Copolyesters Based on Poly(butylene terephthalate)s Containing Cyclohexyl Groups: Synthesis, Structure and Crystallization

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Summary: Poly(butylene terephthalate-co-cyclohexylene dimethylene terephthalate) copolymers PBTCT, were synthesized by melt condensation with compositions ranging from 94/08 to 23/77. ^{13}C NMR spectroscopy was used to study the microstructure of the copolyesters and was found to be completely random. The melting temperature, crystallization temperature on cooling, enthalpy of melting and crystallization followed an eutectic behaviour. Thermal and x-ray diffraction studies indicated that the copolyesters in all composition could crystallize. The XRD studies further indicated that PBT rich copolyesters in the range 75 to 100% BT, crystallized in the PBT lattice while the copolyesters rich in PCT having 38 to 100% CT, crystallized in the PCT lattice.

Keywords: cocrystallization, copolyester, copolymerization, sequence analysis, WAXS

Introduction

Polybutylene terephthalate (PBT) is an important thermoplastic polyester widely used in a range of engineering applications.[1] Because of its very easy processing and rapid crystallization, PBT became a rather widely used thermoplastic material.[2] PBT has good electrical and dielectric properties, making it suitable for applications such as electrical and electronic devices. Because of its excellent ensemble of material properties it is a widely used technical polymer in several application fields either alone or in blends with other thermoplastics.[3] The ability to realize many variable and technically potential modifications of PBT as blends and composites has opened a large window for applications in plastics construction, automotive industry, packaging and electrical industry.[4] However PBT does not have the outstanding impact strength which would be desired. It has a low glass transition temperature (T_g) and hence not suitable for applications involving high heat. Poly(1,4-cyclohexylene dimethylene terephthalate) is a semicrystalline polyester having excellent

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properties[5,6] like high melting temperature (T_m) 278-318°C and T_g 60-90°C depending on the trans diol content of 50-100%. It requires 300°C for injection molding, too close to its decompostion temperature. The resulting molding parts are brittle and require nucleation as with PET. For this reason this polyester is not used as such as a molding plastic. It is well known that copolymers tend to have better properties corresponding to homopolymers. Copolymerization modifies the crystallization behavior and crystallinity degree which, in turn, is strongly influenced by composition and kind and arrangement of structural units in the chain. Copolyesters of PBT containing 5-20% of 1,4-cyclohexane dimethanol units are reported to possess good impact strength.[7]

Another aspect of the copolyesters is the cocrystallization behavior when the component homopolymers are semicrystalline. Only a few systems have been reported, e.g., poly(3-hydroxybutyrate-co-hydroxyvalerate) where melting temperature and some crystallinity are observed over the entrie range of composition.[8,9,10]

In the present study, poly(butylene terephthalate) (PBT), poly (1,4-cyclohexylene dimethylene terephthalate) (PCT) and poly(butylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) (PBTCT) random copolymers were synthesized by melt and solid state polymerization. The sequence analysis was done by ^{13}C NMR spectroscopy. The crystallization behavior of the random copolymers were studied by wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC).

Experimental

Materials

1,4-Dimethyl terephthalate (DMT) (99+%) from Sigma-Aldrich, Inc. was recrystallized from methanol. 1,4-butanediol (BD) (Sigma-Aldrich) was distilled and stored over molecular seives. 1,4-cyclohexanedimethanol (trans/cis 70/30) (CHDM) was dried in vacuum oven before reaction. Tetra isopropyl titanate was distilled under vacuum and used as a solution in dry toluene. Phenol and 1,1,2,2-tetrachloro ethane were used as such.

General Procedure for Synthesis of PBTCT Copolyesters

DMT, BD, CHDM and 0.1 wt% tetraisopropyl titanate 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 recovered by breaking and cutting into pieces.

Synthesis of PCT by Solid State Polymerization

Dimethyl terephthalate 5.01g (0.026 mol), 1,4-cyclohexane dimethanol 7.06g (0.049 mol) and 0.01 wt% titanium isopropoxide were taken in a tube reactor fitted with N_2 inlet, air condensor and spiral trap to collect the distillate, methanol. The transesterification was done at 190-210°C for 1 h till methanol distillation ceased. Polycondensation was done at 270°C for 30 min and at 290°C under reduced pressure for 15 min. The hot polymer was poured into cold water, filtered and washed several times with hot water. The oligomer was dried in vacuum oven. The oligomer was powdered, coated with titanium isopropoxide in toluene and subjected to solid state polymerization at 220°C for 5 h and at 250°C for 5 h under vacuum(0.02 mbar).

