

Characterization of Poly(trimethylene/butylene terephthalate) Copolymer Prepared by the Copolycondensation of Bis(3-hydroxypropyl terephthalate) and Bis(4-hydroxybutyl terephthalate)

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ABSTRACT: Homopolymers and copolymers were synthesized by polycondensation and copolycondensation, with varying feed ratios of bis(3-hydroxypropyl terephthalate) (BHPT) and bis(4-hydroxybutyl terephthalate) (BHBT) at 270°C. In addition, in the mol ratio of 1:1, copoly(trimethylene terephthalate/butylene terephthalate) [P(TT/BT)], with reaction times of 5, 10, 20, 30, and 60 min, was synthesized to identify the chain-growth process of the copolymers. From differential scanning calorimetry (DSC) data, it was found that a random copolymer might be formed during copolycondensation. The molecular structure of copolymers, formed through the interchange reaction of BHPT and BHBT, was investigated using carbon nuclear magnetic resonance spectroscopy (¹³C-NMR). We calculated the se-

quence-length distributions of trimethylene and butylene sequences and randomness in the copolymers using ¹³C-NMR data. From the values of the number-average sequence length calculated, it was determined that a random copolymer was produced: This result coincides with previous DSC data. The lateral spacing of the unit cell of the copolymer increased slowly when the mol percent of one monomer was increased to that of the other monomer, indicating broadening of the unit cell by lateral distortion. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2200–2205, 2003

Key words: poly(trimethylene/butylene terephthalate); bis(3-hydroxypropyl terephthalate) (BHPT); bis(4-hydroxybutyl terephthalate) (BHBT); sequence length

INTRODUCTION

The family of linear aromatic polyesters, poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT), are industrially important and are widely used as commercial fibers, polymeric films, and engineering plastics. PBT is now used primarily in engineering thermoplastics owing to its much higher crystallization rate.^{1–5} Only a small volume of PBT is used in fiber applications. In contrast, PTT is used commercially for textiles and carpets because of its good resilience arising from the chain conformation including the *gauche* configuration.

Generally, to improve the properties of polymeric material, copolymerization and blending are mainly used.^{6–9} Misra and Garg^{10,11} synthesized PET–PBT block copolymers to increase the crystallization rate of PET. Varma et al.^{12,13} synthesized a PET–poly(alkylene terephthalate) copolymer to enhance the dyeability and hydrophilicity of PET. Smith et al.¹⁴ investi-

gated the physical properties of P(ET/TT) and P(ET/BT) copolymers. Ponnusamy and Balakrishnan¹⁵ described the preparation and characterization of P(ET/TT) copolymers in varying compositions. Backson et al.¹⁶ reported on the thermal properties and the number-average sequence lengths of P(ET/BT) copolyesters, synthesized at above and below the melting temperature.

We report here, based on carbon nuclear magnetic resonance (NMR) spectroscopy data, sequence-length distributions of trimethylene and butylene sequences and randomness in the P(TT/BT) copolyester, which were synthesized using bis(3-hydroxypropyl terephthalate) (BHPT) and bis(4-hydroxybutyl terephthalate) (BHBT) with reaction times of 5, 10, 20, 30, and 60 min. Moreover, the thermal properties and molecular structure of the copolyester were measured using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction analysis (WAXD).

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT; Aldrich, Milwaukee, WI, 99%), 1,3-propanediol (1,3-PD, Aldrich, 98%), and 1,4-butanediol (1,4-BD, Yakuri, 99%) were used in synthesizing BHPT and BHBT, respectively, by a transes-

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terification reaction. Zinc acetate and titanium tetrabutoxide (TBT, Aldrich, 99%) were used as catalysts in transesterification, polycondensation, and copolycondensation. Ethyl ether (Showa, Tokyo, Japan, 99.5%) was used to remove the remaining diol after transesterification. Chloroform-*d* (Aldrich, 99.8%) was used as a solvent for a carbon NMR spectroscopy. Other extra-pure reagents were used without further purification.

