

Aliphatic-aromatic poly(butylene carbonate-co-terephthalate) random copolymers: Synthesis, cocrystallization, and composition-dependent properties

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ABSTRACT: A series of aliphatic-aromatic poly(carbonate-co-ester)s poly(butylene carbonate-co-terephthalate)s (PBCTs), with weight-average molecular weight of 113,000 to 146,000 g/mol, were synthesized from dimethyl carbonate, dimethyl terephthalate, and 1,4-butanediol via a two-step polycondensation process using tetrabutyl titanate as the catalyst. The PBCTs, being statistically random copolymers, show a single T_g over the entire composition range. The thermal stability of PBCTs strongly depends on the molar composition. Melting temperatures vary from 113 to 213°C for copolymers with butylene terephthalate (BT) unit content higher than 40 mol %. The copolymers have a eutectic melting point when about 10 mol % BT units are included. Crystal lattice structure shifts from the poly(butylene carbonate) to the poly(butylene terephthalate) type crystal phase with increasing BT unit content. DSC and WAXD results indicate that the PBCT copolymers show isodimorphic cocrystallization. The tensile modulus and strength decrease first and then increase according to copolymer composition. The enzymatic degradation of the PBCT copolymers was also studied. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41952.

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INTRODUCTION

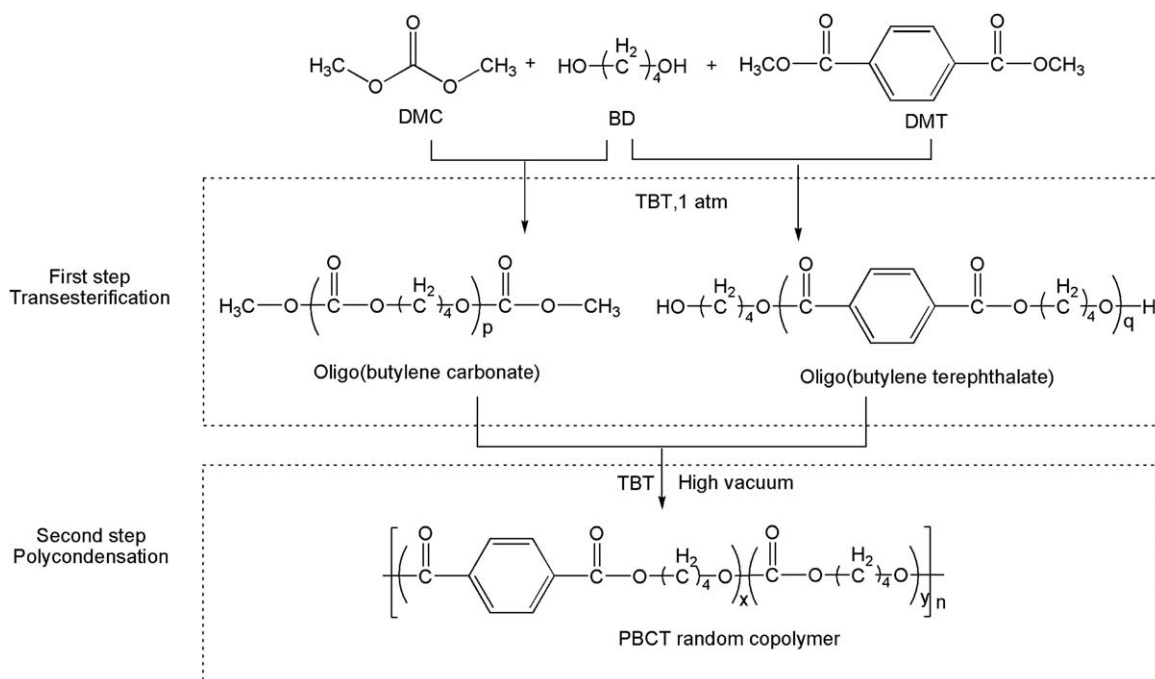
Aliphatic polycarbonates (APCs) have aroused great concern as biodegradable polymers recently, due to their nontoxicity, biocompatibility, and biodegradability.^{1–13} Compared with aliphatic polyesters, APCs are more feasible candidates for biomedical applications, owing to the absence of acidic compounds during the *in vivo* degradation. APCs can be prepared by copolymerization of CO₂ and epoxides or ring-opening polymerization method.^{14–18} The best method to obtain APCs in which the carbonate linkages are connected by more than three carbon atoms is the condensation polymerization of dimethyl carbonate (DMC) and aliphatic diols.¹⁹ DMC is renowned because it can be easily handled and is cheap, nontoxic, and high biodegradability, which make them true green materials. In addition, it now can be produced on a large scale using carbon monoxide or carbon dioxide. We have recently prepared high-molecular-weight APCs (weight-average molecular weight (M_w) \geq 166,000 g/mol) using DMC and different types of aliphatic diols with a two-step polycondensation method.^{19–22}

Among the resulting APCs, poly(butylene carbonate) (PBC) has attracted most interest because of its favorable comprehensive properties and competitive cost.^{23–26} It can be economically prepared from DMC and BD through the condensation polymerization. Recently, PBC has been chosen as a toughening blend partner for polylactide (PLA) and poly(butylene succinate) (PBS) due to its high flexibility. The addition of PBC significantly changed the tensile behavior, from brittle fracture of neat PLA or PBS to ductile fracture of the blends.^{27,28} Moreover, PBC can also be used as the flexible segment to toughen PBS according to block copolymerization.²⁹

However, PBC has a low melting point ($T_m = 60^\circ\text{C}$) and a slow crystallization rate, which limit its application range and processing window. Random copolymerization is a good way to modulate the properties of homopolymer.³⁰ PBC based random copolymers incorporating with aliphatic polyesters, aliphatic poly(carbonate-co-ester)s, have been reported to tune its properties.^{31–38} It was found that the crystallization property of PBC could be improved by copolymerizing with aliphatic polyesters.

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Scheme 1. Synthetic route to PBCT via two-step melt polycondensation.