Characterization

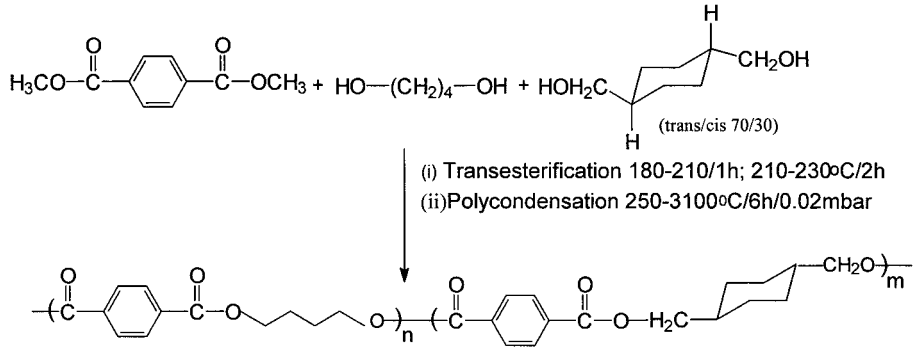
Inherent viscosities were measured at 30°C in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer in phenol/1,1`,2,2`-tetrachloroethane(TCE) (60:40 w/w) at a polymer concentration of 0.5 wt%. The PCT prepared by SSP was melted and cooled under vaccum for viscosity measurement as the polymer did not dissolve in the solvent. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide-angle powder goniometer and a slit collimated Rigaku SAXS goniometer(model CN2203E.5). 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 scaned between 2θ = 5-35 deg at a speed of 1 deg/min. The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10°C/min under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization temperature upon cooling (T_{cc}) from the cooling thermogram.

^1H and ^{13}C NMR were performed in a Brucker DRX 500 spectrometer at 25 ± 1°C, operating at 500 and 125 MHz. Polyesters and copolyesters were dissolved in a mixture of deuterated chloroform ($CDCl_3$)/trifluoroacteic acid(TFA-d_1) and spectra were internally referenced to tetramethyl silane. About 12 and 100 mg of sample dissolved in 0.5 ml of solvent for ^1H and

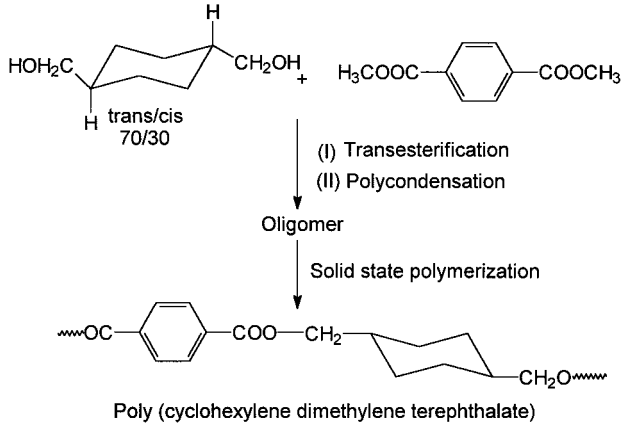
^{13}C NMR. For quantitataive ^{13}C NMR analysis of the microstructure, the relaxation delay and spectral width was 2 μs and 250 ppm, respectively., and the relaxation delay was 10s. 1000 FID's were acquired with 3K data points and Fourier transformed.

Results and Discussion

PBT and PBTCT copolymers were prepared by standard melt condensation procedure from dimethyl terephthalate, butanediol and 1,4-cyclohexane dimethanol (trans/cis 70/30) using tetraisopropyl titanate catalyst. The reaction scheme is depicted in Scheme 1. A series of copolyesters were synthesized by changing the ratio of BD/CHDM from 94/6 to 22/78.



Scheme 1. Synthesis of Poly(butylene terephthalate-co-cyclohexane dimethylene terephthalate).



Scheme 2. Synthesis of Poly(cyclohexane dimethlene terephthalate) by melt and SSP.