Synthesis and purification of BHPT and BHBT

The transesterification of DMT (97.1 g, 0.5 mol) with 1,3-PD (83.6 mL, 1.5 mol) in the presence of zinc acetate (2960 ppm: 2.5×10^{-3} mol) as a catalyst was performed in a four-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The mixture of DMT, 1,3-PD, and the catalyst was purged with nitrogen and stirred continuously throughout the reaction at 160°C. After 5 h, the temperature was gradually increased to 210°C and maintained for 30 min with stirring. After reaction completion, the product was washed several times with ethyl ether, then dissolved in hot water. White needle-shaped crystals were obtained by recrystallizing the above-dissolved BHPT. The transesterification of DMT (39 g, 0.2 mol) with 1,4-BD (355 mL, 3.95 mol) in the presence of TBT (0.039 g, 1.145×10^{-4} mol) as a catalyst was also performed under the same conditions.

Homopolycondensation and copolycondensation of BHPT and BHBT

Purified BHPT (10 g, 0.035 mol) was melted under a nitrogen atmosphere in a polycondensation tube, equipped with a mechanical stirrer and silicone sealing apparatus. Molten BHPT was stirred at 50 rpm. At 200°C, nitrogen purging was stopped and the TBT (400 ppm: 1.18×10^{-5} mol) catalyst was added into the polycondensation tube. Pressure was decreased to about 20 mmHg by a vacuum pump and then slowly reduced to the pressure of 0.3 mmHg. This pressure was maintained during the polycondensation time. The reaction temperature was increased to 270°C and maintained at that level during a given polycondensation reaction time (10, 20, 35, 50, and 70 min). The polycondensed material was quenched in cold water immediately after the reaction was stopped and dried in a vacuum oven at room temperature for 1 day. BHBT (10 g, 0.031 mol) was also polymerized under the same conditions (TBT: 1.18×10^{-5} mol). The copolycondensation was conducted for 10 min under the same conditions used in The homopolycondensation. The amount of the TBT catalyst was fixed as listed in Table I. With a mol ratio of 1:1, copolycondensations were conducted for 5, 10, 20, 30, and 60 min under the

TABLE I
Feed Ratios of Monomer and Catalyst
for Copolycondensation

BHPT (mol)	BHBT (mol)	TBT catalyst (mol)
0.000	0.032	1.18×10^{-5}
0.007	0.026	1.18×10^{-5}
0.011	0.023	1.18×10^{-5}
0.014	0.019	1.18×10^{-5}
0.017	0.017	1.18×10^{-5}
0.021	0.013	1.18×10^{-5}
0.025	0.010	1.18×10^{-5}
0.028	0.007	1.18×10^{-5}
0.036	0.000	1.18×10^{-5}

same conditions as used in the polycondensation described above.

Characterization

For ^{13}C -NMR experiments, specimens of each copolymer were dissolved in CDCl_3 in the range of 5–25% (w/v). In this concentration range, no significant shift in the peak positions was noted. Newmark et al.^{17,18} reported similar spin-lattice relaxation times (T_1) and nuclear Overhauser enhancement (NOE) of the aromatic quaternary and the carbonyl carbon of the PET–PBT copolymer. PET, PTT, and PBT differ only in the number of methylene groups in the aliphatic moiety of the repeating unit. If signals arising from similar environments within each polymer molecule, for example, ester groups, have the same T_1 and NOE, the integral of that peak can be used in quantitative analysis.

The thermal properties of specimens were carried out using a DSC (TA 2010) with a sample weight of 10 mg and a heating rate of 10°C/min. WAXD scans were recorded using a Rigaku (Japan) diffractometer with a scintillation counter in the transmission mode. These data were collected in increments of 1.5° ($\Delta 2\theta$) with a counting time 1 min for each step. $\text{CuK}\alpha$ radiation was used in all the measurements.