However, the melting temperature was not improved obviously. In contrast, aromatic polyesters such as poly(ethylene terephthalate) and poly(butylene terephthalate) (PBT) have been widely used as an engineering thermoplastic or as a component in blends and copolymers because of their excellent thermal and mechanical properties.^{39–44} Consequently, randomly introducing terephthalate units into the aliphatic polyesters main chain is a promising way to enhance the thermal and mechanical performance, without sacrificing the biodegradability^{45–48} Specially, the well-known aliphatic–aromatic copolyester poly(butylene adipate-*co*-terephthalate) has been commercially produced as a biodegradable polymer under the trade name Ecoflex of BASF Co.^{49–53} It has been widely used as packaging films, agricultural films, and compost bags. Thus, incorporating terephthalate unit into PBC main chain might result in an aliphatic–aromatic copolymer with desirable thermal, crystallization, and mechanical properties.

Therefore, this article aims at synthesizing random poly(butylene carbonate-*co*-terephthalate)s (PBCTs) copolymers with desirable properties via transesterification and polycondensation route. However, such a series of aliphatic–aromatic random copolymers based on PBC were rarely reported. As such copolymers, similarly to commercially available Ecoflex, are potential candidates for uses in polymer applications. Their macromolecular structures and thermal properties were intensively characterized and discussed by gel permeation chromatography (GPC), viscometry, proton nuclear magnetic resonance (¹H NMR), and thermogravimetric analysis (TGA). The cocrystallization behavior of the random copolymers was investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). Their tensile properties were also analyzed. Results herein show that, PBCTs possess expectable thermal, cocrystallization, and mechanical properties in an appropriate composition range.

EXPERIMENTAL

Materials

DMC were purchased from Shandong Shida Shenghua Chemical (China) and were used as received. DMT, BD, and tetrabutyl titanate (TBT) were purchased from Beijing Chemical Reagents Corp. (China). TBT was distilled before use.

Synthesis of PBCTs

The copolymers were prepared by a two-step melt polycondensation method, transesterification, and polycondensation, as shown in Scheme 1. The copolymers are named as PBCT_{φ_{BT}} where φ_{BT} % is the molar percentage of BT unit in feed, i.e., φ_{BT} mol % = BT/(BT + BC) × 100%.

Hydroxyl terminated oligo(butylene terephthalate) (BHBT) and methyl carbonate terminated oligo(butylene carbonate) (BMBC) were prepared in the first step. For the synthesis of BHBT, DMT, and BD at a molar ratio of 1 : 1.8 and the catalyst TBT (0.1 wt % of the final polymer) were added into a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, reflux condenser, thermometer, and feeding funnel. Then the mixture was heated to 170°C for 1 h under a nitrogen atmosphere and stirring. The temperature was then increased to 230°C slowly. The reaction was controlled by the amount of the distilled methanol as the reaction byproduct of transesterification. The ¹H NMR spectrum of the obtained BHBT is shown in Figure 1. For the synthesis of BMBC, DMC, and BD at a molar ratio of 2.5 : 1 with the catalyst TBT (0.1 wt % of the final polymer) were added into the same reactor and then heated to 98°C under a nitrogen atmosphere and stirred continuously. The temperature was then gradually increased to 180°C and maintained for 1 h to ensure unreacted DMC and methanol formed as transesterification byproducts removed completely. The temperature of the distillation head was kept

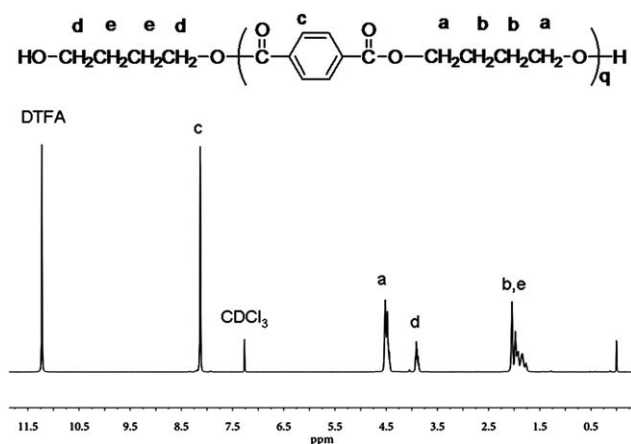


Figure 1. Chemical structure of BHBT, ^1H NMR spectrum of BHBT, and peak assignments.

between 60 and 66°C to prevent too much volatilization of DMC. The ^1H NMR spectrum of the obtained BMBC is shown in Figure 2. There is no methylene protons adjacent to the terminal hydroxyl group observed at 3.6–3.7 ppm, indicating that all the hydroxyl groups of BD in feed were involved in the transesterification reaction.

In the second step of polycondensation, the fractionating column was replaced by a short path distillation, and a vacuum system was connected to the reflux condenser through a cold trap immersed in liquid nitrogen. To obtain the desired butylene carbonate (BC) and butylene terephthalate ratio in the final copolymer, appropriate amounts of each oligomer and TBT (0.1 wt % of the final copolymer) were added into the reactor under nitrogen. The four-necked flask was moved to a silicone oil bath and heated to 210°C, for samples with terephthalate unit content up to 70 mol %, and 240°C for the rest. A high vacuum (ca. 10 Pa) was applied slowly over a period of about 20 min to avoid excessive foaming and to minimize oligomer sublimation. The polycondensation reaction was carried out for 2–6 h for all prepared samples. After completion, the copolymers were cooled to room temperature naturally and were used

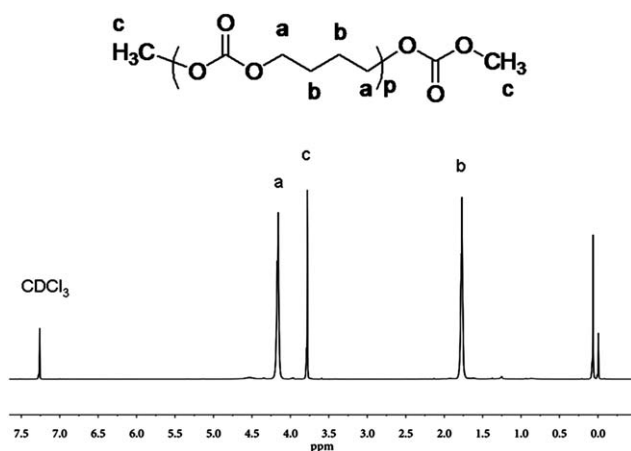


Figure 2. Chemical structure of BMBC, ^1H NMR spectrum of BMBC, and peak assignments.

without any purification. PBT homopolymer was synthesized using the same procedure and PBC homopolymer was synthesized according to the procedure described in the literature.²⁰ The specific polycondensation reaction conditions are shown in the Table SI, Supporting Information.