The copolyesters have viscosities in the range of 0.5-0.9 dL/g and there was no change in the trans/cis ratio of CHDM after the polymerization. However, PCT could not be synthesized by melt method as it underwent degradation. Hence it was synthesised by solid state polymerization[11] (Scheme 2). Oligomer with an inherent viscosity (ηi_{nh}) of 0.1 dL/g was synthesized by melt condensation and subsequently subjected to SSP to obtain high molecular weight PCT of viscosity 0.66 dL/g. Table 1 gives the SSP conditions and other relevant data.

Table 1. Thermal and viscosity data of PCT samples during SSP.

Sample/conditions	η_{inh} [a] (dL/g)	Melting Peak		Crystallization peak	
		T_m (°C)	[ΔH J/g]	T_c(°C)	[ΔH J/g]
Oligomer	0.10	267	35	258	68
220°C/5.25 h	0.45	297	79	249	55
250°C/5 h	0.66	299	86	246	58

[a]The inherent viscosities were measured after melting the samples under vacuum in 60/40 w/w phenol/TCE mixture

Copolymer Composition and Sequence Analysis

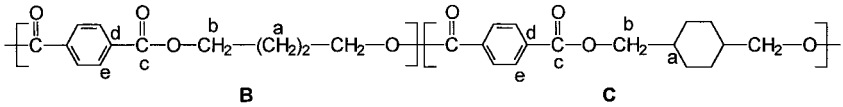


Fig. 1. Chemical structure of PBTCT copolyesters with notations used for NMR assignments.

The chemical structure of PBTCT copolyester with notations used for NMR assignments are shown in Figure 1. The composition of the copolyesters is determined by the ^{1}H NMR and the spectra is shown in Figure 2. The cyclohexylene dimethylene groups of CT unit have two isomers *cis*(equatorial, axial) and *trans* (equatorial, equatorial or axial, axial), the latter (*trans* CT) is more stable than former (*cis* CT). The oxymethylene protons are divided into three groups, viz, BT, *cis* CT and *trans* CT. The copolymer composition of BT, *cis* CT, *trans* CT was estimated from relative peak intensities of oxymethylene proton resonance of butylene and cyclohexylene dimethylene peaks. The ^{1}H and ^{13}C NMR peak assignments of PBT, PCT and PBTCT copolyester is shown in Table 2. The *trans/ cis* ratio determined for all the copolymers are found to be the same as the feed ratio.

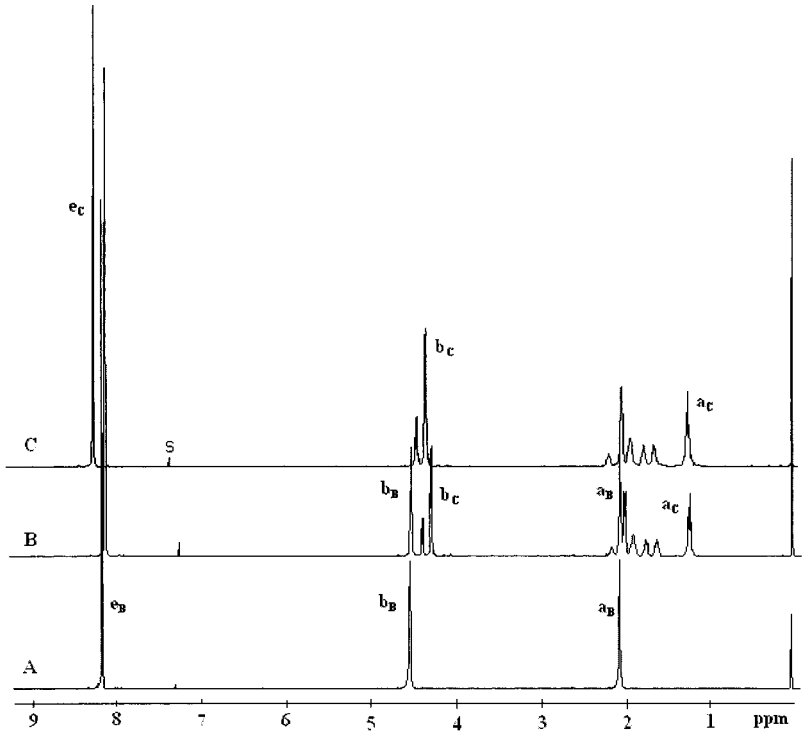


Fig. 2. ^{1}H NMR of (A)BT, (B)$PBT_{45}CT_{55}$ and (C)PCT in $CDCl_3$/TFA-d_1.

Table 2. ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PCT and PBTCT copolyesters in $CDCl_3$/TFA-d_1.

