26%). It was argued that the rigid structure of PCT controls the crystallization. The length of CPDT unit was calculated using the conjugate gradient and Newton−Raphson method using Cerius 2 software and found to be 1.29 nm, which was 0.056 nm longer than that observed for the BT unit. Similar lengths of the BT and CPDT units cause them to cocrystallize even though the average sequence length was lower than the required length for crystallization to occur.[19]

Figure 9c shows the WAXS patterns of poly(BT-*co*-BCD) along with patterns of PBT and PBCD. In the case of PBCD, which does not crystallize readily from the melt, thin film sample had been cast from the solution and the film sample was scanned to obtain the WAXS pattern. The diffraction pattern of PBCD indicates that the packing of chains in the lattice is different from that other polyesters discussed here. The *d*-spacings of the reflections are plotted in Figure 10c. The *d*-spacings change linearly with increase in comonomer content. The smooth changeover of PBT lattice into PBCD shows that the cocrystallization is isomorphic in nature and consistence with the thermal data. A similar kind of changeover in lattice and isomorphic cocrystallization behavior has also been observed for poly(hexamethylene naphthalate-*co*-cyclohexylene dimethylene naphthalate).[13]

The WAXS patterns of poly(BT-*co*-BCP) copolyesters are shown in Figure 9d. All samples were annealed for 2 h at temperature10 °C below their T_m to sharpen the diffraction patterns. The diffraction patterns of the copolymers appear similar to that of PBT, indicating that all the copolyesters crystallized in PBT lattice. Copolyesters having more than 50% incorporation of BCP do not crystallize, since PBCP is an amorphous polymer. The *d*-spacings calculated from the patterns are shown in Figure 10d. It is interesting to observe that PBCP on its own cannot arrange into a lattice, but BCP units can get into the lattice along with PBT. According to Jun et al.,[39] an average sequence length higher than 3 is required to form crystallites. In the present case, copolyesters with compositions close to 50:50 could crystallize even though the sequence length

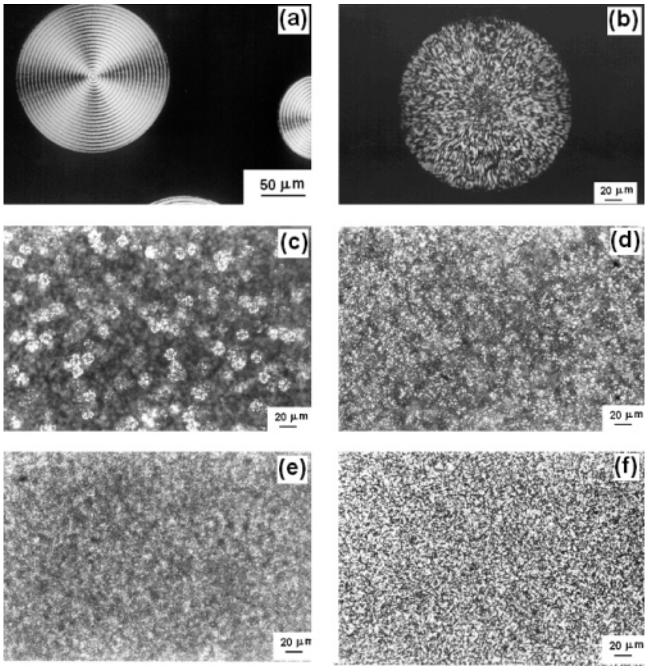


Figure 11. Polarized light micrographs of the spherulites of (a) PCPDT, (b) $PBT_{15}CPDT_{85}$, (c) $PBT_{45}CPDT_{55}$, (d) $PBT_{78}CPDT_{22}$, (e) $PBT_{85}CPDT_{15}$, and (f) PBT.

is less than 3, indicating the inclusion of comonomer in the lattice. Incorporation of the BCP unit in the PBT lattice is more apparent from the 001 spacing. The 001 *d*-spacing, which is related to the *c*-axis and the chain repeat length, showed marginal decrease with increase in BCP content and is in agreement with the BCP unit's length 1.04 nm (calculated using the conjugate gradient and Newton−Raphson method using Cerius 2 software), which was lower than the length of BT unit (1.234 nm).

Among the polyesters synthesized, PBT and PCT show high crystallization rates and very high nucleation density under crossed polars upon crystallization from the melt. PBCP is an amorphous polymer, and PBCD does not crystallize easily from the melt. However, PCPDT has lower crystallization rate and showed well-defined spherulitic morphology on crystallizing from the melt and provides an opportunity to study the effect of incorporating another monomer in the chain on the sperulitic morphology. The crystallization and spherulitic morphology of PCPDT and the poly(BT-*co*-CPDT) copolyesters were observed using a polarized optical microscope. Figure 11 shows the spherulitic morphology of PBT, PCPDT, and the copolyesters. PCPDT exhibits well-defined banded spherulites, which were highly birefringent. Banded spherulites are also observed in poly(trimethylene terephthalate) (PTT).[40,41] The formation of banded spherulites is attributed to the lamellar twisting. In the case of PTT, the banded spherulites grow in the lower half of the bell-shaped curve (spherulitic growth rate vs temperature);[42] however, in the case of PCPDT the spherulites are observed in the high-temperature region, viz., 140−175 °C. Below 140 °C, the nucleation density was too high to discern the single spherulite. The banded spherulitic morphology changed with increasing comonomer content. When 20% PBT was included as comonomer, the banded spherulitic morphology was highly distorted (Figure 11b) apparently due to the disturbance in the sequence of CPDT units by BT units. Other specific features are lower growth rates and increased nucleation density. For the sample $PBT_{45}CPDT_{55}$, the banded structure (Figure 11c**)** is extremely distorted and the excessive nucleation density reduces the size of spherulites also. The PBT-rich blend, $PBT_{78}CPDT_{22}$, shows spherulitic morphology (Figure 11d) similar to that of PBT (Figure 11e). These results are consistence with the DSC and WAXS data presented in the preceding sections.

Conclusions

Polyesters having systematic variation in molecular structure, viz., PBT, PCT, PCPDT, PBCD, and PBCP, have been synthesized and their thermal and crystallization behaviors compared. Among these polyesters, PCPDT and PBCP have been synthesized for the first time. PCT and PCPDT possess a rigid structure when compared to PBT and therefore exhibited higher T_g than PBT. PCPDT structure is more nonplanar compared to PBT and PCT and accordingly exhibits lower crystallization rate and lower melting temperature. Interestingly, PCPDT exhibits well-defined banded spherulites similar to PTT.

When less planar and conformationally more mobile cyclohexyl and cyclopentyl groups replace the planar and rigid phenyl ring of the PBT, the resulting polyesters, namely PBCD and PBCP, exhibit rubbery behavior at room temperature. PBCP is an amorphous polymer and PBCD is very poorly crystallizing and may be considered as an amorphous polymer.

Random copolyesters containing butylterephthalate units were synthesized for the first time and show interesting thermal and crystallization behavior. P(BT-*co*-CT) and P(BT-*co*-CPDT) copolyesters show eutectic melting and isodimorphic crystallization behavior with composition. On the other hand, P(BT-*co*-BCD) and P(BT-*co*-BCP) copolyesters do not exhibit eutectic melting behavior. They exhibit a linear change in melting temperature with composition and show isomorphic crystallization behavior.

Acknowledgment. Ms. T. E. Sandhya thanks CSIR for the Senior Research Fellowship.

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MA071272Q