Characterization

The intrinsic viscosities of all samples in the mixture of phenol/1,1,2,2-tetrachloroethane (1/1, w/w) were measured using Ubbelohde viscometer at 25°C. The samples were maintained in the above solvent at 60°C for some time to dissolve completely. ^1H NMR spectroscopy obtained with a Bruker spectrometer operating at a frequency of 400 MHz was used for determining both the copolymer composition and the dyad sequence distribution in the copolymers. A mixture of deuterated trifluoroacetic acid (DTFA) and chloroform (CDCl_3) in a ratio 3/1 w/w (DTFA/ CDCl_3) was used as solvent and the concentration of each sample solution was of about 5% (w/v). Molecular weight determinations were estimated by GPC performing on a Waters 1515 HPLC pump and a refractive index detector (Waters 2414) at 35°C. Chloroform was used as the solvent. Polystyrene standards were used for calibration. The M_w of PBCT60, PBCT70, PBCT80, PBCT90, and PBT was not measured because they are insoluble in chloroform.

WAXD Analysis

The diffraction pattern was obtained with a Ragakumodel D/max-2B diffractometer using Ni-filtered Cu-K α radiation ($\lambda = 0.1542$ nm, 40 kV, 200 mA) in the range from 5° to 60° at a scanning rate of 5°/min. The samples were compression-molded into the films using a hot press at 20°C higher than their melting temperature values.

Thermal Analysis

The thermal properties of the samples were recorded with a Pyris Diamond DSC apparatus (PerkinElmer) equipped with a Cryo-Fill liquid nitrogen cooling system under a nitrogen atmosphere to minimize the oxidative degradation. Relatively small sample sizes (5 ± 0.3 mg) were used to minimize the effect of thermal conductivity of polymers. The samples were sealed in aluminum pans and heated to 20°C above the melting temperature at a rate of 10°C/min. Then the samples were cooled to -50°C with the highest achievable rate in order to obtain amorphous materials and reheated to 100°C at a rate of 10°C/min. The melting temperature and melting enthalpy were obtained during the first heating step, while the glass transition temperature was obtained during the second heating step. For isothermal crystallization the same melting procedure as mentioned above was followed, and then the samples were cooled to the designated crystallization temperature. The curves of heat flow as a function of time were recorded. TGA was carried out using a TA Instruments TGA2950 thermogravimetric analyzer from room temperature to 700°C under a nitrogen atmosphere, with a heating rate of 10°C/min. Sample weight was 2–3 mg.

Mechanical Properties

The tensile properties were measured with a universal tester (Instron 1122, UK) according to ASTM D638. Relatively thin films of about 300 ± 30 μm were prepared using a laminator (KT-0906, China) machine and conditioned at 23°C and 50%

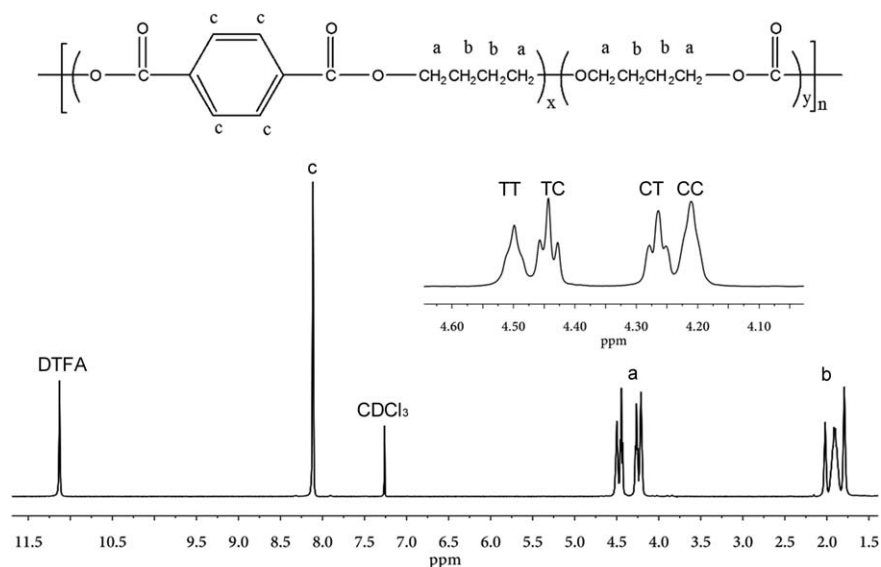


Figure 3. Chemical structure of PBCT, ^1H NMR spectrum of PBCT40, and peak assignments.

relative humidity for 48 h prior to testing. The crosshead speed was 80 mm/min. At least five specimens were tested for each sample.

Enzymatic Degradation

Sample films sized $1\text{ cm} \times 1\text{ cm} \times 50\ \mu\text{m}$ were prepared in duplicate. The samples were placed in vial tubes containing enzyme and potassium phosphate buffer solution ($\text{pH} = 6.86$) at $37 \pm 0.1^\circ\text{C}$. The enzyme used was lipase from *Pseudomonas* sp. (activity of 35 units/mg). The initial concentration of enzyme in the buffer solution was 10 units/mL. The enzymatic concentration for the samples was 5 units/mg. The films were removed from the enzymatic solution after 24 h, washed with distilled water several times, and dried under vacuum at room temperature to constant weight. The degree of biodegradation was estimated by the sample weight loss.