	^{1}H Chemical shifts					
	$^{B}H_a$	$^{B}H_b$	$^{B}H_e$	$^{C}H_a$	$^{C}H_b$	$^{C}H_e$
PBT	2.02	4.5	8.12			
PCT				1.2-1.99	4.37(d), 4.27(d)	8.15
$PBT_{45}CT_{55}$	2.04	4.52	8.14	1.2-2.00	4.38(d), 4.27(d)	8.15

	^{13}C Chemical Shifts							
	$^{B}C_b$	$^{B}C_c$	$^{B}C_d$	$^{B}C_e$	$^{C}C_b$	$^{C}C_c$	$^{C}C_d$	$^{C}C_e$
PBT	65.9	167.6	133.7	129.8				
PCT					71.3, 69.2	167.9	133.9	129.8
$PBT_{45}CT_{55}$	65.9	167.6	133.7	129.8	71.3, 69.2	167.7	133.9	129.8

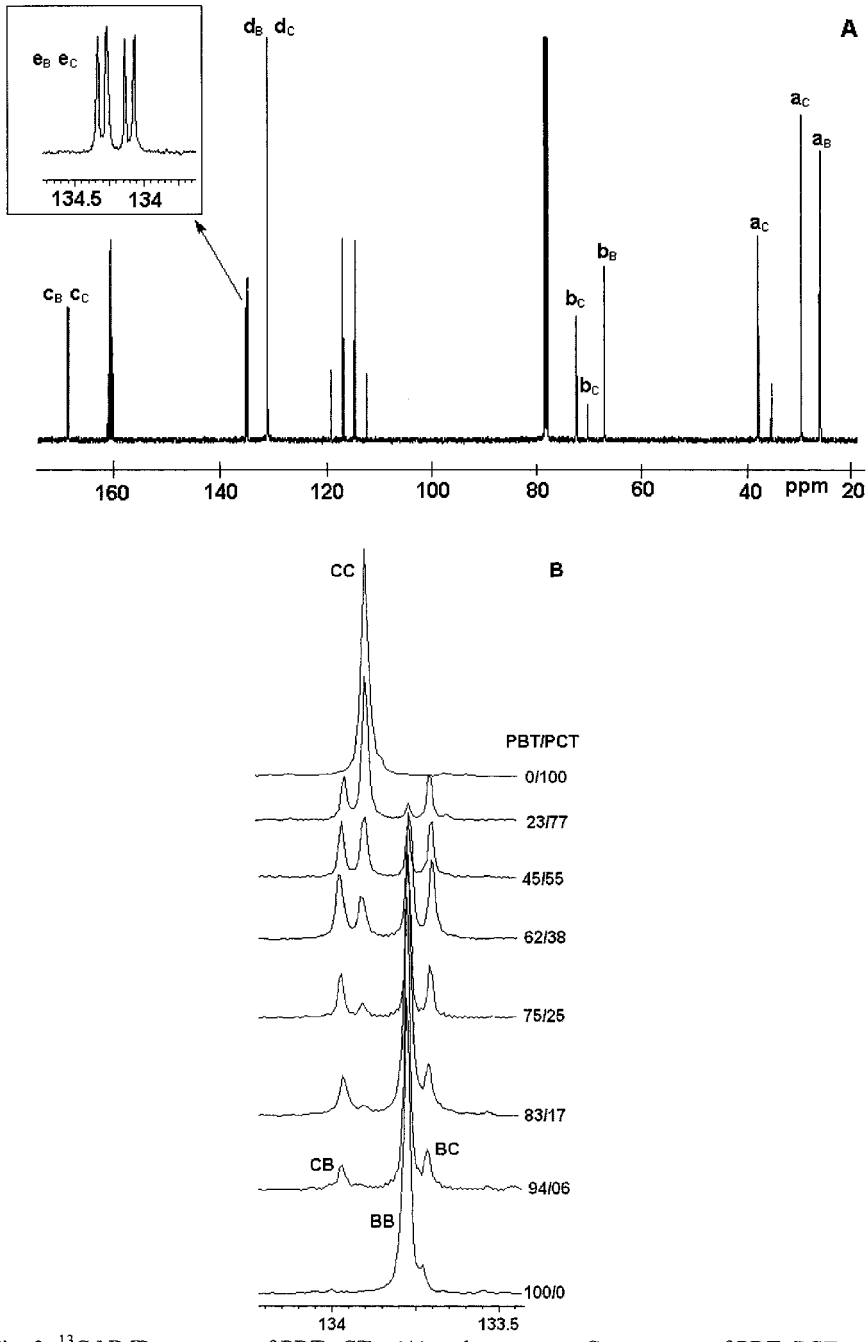


Fig. 3. ^{13}C NMR spectrum of $PBT_{45}CT_{55}$ (A) and quaternary C resonance of PBT, PCT and PBTCT copolyesters (B).