RESULTS AND DISCUSSION

In this study, to evaluate the effect of the monomer feed ratio on the molecular structure of the P(TT/BT) copolyester, BHPT and BHBT were homopolymerized and copolymerized in various monomer feed ratios. The NMR spectrum, recorded for the P(TT/BT) copolymer with a reaction time of 10 min and mol ratio of 1:1, is shown in Figure 1 and the assignment of the peaks in the spectra of the copolymer is given in Table II. From Table II, we note that chemical shifts of the quaternary aromatic carbon atoms are sensitive to the nature of the alkyl group adjacent to the phenylene ring and associated with the environment of the atoms, that is, whether a propanediol or butanediol

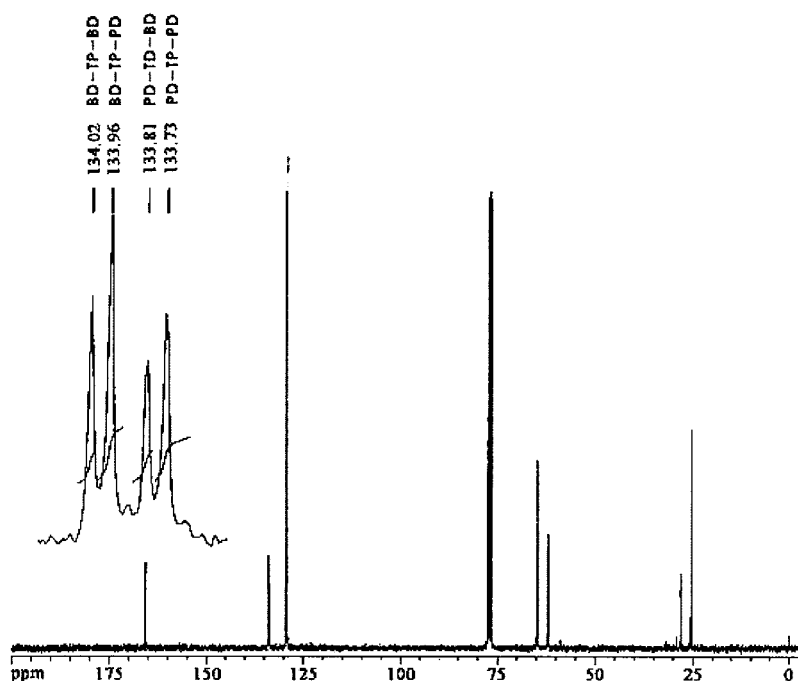


Figure 1 Typical ^{13}C -NMR spectrum of P(TT/BT) copolymer by copolycondensation of BHPT and BHBT using the mol ratio of 1/1.

alkyl residue is neighboring on the aromatic ring. The chemical shifts due to the quaternary carbon atoms are diagnostic of their environment and can be used in the characterization of the changes in the chain structure.

In discussing the NMR spectra, we used the homogeneous (PD-TP-PD and BD-TP-BD) and heterogeneous (PD-TP-BD and BD-TP-PD) dyads to describe sequences where a phenylene ring is flanked by the same or different alkyl chain residues, respectively. From the dyad sequences, mol fractions of the PT (f_p) and BT (f_B) units were calculated as follows:

$$f_p = f_{\text{PTP}} + 0.5f_{\text{PTB}} \quad (1)$$

$$f_B = f_{\text{BTB}} + 0.5f_{\text{PTB}} \quad (2)$$

where f_{PTP} and f_{BTB} are mol fractions of each homogeneous dyad. f_{PTB} is the mol fraction of both heterogeneous dyads. The values of f_{PTP} , f_{BTB} , and f_{PTB} are directly proportional to the area under the spectral peaks associated with the dyad sequence concerned.

If P_{PB} is the probability of a BT unit existing next to a PT unit and P_{BP} is the probability of a PT unit existing next to a BT unit, respectively, P_{PB} and P_{BP} can be calculated as follows:

$$P_{\text{PB}} = \frac{f_{\text{PTB}}}{2f_p} \quad (3)$$

$$P_{\text{BP}} = \frac{f_{\text{PTB}}}{2f_B} \quad (4)$$

The degree of randomness (B) can be defined as the summation of the two probabilities:

$$B = P_{\text{PB}} + P_{\text{BP}} \quad (5)$$

If B is below 1, the PT and BT units in the copolymer tend to cluster in blocks of each unit and B will be 0 in a homopolymer mixture. In contrast, if B is over 1, their sequence lengths become shorter with increasing B . When B is 2, PT and BT units form a perfect alternating copolymer. The number-average sequence lengths are given by