RESULTS AND DISCUSSION

Synthesis and Characterization

Random aliphatic–aromatic poly(carbonate-ester)s PBCTs were prepared following the two-step melt polycondensation method. In the first step, methyl carbonate terminated oligo(butylene carbonate) and hydroxyl terminated oligo(butylene terephthalate) were prepared. The number-average molecular weight of BMBC, calculated via ^1H NMR spectroscopy (Figure 1), is 759 g/mol, and that of BHBT (Figure 2) is 936 g/mol. In the second step, proper amounts of BMBC and BHBT were mixed and polycondensation under high vacuum was followed. The detailed synthetic route is presented in the experimental section.

A typical ^1H NMR spectrum of PBCT40 together with the assignment of each peak is shown in Figure 3. All the resonance signals are reasonably attributed to the proton nuclei locating at different sites. The copolymer composition is calculated according to the relative areas of the *c* aromatic protons of the BT unit located at 8.12 ppm and the a_{CC} and a_{CT} $-\text{OCH}_2$ protons of the BC unit at 4.24 and 4.29 ppm. Partial of other samples of the ^1H NMR spectrums are provided in the Figures S5–S9,

Supporting Information. It is worth noticing that the BC unit content in copolymer is always slightly lower than that in feed, as seen in Table I. This might be attributed to the sublimation of BMBC and thermal degradation of BC unit during the polycondensation stage. It has been clarified in our early work, during the PBC homopolymer polycondensation, which oligomer sublimation and thermal degradation of main chain happen, giving BMBC, cyclic tetramethylene carbonate dimer (TeMC_2), tetrahydrofuran (THF), and a small quantity of cyclic tetramethylene carbonate monomer (TeMC).²⁰

Because the random, alternate, or block nature is a vital factor for a copolymer, significantly influencing its final properties. The degree of randomness (*R*) is calculated using eqs. (1–3)⁵⁴

$$R = P_{\text{TC}} + P_{\text{CT}} \quad (1)$$

$$P_{\text{TC}} = \frac{\frac{f_{\text{TC}} + f_{\text{CT}}}{2}}{\frac{f_{\text{TC}} + f_{\text{CT}}}{2} + f_{\text{TT}}} = \frac{1}{L_{\text{nT}}} \quad (2)$$

$$P_{\text{CT}} = \frac{\frac{f_{\text{TC}} + f_{\text{CT}}}{2}}{\frac{f_{\text{TC}} + f_{\text{CT}}}{2} + f_{\text{CC}}} = \frac{1}{L_{\text{nC}}} \quad (3)$$

where P_{TC} and P_{CT} are the probability of finding a BT unit next to a BC unit and the probability of finding a BC unit next to a BT unit, respectively. f_{TB} , f_{TC} , f_{CT} , and f_{CC} represent the dyads fraction, calculated from the integral intensities of the resonance signals of TT, TC, CT, and CC, respectively. L_{nC} and L_{nT} stand for the number-average sequence length of the BC and BT units, respectively. In the case of a random copolymer *R* takes a value equal to 1, while for an alternate copolymer equals to 2 and for a block copolymer close to zero.

As summarized in Table I, the degree of randomness calculated by ^1H NMR is equal or very close to 1, indicating random structure of the copolymers. The L_{nC} decreased and L_{nT} increase with increasing BT unit content. We also use ^{13}C NMR to calculate the average length of the microblocks, and specify the degree of randomization. The data calculated from ^1H NMR and ^{13}C NMR were very similar to each other. The ^{13}C NMR

Table I. Molecular Characteristics of PBC, PBCT Copolymers, and PBT

Sample	[BT] ₀ /[BC] ₀ in feed	[BT]/[BC] in polymer	L_{nC}^a	L_{nT}^a	R^a	M_w (g/mol)	PDI	$[\eta]$ (dL/g)
PBC	–	–	–	–	–	139,000	1.76	1.57
PBCT10	10/90	12/88	6.45	1.10	1.07	132,000	1.71	1.52
PBCT20	20/80	23/77	3.53	1.26	1.07	113,000	1.74	1.36
PBCT30	30/70	34/66	2.85	1.49	1.03	126,000	1.49	1.21
PBCT40	40/60	45/55	2.00	1.67	1.10	146,000	1.77	1.44
PBCT50	50/50	54/46	1.75	2.20	1.02	140,000	1.73	1.30
PBCT60	60/40	64/36	1.53	2.65	1.03	nd ^b	nd ^b	1.24
PBCT70	70/30	75/25	1.32	3.67	1.03	nd ^b	nd ^b	1.49
PBCT80	80/20	83/17	1.17	6.56	1.00	nd ^b	nd ^b	1.23
PBCT90	90/10	94/6	1.4	21	0.99	nd ^b	nd ^b	1.53
PBT	–	–	–	–	–	nd ^b	nd ^b	1.41

^a L_{nC} , L_{nT} , and R were measured by ¹H NMR analysis.

^bNot determined because of the insolubility of PBCT60, PBCT70, PBCT80, PBCT90, and PBT in chloroform.

spectrum of PBCT40 and the corresponding data can be seen in the Figure S10 and Table SII, Supporting Information. The number-average sequence length of aromatic unit is the crucial factor in aliphatic–aromatic copolyester biodegradability. When the number-average sequence of aromatic unit is less than 3, the PBT based aliphatic–aromatic copolyesters exhibit a fast and complete biodegradation.⁵⁰

The weight-average molecular weight and PDI were detected by GPC (Table I). Partial samples of the GPC traces are reported in the Figures S1–S4, Supporting Information. The weight-average molecular weight of the obtained polymers ranges from 113,000 to 146,000 g/mol, with narrow dispersities of around 1.7. Similar narrow dispersities were also found in poly(propylene terephthalate-*co*-succinate) and poly(propylene terephthalate-*co*-adipate) random copolymers.^{46,47} The measured intrinsic viscosities of the samples are in the range of 1.21–1.57 dL/g, as shown in Table I. These results reveal that high-molecular-weight aliphatic–aromatic random poly(carbonate-ester)s were successfully synthesized.