The sequence of the BT and CT units in the copolymer could be determined from the ^{13}C NMR spectra. The quaternary aromatic carbon peak is more sensitive to sequence effects than any other aromatic carbons due to the occurrence of through space and through-bond interactions between neighboring units and was used for sequence quantification.[12,13,14] The spectrum is shown in Figure 3A and the peak assignments is given in the Table 2. The quaternary carbon of the terepthalate (labelled as d) is split into four different signals corresponding to the four dyads, BB(133.8), CC(133.88), BC(133.68), CB(133.95) as shown in Figure 3B and Figure 4. According to Yamadera and Murano,[15] 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 cyclohexylene (C) units were obtained from integration of the peaks.

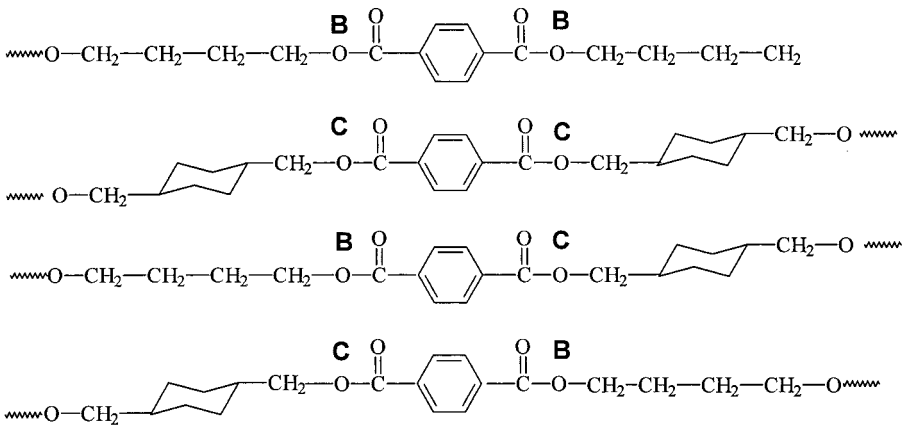


Fig. 4. Possible dyad sequences of the quaternary carbon in the PBTCT copolyester.

$$P_B = \frac{f_{BC} + f_{CB}}{2} + f_{BB} \qquad P_C = \frac{f_{BC} + f_{CB}}{2} + f_{CC} \qquad (1)$$

Where P_B is the molar fraction of the butylene unit, P_C the molar fraction of the terephthalate unit and f_{BB}, f_{CC}, f_{BC} and f_{CB} correspond to the proportion of the integrated intensities of BB, CC, BC and CB.

If one could inspect the units along the copolymer chain from one end to the other, the probability of finding a butylene unit placed next to a cyclohexylene unit (or cyclohexylene unit placed next to a butylene unit) would be given by P_{BC} and P_{CB} as given in equation (2)

$$P_{BC} = \frac{f_{BC} + f_{CB}}{2P_B} \qquad P_{CB} = \frac{f_{BC} + f_{BC}}{2} + f_{CC} \qquad (2)$$

The number-average sequence length of butylene terephthalate (BT) and cyclohexylene dimethylene terephthalate (CT) units L_{nB} and L_{nC} repectively and the degree of randomness (B) were calculated using following equations (3) and (4)

$$L_{nB} = \frac{2P_B}{f_{BC} + f_{BC}} \qquad L_{nC} = \frac{2P_C}{f_{BC} + f_{CB}} \qquad (3)$$

$$B = P_{BC} + P_{CB} \qquad (4)$$

For random copolyesters B is unity. A value of B equal to zero indicates a mixture of homopolymers, whilst a value of 2 indicates an alternating distribution.[15] Table 3 shows the average sequence length and degree of randomness. The dyad distribution is also calculated based on Bernoullian statistical model[16] and plotted in Figure 5 along with the experimentally determined values.

Table 3. Sequence distribution and randomness of PBTCT copolyesters determined by ^{13}C NMR.