$$\overline{LnP} = \frac{2f_p}{f_{\text{PTB}}} = \frac{1}{P_{\text{PB}}} \quad (6)$$

$$\overline{LnB} = \frac{2f_B}{f_{\text{PTB}}} = \frac{1}{P_{\text{BP}}} \quad (7)$$

where \overline{LnP} is the number-average sequence length of PT unit sequences and \overline{LnB} is the number-average sequence length of BT unit sequences. The values of number-average sequence length should lie between 1 and infinity. A value of 1 corresponds to a strictly alternating copolymer and a value of infinity pertains to a homopolymer. In contrast, a value of 2 is characteristic of a random distribution of the minor component repeating units over all molecules in the system. The calculated number-average sequence lengths and f_B are given in Table III.

TABLE II
 ^{13}C -NMR Chemical Shifts Assigned to the P(TT/BT) Copolymer

Chemical shift (ppm)	Environment
133.73	
133.81	
133.96	
134.02	

Figure 2 shows the change of randomness with the reaction time. As presented in Table III and Figure 2, the randomness of a copolymer decreased slightly and is very close to 1, which means that random copolymers were formed during the copolycondensation, but with no significant changes in the randomness with the copolycondensation time. The mol fraction of the heterogeneous dyad decreased slightly with the reaction time, which shows that the blockiness of PTT or PBT in the main chain increased very slightly. This result shows good agreement with the decrease of randomness.

TABLE III
 Sequence Length and Randomness
 of P(TT/BT) Copolymer

Reaction time (min)	f_{PTB}	B	\overline{LnP}	\overline{LnB}
5	50.17	1.021	1.733	2.253
10	49.37	1.005	1.757	2.294
20	49.10	1.000	1.763	2.310
30	49.08	1.000	1.761	2.314
60	48.92	0.997	1.762	2.326

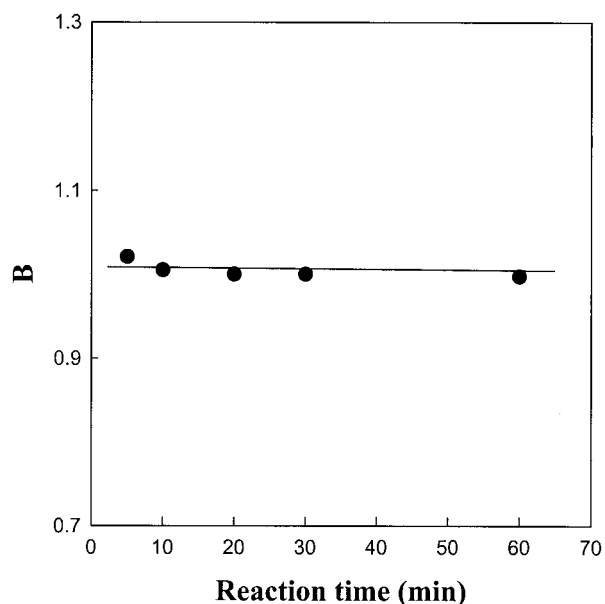


Figure 2 Change of randomness of P(TT/BT) copolymer during copolycondensation.

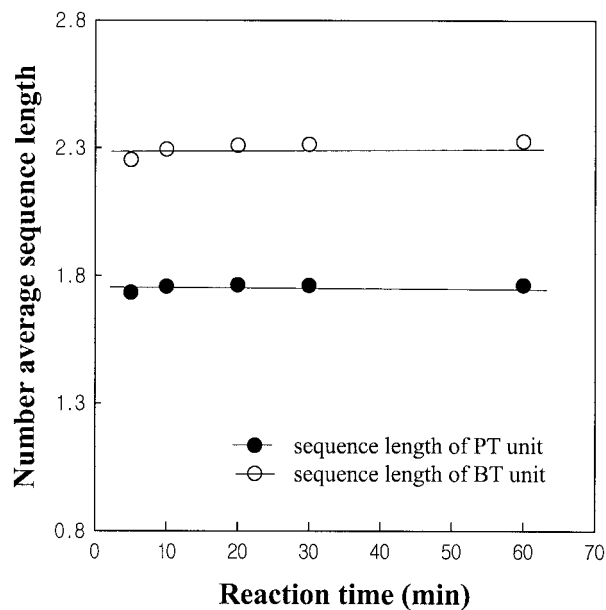


Figure 3 Changes of number-average sequence lengths during copolycondensation.