For comparison, another two different synthetic protocols are chosen to prepare PBCT50. For the first one, hydroxyl terminated oligo(butylene carbonate) (BHBC) was prepared instead of BMBC in the first step. BHBC was synthesized from DMC and BD with a molar ratio of 1:2, using TBT as a catalyst. Then BHBC and BHBT were mixed and polycondensation was executed under the same condition as PBCT50 mentioned in the experimental section. The molar ratio of BC and BT units of the resulted PBCT50, characterized by ¹H NMR, is 38 : 62, which is much lower than that of PBCT50 preparing from BMBC and BHBT (46 : 54). This might be explicated that the thermal degradation of BHBC is much severer than that of BMBC during the polycondensation step. Actually, PBC oligomer with methyl carbonate end group shows much higher thermal stability than PBC oligomer with hydroxyl terminal group.²² To confirm the influence of side reaction, PBC homopolymer was prepared via direct polycondensation of oligomers with different end groups, under the same polycondensation temperature and time as PBCT50. The volatile byproduct was

collected in the cold trap immersed in liquid nitrogen. Fourteen grams of THF was collected in the cold trap during the polycondensation of BHBC when 100 g PBC was obtained, resulting in low synthetic yield (54%) of PBC, while only 5 g THF was found for BMBC, giving a satisfactorily high yield of 91%. For the second protocol, PBCT50 was synthesized via one-pot route, in which DMC, DMT, and BD were charged together at the beginning. However, the melting temperature of DMT is 140.6°C, which is much higher than the boiling point of DMC of 90°C. Correspondingly, this procedure is failed due to significant distillation of DMC during the transesterification reaction. As discussed above, the initial strategy, using BMBC and BHBT as the intermediates, is the most effective method to synthesize high-molecular-weight PBCT random copolymers with high yield.

Calorimetric Properties

To investigate the BT unit content dependence of thermal properties of PBCTs, thermal analyses were carried out by DSC for PBC, PBCTs, and PBT, shown in Figure 4. The first heating scan indicates that the homopolymers and all the copolymers are semicrystalline. The results of thermal transition data are summarized in Table II.

It can be seen that the thermal transition behavior of PBCT significantly depends on composition. PBT is a typical crystalline polymer and exhibits high melting enthalpy ($\Delta H_m = 62.8$ J/g) at 222°C, while PBC shows poor crystallization ability and low melting point of 52°C. Introducing BT units into the PBC main chain can improve its thermal and crystallization properties. All the copolymers rich in BT units (i.e., ≥ 60 mol %, Figure 4: PBCT60–90 and PBT) show a sharp endotherm reminiscent of that of PBT. The copolymers with BT unit content of 40 mol % show a favorable high melting point of 113°C. The PBCT20 and PBCT30, crystallizing slowly during storage at room temperature, with broad peaks and less heat of crystallization are nearly amorphous, which influences the mechanical performance negatively. Furthermore, the change of the melting temperatures with the BT unit composition exhibits a typical eutectic behavior, with the eutectic composition at about 10 mol % BT

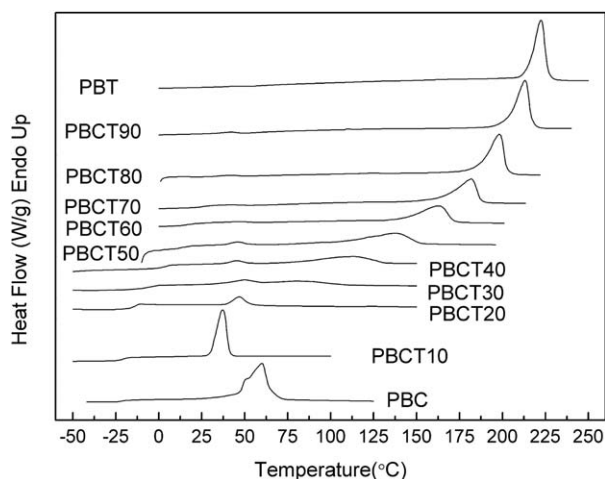


Figure 4. DSC curves of the first heating of PBC, PBCT copolymers, and PBT.

unit content. For PBCTs with those of reference PBC and PBT homopolymers, the melting temperature (T_m) and melting enthalpy (ΔH_m) of the first scan are also plotted in Figure 5 to better understand their composition dependence. Both T_m and ΔH_m of the copolymers are composition-dependent. The eutectic behavior is also observed in the relationship between the melting temperature and the copolymer composition. A similar variation tendency of melting temperature dependent on copolymer composition was also discovered in poly(ω -pentadecalactone-*co*-butylene-*co*-succinate)³⁵ and poly(butylene succinate-*co*-butylene furandicarboxylate) random copolyesters,⁵⁵ indicating isodimorphic cocrystallization in nature.

In amorphous random copolymers, glass transition temperature (T_g) is usually a monotonic function of composition. All the copolymers have a single T_g in agreement with the random sequence structure validated by ¹H NMR. The T_g of samples increase monotonically with increasing BT unit content between the two values of the homopolymers, which are -30.1 and 44.2°C for PBC and PBT, respectively.

To evaluate the crystallization rate, the crystallization half-time ($t_{1/2}$), defined as the time at which the polymer reaches a

Table II. Thermal Properties of PBC, PBCT Copolymers, and PBT

Sample	$T_{d,5\%}$ ($^\circ\text{C}$)	$T_{d,max}$ ($^\circ\text{C}$)	ΔH_m (J/g)	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
PBC	256	297	42.8	52.0	-30.1
PBCT10	293	(342,391)	27.0	37.1	-20.4
PBCT20	300	(334,393)	7.30	45.9	-14.5
PBCT30	304	(346,392)	8.40	46.4	-6.90
PBCT40	314	(350,394)	17.8	113	3.90
PBCT50	322	(344,393)	24.8	140	13.6
PBCT60	331	(342,392)	33.8	163	16.6
PBCT70	343	(349,392)	38.9	182	23.6
PBCT80	352	394	40.1	199	28.2
PBCT90	358	391	55.9	213	36.8
PBT	362	393	62.8	222	44.2