	Composition[b]		CHDM isomer compostion[b]		Average sequence length		Randomness
Copolyester[a]	X_B	X_C	*cis*	*Trans*	L_{nB}	L_{nC}	B
PBT	100	0	-	-	-	-	-
$PBT_{94}CT_{06}$	93	07	30	70	7.7	1.2	0.95
$PBT_{83}CT_{17}$	84	16	28	72	5.3	1.3	0.98
$PBT_{75}CT_{25}$	74	26	25	75	3.7	1.4	0.99
$PBT_{62}CT_{38}$	61	39	25	75	2.4	1.7	1.01
$PBT_{45}CT_{55}$	45	55	25	75	1.8	2.3	0.98
$PBT_{23}CT_{77}$	22	78	23	77	1.4	5.0	0.93
PCT	0	100	26	74	-	-	-

[a] Experimetnal values were obtained from integration of ^{13}C NMR peaks and ref 16.
[b] calculated from the oxymethylene proton resonance of butanediol and cylohexanedimethanol from ^{1}H NMR spectra.

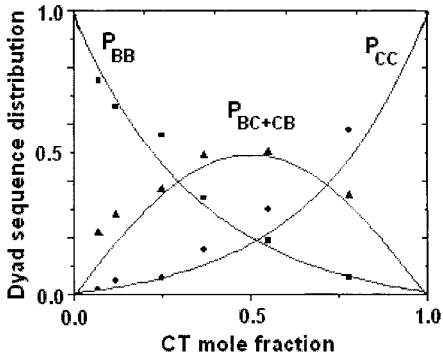


Fig. 5. Dyad sequence distribution as a function of copolymer composition. The solid lines represent the distribution calculated by Bernoullian statistics.

It is observed that the experimentally determined average sequence lengths were in all cases in accordance with that predicted on the basis of ideal copolycondensation statistics with randomness close to unity.[15,17,18]

Crystallization and Melting Behavior of the Copolyesters

The thermal behavior of the copolyesters was studied by differential scanning calorimetry. The copolyesters, in all composition range showed melting endotherm on heating and crystallization exotherm on cooling. The presence of clear melting and crystallization peak indicates cocrystallization behavior of the copolyesters over the entire range of composition. Only few systems show such a behavior.[8,9,10] Figure 6 shows the crystallization exotherms on cooling and the melting endotherms of the copolyesters during the second heating. It may be noted that the as polymerized samples have varying thermal history and hence the thermal properties obtained during the first heating cannot be compared. The various parameters extracted from the thermograms are shown in Table 4. The crystallization, melting and glass transition temperatures of the copolyesters are shown in Figure 7. All the copolyesters have single T_g and show a linear increase with increase in CHDM content. The melting and crystallization temperatures of the copolyesters show eutectic behavior and the eutectic composition is $PBT_{62}CT_{38}$. The typical eutectic behavior indicates that the cocrystallizaion is isodimorphic in nature and monomer units of one type are included in the crystal lattice of the other type.