Figure 3 presents the change of \overline{LnP} and \overline{LnB} with the reaction time. The sequence lengths of the PT unit and the BT unit are slightly increased and close to 2, the value of a random copolymer, but show no significant change with the reaction time. It is thought that the sequence length of a copolymer has a close relation to the monomer reactivities. The sequence length of the BT unit is longer than that of the PT unit, probably due to the reactivity of BT being higher than that of PT. This is in good agreement with our previous result¹⁹ showing the monomer reactivities calculated from the ¹H-NMR peaks, which are 1.25 and 0.78 for BT and PT, respectively.

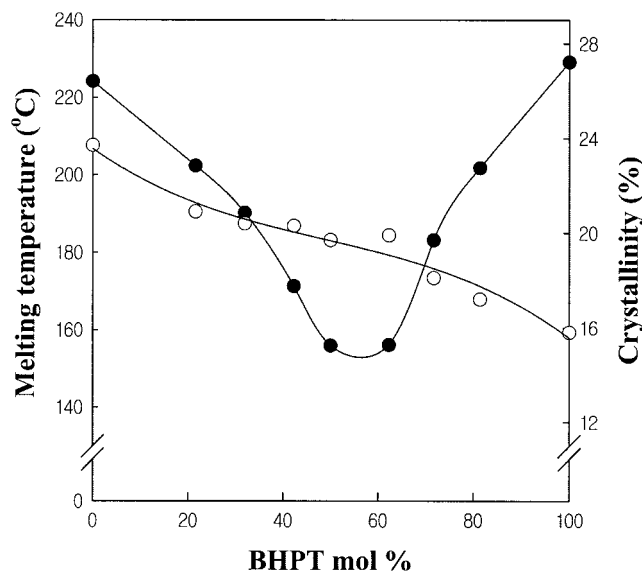


Figure 5 Melting temperature and crystallinity of copolymers with BHPT mol percent.

Typical DSC curves of the PTT, PBT, and P(TT/BT) copolymers, obtained after cooling from the melt, are shown in Figure 4. Endothermic baseline shifts associated with the glass transitions were observed in the temperature range between 40 and 60°C in the first scan, but were not found in the second run. These calorimetric results indicate that an increase in the amount of the comonomer leads to a depression of the melting temperature in the copolymers which experienced the same thermal history. Figure 5 shows the melting temperature and crystallinity of the copolymers with the BHPT mol percent. The melting temperatures for The BHPT mol % of 50 and 62.3 show a large difference compared to the melting temperatures

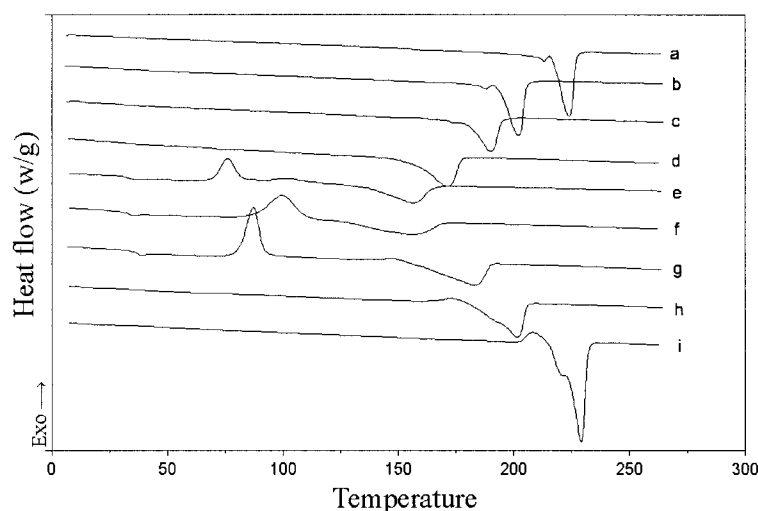


Figure 4 DSC thermograms of PTT, PBT, and copoly(TT/BT): BHPT/BHBT mol %: (a) 100/0; (b) 78.4/21.6; (c) 68.1/31.9; (d) 57.7/42.3; (e) 50/50; (f) 37.7/62.3; (g) 28.3/71.7; (h) 18.6/81.4; (i) 0/100.