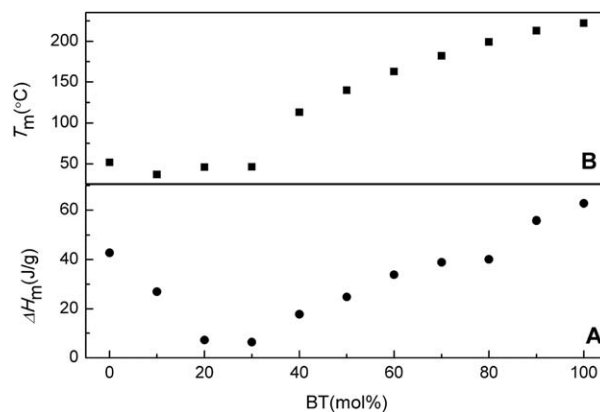


Figure 5. Composition dependences of T_m and ΔH_m .

crystalline fraction equal to 0.5, was used. Figure 6, which describes the trend of $t_{1/2}$ as a function of crystallization temperature (T_c), shows $t_{1/2}$ for PBC homopolymer and PBCT40 copolymer. For both samples, the crystallization rates decrease as T_c increase. The introduction of BT unit considerably improves the melting temperature and crystallization rate, as shown in Figures 5 and 6. On the basis of these results, it can be concluded that randomly copolymerizing with certain amounts of aromatic units can enhance the melting temperature and crystallization ability of PBC.

WAXD Analysis

Isomorphism is a general term for cocrystallization of different polymeric units or segments. As stated by Allegra and Bassi, isomorphism should meet several requirements: (i) the different types of monomer units must have the similar chemical structure and occupy the same volume, and (ii) the chain conformation of both corresponding homopolymers must be compatible with either crystal lattice. Cocrystallization in copolymer can be classified into two types, i.e. isomorphism and isodimorphism. In isomorphism, there is only a unique crystal modification is observed over the entire copolymer composition.⁵⁶ In isodimorphism, two crystalline phases can be observed.^{57–60}

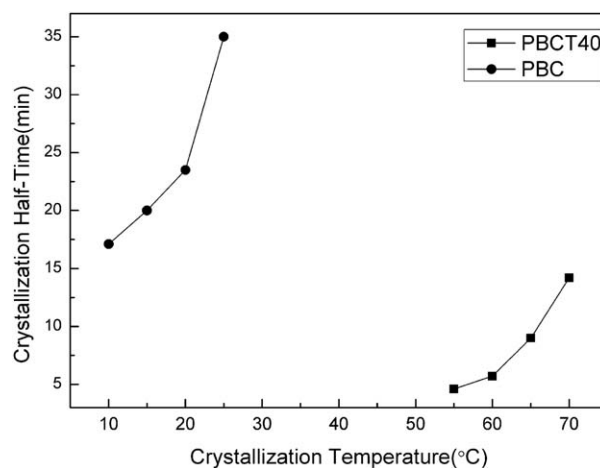


Figure 6. Crystallization half-time for PBC and PBCT40 polymers measured from isothermal experiments from the melt.

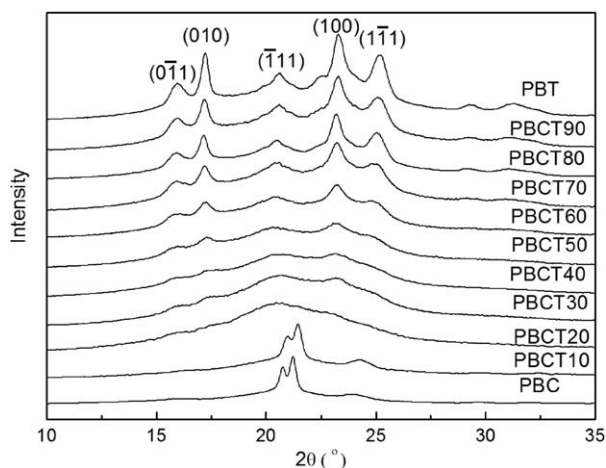


Figure 7. WAXD diffractograms of PBC, PBCT copolymers, and PBT.

Figure 7 shows the WAXD patterns of PBC, PBT, and PBCT copolymers in order to investigate the nature of the crystalline phase. As previously reported, PBT is characterized by two different crystal structures, denoted as α -form and β -form; the latter form exists only under tension and consists of more extended molecular chains.⁶¹ As in Figure 7, PBT shows main reflections at 16.0° ($0\bar{1}1$), 17.2° (010), 20.6° ($\bar{1}11$), 23.3° (100), and 25.2° ($1\bar{1}1$), presenting α -form crystal,⁶² while the main reflections of PBC appear at 20.7° and 21.2° . In addition, the patterns of all the copolymers can be easily divided into two classes, according to the BT unit content. The copolymer containing 10 mol % of BT unit develops PBC type crystal. This means that the formation of PBT crystals should be excluded for the specific copolymer. Whereas the copolymers with BT unit content higher than 20 mol % assume the lattice of PBT α -form. It must be noted that it is difficult to be explained for PBCT20 copolymer because of the very weak crystalline reflection peaks. The broadening peak of PBCT20 indicate that a shortening of mean extension of the ordered domains takes place, on account of the presence of an increasing number of “foreign” units which induces defects and less ordered crystals. These observations combined with the eutectic behavior of melting temperature lead to conclusion that these copolymers show isodimorphic cocrystallization and confirm the DSC results discussed above.

Thermal Stability

The thermal stability of polymers is an important factor for their synthesis, process, and application. Therefore, the thermal stability of the resulted copolymers was characterized by the thermogravimetric analysis under a nitrogen atmosphere, compared with PBC and PBT homopolymers.