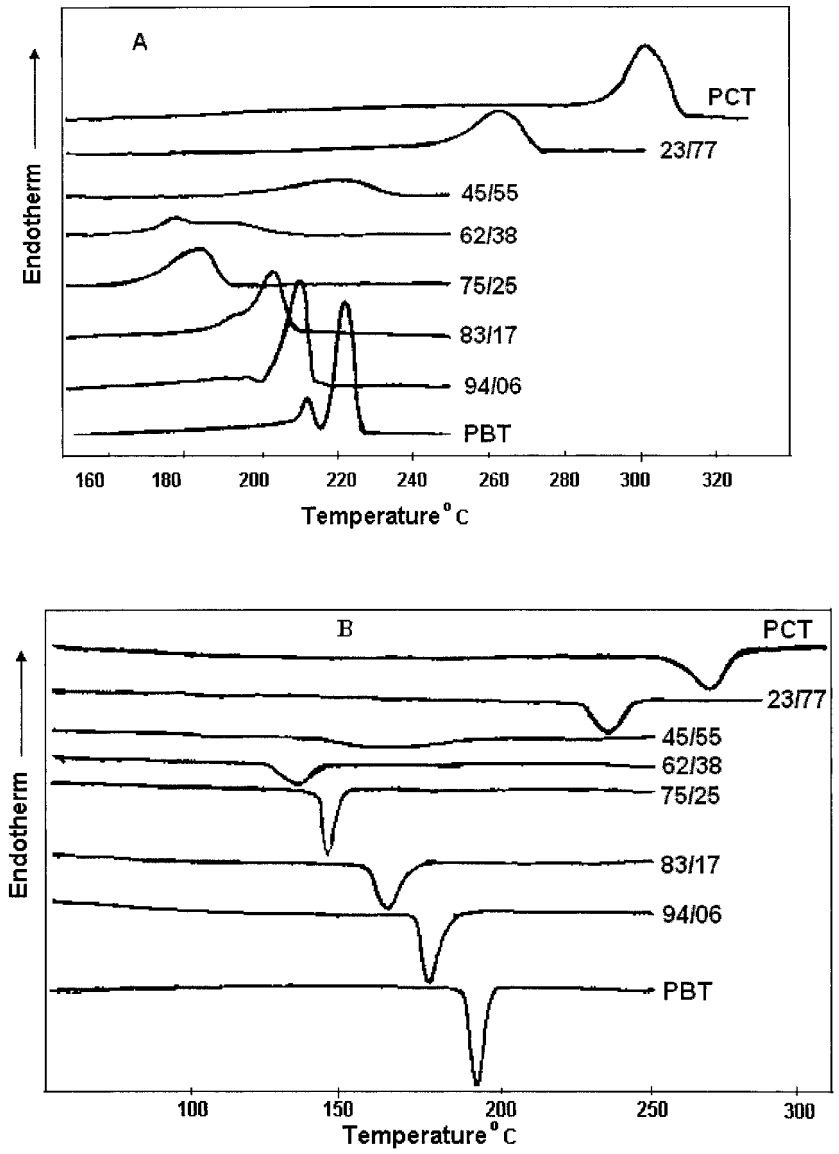


Fig. 6. DSC scans of PBT, PCT and PBTCT copolyesters. (A) second heat (B) first cooling.

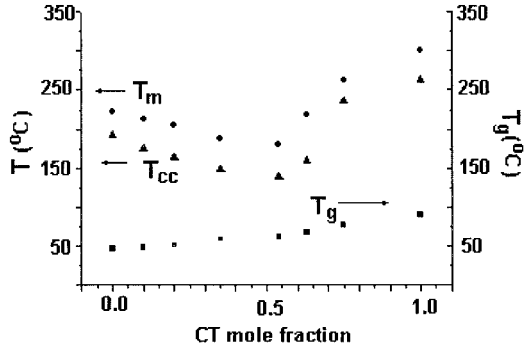


Fig. 7. Melting temperature (T_m), crystallization temperature (T_{cc}) and glass transition temperature (T_g) as a function of comonomer (CHDM) content expressed as molar fraction.

Table 4. Thermal properties of poly(butylene-co-1,4-cyclohexylene dimethyle terephthalate) (PBTCT) copolyesters.

Polyester	η_{inh} dL/g	T_g[a] (°C)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_c (J/g)	T_m[b] (°C)	ΔH_m[b] (J/g)
PBT	0.90	40	226	41	193	49	223	54
$PBT_{94}CT_{06}$	0.50	48	212	36	175	45	211	53
$PBT_{83}CT_{17}$	0.57	51	205	34	163	41	206	45
$PBT_{75}CT_{25}$	0.66	59	187	27	149	30	188	37
$PBT_{62}CT_{38}$	0.60	61	180	25	139	26	183	32
$PBT_{45}CT_{55}$	0.75	67	218	19	159	24	210	30
$PBT_{23}CT_{77}$	0.51	77	262	30	237	31	264	40
PCT	0.66	90	296	43	246	58	294	67

[a] Measured by DSC with a heating rate of 10°C/min after quenching from the melt.
[b] Measured from first heating of the annealed samples. Annealing was performed at 15°C below the T_m onset for 2 h.

X-ray Diffraction Studies

The room temperature structure of the samples was analyzed by WAXS. As obtained samples showed diffraction pattern typical of semicrystalline polymers. The diffraction patterns of the samples having compositions close to the eutectic composition are not well resolved. Hence, all the samples were annealed close to their melting temperature for 2 h. After annealing the

diffraction peaks are well developed. From the peak position the d-spacings are calculated using Bragg equation. Figure 8 shows the WAXS pattern of the annealed PBT, PCT and PBTCT copolymers. The crystal structure of PBT[4,19] and PCT[20] 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 010, 101, 100 and 111 planes of triclinic. PCT shows peaks at 15.63, 16.63, 23.41 and 25.6 and are assinged to 011, 010, 100 and 111 planes. The variation of d-spacing with composition 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. The change in the lattice also ocuurs close to the eutectic composition. This shows the ability of PCT to control the crystallization even when it is present in minor proportion. This could arise due to the higher rigidity of PCT when compared to PBT.