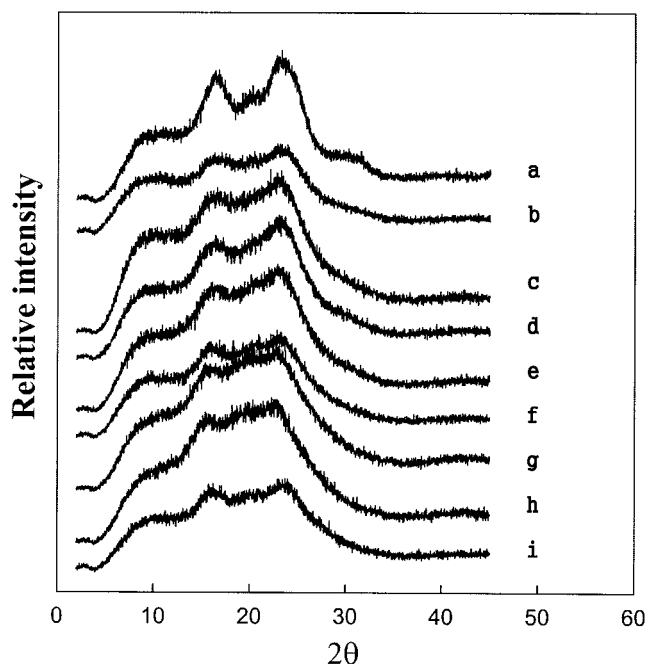


Figure 6 X-ray diffraction patterns of homopolymers and copolymers: BHPT/BHBT mol %: (a) 100/0; (b) 78.4/21.6; (c) 68.1/31.9; (d) 57.7/42.3; (e) 50/50; (f) 37.7/62.3; (g) 28.3/71.7; (h) 18.6/81.4; (i) 0/100.

of PTT and PBT. These two values are similar, so it is expected that there is further depression of the melting temperature in a BHPT mol % between 50 and 62.3. In contrast, the crystallinity obviously decreased with an increase in the PT fraction in the copolymer. This can be explained by the fact of a much higher crystallization rate of the BT unit than that of the PT unit after copolycondensation.

To determine the crystal structure variations of the P(TT/BT) copolymers with the monomer feed ratio (copolymer composition), WAXD analyses were carried out. In the WAXD measurement, homopolymers and copolymers were used without any pretreatment. Figure 6 shows typical WAXD patterns of PTT, PBT, and their copolymers. As expected, the crystal structure variations with the copolymer compositions are well represented, that is, the lateral spacing of the unit cell of the copolymer increased slowly when the mol percent of one monomer was increased relative to the other monomer, indicating that the unit cell was broadened by lateral distortion.

CONCLUSIONS

Considering the effects of various copolycondensation parameters on the characteristics of the P(TT/

BT) copolymer, we may conclude as follows: Using the BHPT/BHBT mol ratio of 1:1 at a copolycondensation temperature of 270°C, P(TT/BT)s, with reaction times of 5, 10, 20, 30, and 60 min, were prepared to investigate the chain-growth process of the copolyester. It was found that a random copolyester might be formed during copolycondensation. Sequence-length distribution and randomness of the copolyester were calculated from the ^{13}C -NMR data. From the calculated number-average sequence length, it was confirmed that random copolymers were produced, which agreed with the DSC data. The lateral spacing of a unit cell of the copolyester was increased slowly when the mol percent of one monomer increased relative to the other monomer, indicating that the unit cell was broadened by lateral distortion. In the near future, we will report on the preparation and characterization of P(ET/TT/BT) copolymers using three different monomeric forms.

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