Figure 8 presents (a) TGA and (b) DTG curves of PBCT copolymers, PBC, and PBT homopolymers. The decomposition temperature at 5% weight loss, $T_{d,5\%}$ and decomposition temperature at the maximum rate, $T_{d,max}$ are shown in Table II. Before 250°C , all the copolymers do not have any weight loss. Figure 8(a) shows that the main weight loss of all copolymers lies between those of the two homopolymers and that the $T_{d,max}$ shifts from 297°C (for PBC homopolymer) to 393°C (for PBT

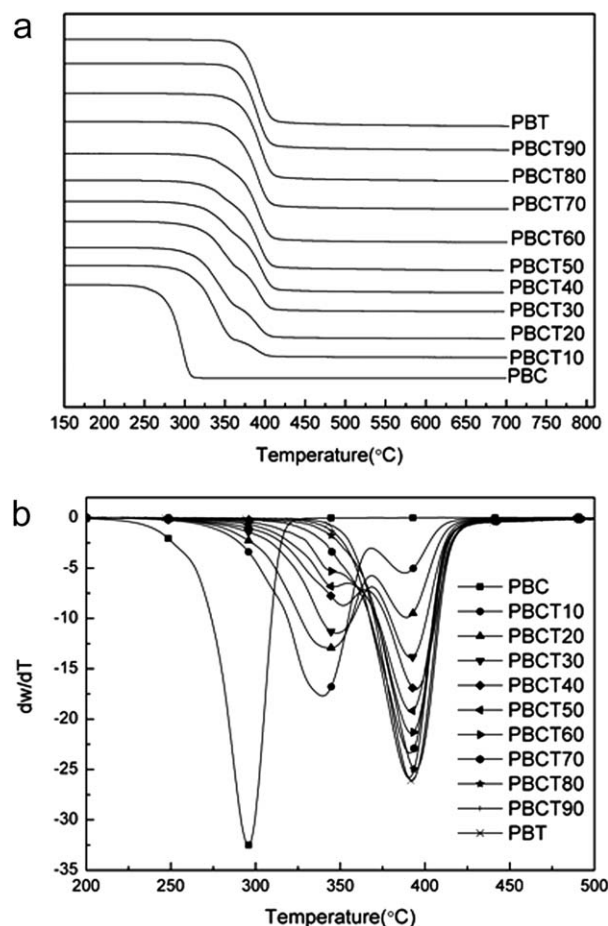


Figure 8. (a) TGA and (b) DTG curves of PBC, PBCT copolymers, and PBT.

homopolymer). The lower thermal stability of the polycarbonate is attributed to thermally induced decarboxylation reactions.⁶³ The results suggest that the insertion of BT sequences in PBC chains hinders to some extent the degradation of PBC.^{63,64} Thus, copolymerization with aromatic unit is demonstrated to be capable of improving the thermal stability of PBC.

As shown in the Figure 8 curves, both PBC and PBT homopolymers degrade in a single step. Generally, in random copolymer where the corresponding homopolymers degrade in one-step, the copolymer should degrade in one-step too.³³ It is interesting to note that, PBCT10–70 show a peculiar two-step degradation behavior. The first degradation step starts well above the thermal degradation range of PBC homopolymer, and its location and steepness depend on the specific copolymer analyzed. The second step occurs at a higher temperature comparable with that of PBT. Similar two-step degradation behaviors were also reported in aliphatic poly(carbonate-ester)s, such as poly(butylene carbonate-*co*-butylene succinate) and poly(ω -pentadecalactone-*co*-trimethylene carbonate) copolymers.^{65,66} However, the origin of the degradation behavior was not clarified. We speculate that this two-step degradation behavior is attributed to the special thermal degradation mechanism of PBC homopolymer. On the basis of our previous research, the intramolecular transesterification of PBC chain takes place during the thermal

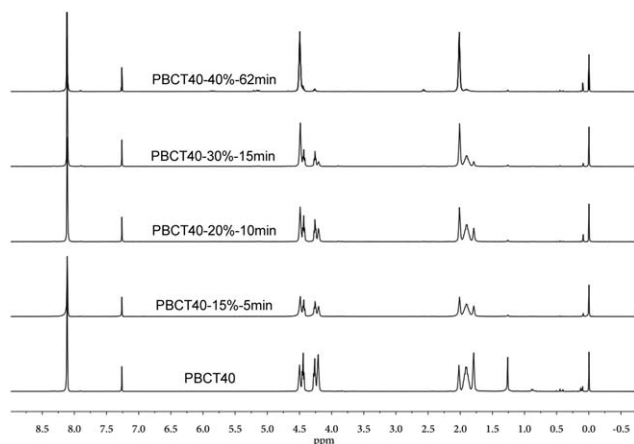


Figure 9. ^1H NMR spectra of PBCT40 residues under different isothermal degradation time.

degradation, producing TeMC monomer and dimer and not changing the chain structure.²²

To confirm our speculation, further isothermal thermal degradation analyses were performed. Isothermal degradation of PBCT40 was carried out under a nitrogen atmosphere at 330°C for 5, 10, 15, and 62 min, resulting in 15%, 20%, 30%, and 40% weight losses, respectively. After the isothermal degradation, the molecular structure of residues was characterized by ^1H NMR presented in Figure 9. There is no new peak observed after the isothermal degradation, while the intensities of resonance signals are changed. These results indicate that the chemical structure of the residues does not change. In contrast, the molar ratios of BC and BT unit of the residual samples vary from 55/45 to 40/60, 35/65, 25/75, and 7/93, respectively, indicating that the BC unit content decrease with degradation time. On the basis of the above analyses, it can be concluded that intramolecular transesterification of BC units occurs during the first step of PBCT thermal degradation (Scheme 2).