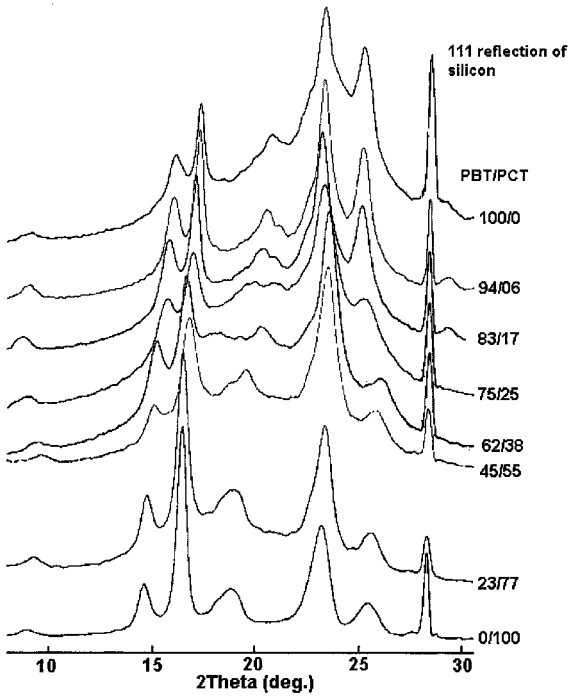


Fig. 8. X-ray diffraction patterns of annealed samples.

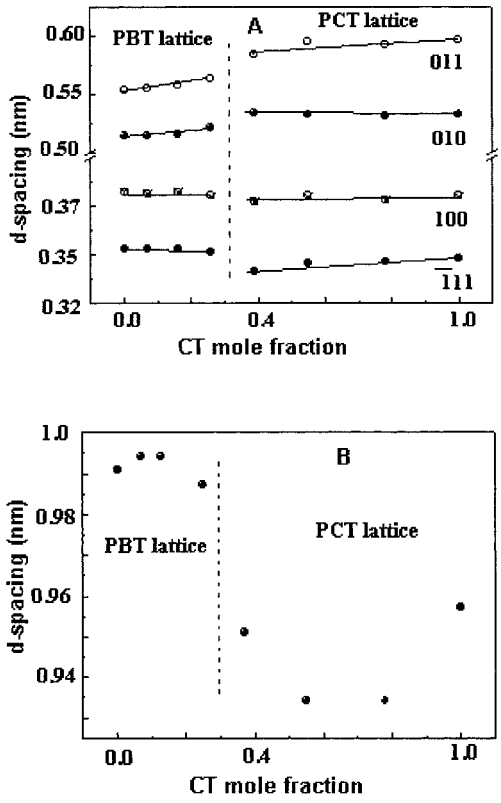


Fig. 9. (A) d-spacigs of 011, 010, 100 and 111 reflections and (B) 001 spacing(along chain direction)as a function of copolymer composition.

According to Jun etal,[21] an average sequence length higher than 3 is required to form crystallites. However, in the present case, copolyesters could crystallize even when the sequence length is less than 3. This indicates similarity in the repeat unit of PBT and PCT. The length of BT and CT units are calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software and found to be similar(1.23 nm for PBT and 1.33 nm for PCT). It appears that similar repeat unit lengths makes the copolyesters to cocrystallize in the same lattice even when the individual sequence length is less than 3.

Conclusions

Poly(butylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) (PBTCT) copolymer is synthesized by melt condensation. The NMR spectroscopic analysis indicates that the coploymer is statistically random, irrespective of the composition. The thermal analysis and XRD studies have shown that PBTCT is one of the few copolymers that can be crystallized in all composition. The melting and crystallization from the melt shows typical eutectic behaviour. The eutectic composition is $PBT_{62}CT_{38}$. The T_g shows a linear dependency on the composition and increases with increase in the CHDM proportion in the copolyesters. The copolyesters crystallize in either PBT or PCT lattice depending on the composition, however, only PBT rich compositions favour PBT lattice.

Acknowledgements

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