Mechanical Properties

The tensile properties, namely, tensile strength (σ_b), tensile modulus (E), and elongation at break (ε_b), are listed in Table III. In comparison with PBC, PBT has much higher modulus (2030 MPa), better strength (53 MPa), but lower elongation at

Table III. Mechanical Properties of PBC, PBCT Copolymers, and PBT

Sample	σ_b (MPa)	E (MPa)	ε_b (%)
PBC	27 ± 1.4	340 ± 22	470 ± 22
PBCT10	21 ± 1.2	150 ± 20	nb ^a
PBCT20	5.7 ± 0.4	15 ± 9.1	nb ^a
PBCT30	18 ± 2.6	65 ± 4.8	700 ± 53
PBCT40	34 ± 5.1	150 ± 11	610 ± 20
PBCT50	37 ± 11	340 ± 37	580 ± 29
PBCT60	40 ± 1.2	570 ± 18	280 ± 50
PBCT70	43 ± 6.5	1120 ± 110	240 ± 80
PBCT80	48 ± 7.4	1860 ± 240	7.1 ± 3.1
PBCT90	53 ± 4.7	2010 ± 190	6.8 ± 1.1
PBT	53 ± 3.1	2030 ± 120	7.9 ± 0.9
Ecoflex ^b	18 ± 3.0	68 ± 8.0	1204 ± 264

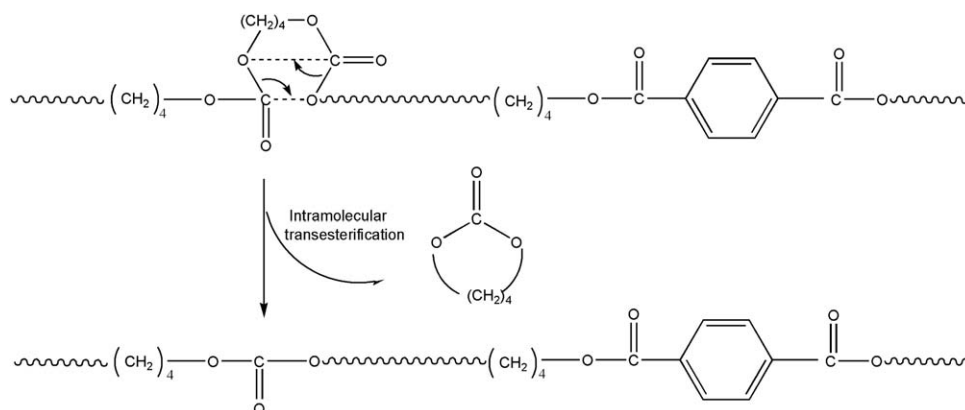
^a Specimens could not break.

^b Data cited from Ref. 67

break (7.9%). As seen in Table III, there is a direct dependence of the mechanical properties on copolymer composition. From neat PBC to PBCT20, the modulus and strength decrease, and the elongation increases because the crystallizability decreases with increasing BT unit content as discussed above. PBCT20 exhibits the lowest strength (5.7 MPa) and modulus (15 MPa) because of its poor crystallization capacity. From PBCT30 to neat PBT, the tensile strength and modulus systematically increase with increasing BT unit content, approximating those values for neat PBT. The mechanical properties of the copolymers are also composition-dependent. Thus, with changing composition, the PBCT copolymers can vary from rigid semi-crystalline materials to near amorphous, soft substances.

Enzymatic Degradation

To examine the biodegradability of the synthesized copolymers in a short time scale, enzymatic hydrolysis degradation was carried out. Figure 10 shows the weight losses of PBC PBCT20 and PBCT40 during enzymatic hydrolysis for several days. As can be seen, all samples are biodegradable. PBCT40 showed a biodegradation rate with a weight loss of 4.9 wt % after 10 days, while PBC had a higher biodegradation rate with a weight loss close



Scheme 2. Intramolecular transesterification of BC units during PBCT thermal degradation.

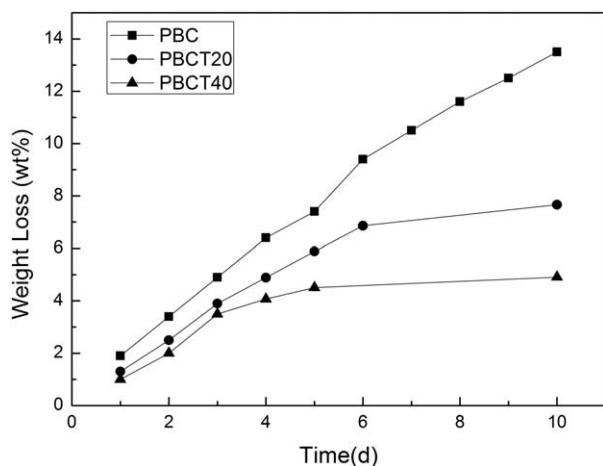


Figure 10. Weight loss against time of enzymatic degradation of the PBCT copolymers.

to 13.5 wt % for the same time. The biodegradation rate of PBCT20 was between that of PBC and PBCT40. It could be concluded that the introduction of BT units decrease the biodegradability of the copolymers, but that the PBCT copolymers are still biodegradable.

In conclusion, the PBCT random copolymers show an isodimorphic cocrystallization behavior, which determines that the melting temperature, crystallization ability, thermal, and mechanical properties of PBC can be enhanced by randomly incorporating with a moderate amount of BT units. As aforementioned, among the PBCT copolymers, PBCT40 has a favorable thermal property with T_m of 113°C similar to Ecoflex (110–120°C).⁵¹ Moreover, it has higher σ_b and E than Ecoflex in the mechanical property. Hence, PBCT40 illustrates a promising application in biomedicine, packaging film, agricultural film, and compost bag.

CONCLUSIONS

Here we successfully synthesized aliphatic–aromatic poly(carbonate-ester)s, PBCTs in full composition range using DMT, DMC, and BD via a transesterification and polycondensation process. The copolymers possessed the expected chemical structure attested by ¹H NMR spectrum. All the copolymers process almost ideal random microstructure with R independent of the copolymer composition. DSC showed a single T_g increasing continuously with BT unit content, and approaching the T_g of PBT. The T_m decreased with increasing BT unit content from 0 to 20 mol %, but rose again at BT unit content of 30–100 mol %. WAXD suggested a crystalline structure shifting from that of PBC to PBT. Both the DSC and WAXD results indicate that the PBCT copolymers show isodimorphic cocrystallization. The mechanical properties are varied to a large extent by the selected monomer feed composition based on the fact that PBT is a stiff material and PBC is a soft material. Consequently, the tensile modulus and strength decreased in the range of 0–20 mol %. At higher BT unit content, the modulus and strength increased. With changing composition, the PBCT copolymers vary from rigid semicrystalline materials to near amorphous, soft substances. Thus, by judicious selection of

copolymer composition, PBCT copolymer properties can be fine-tuned to obtain the expected balance of material rigidity, ductility, and melting point.

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