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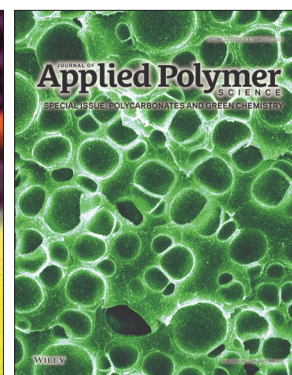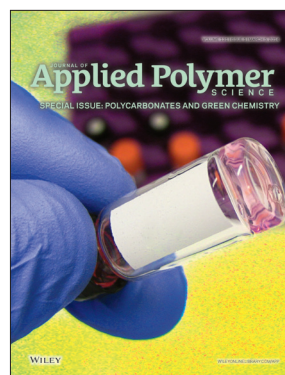
JOURNAL OF Applied Polymer SCIENCE

Synthesis and Properties of Biodegradable Multiblock Poly(ester-carbonate) Comprising of Poly(L-lactic acid) and Poly(butylene carbonate) with Hexamethylene Diisocyanate as Chain-Extender

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ABSTRACT: A series of novel biodegradable poly(ester-carbonate) consisting of poly(L-lactic acid) (PLLA) and poly(butylene carbonate) (PBC) (PLLA-b-PBC) have been successfully synthesized by chain-extension reaction of dihydroxyl-terminated poly(L-lactic acid) prepolymer (PLLA-OH) and dihydroxyl-terminated poly(butylene carbonate) prepolymer (PBC-OH) using hexamethylene diisocyanate as a chain-extender. The chemical structures and molecular weights of copolymers are characterized by ^{1}H NMR and gel permeation chromatography. The thermal properties, morphology, and mechanical properties of PLLA-b-PBC are investigated by differential scanning calorimetry, thermogravimetric analysis, phase contrast optical microscopy, and mechanical testing. The results indicate that PBC soft segment slightly increases the thermal stabilities and effectively enhances the impact strength of the copolymers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39158.

INTRODUCTION

In recent years, biodegradable and renewably derived polymers are of active academic and industrial research interests for environmental reasons and sustainable issues.[1–3] As one of the most representative and generally acknowledged biopolymers, poly (L-lactic acid) (PLLA) possesses good degradability, excellent strength, and good melt processability, and thus has been used in many fields.[1,3–5] However, disadvantage of brittleness greatly restricts its wide application. Therefore, various modifications have been carried out to conquer this weakness of PLLA, such as blending and copolymerization.[6,7] Among these modifications, copolymerization is regarded as a useful and relatively economical way to produce new materials with a variety of properties. As a result, various PLLA-based random or block copolymers have been successfully prepared either through polycondensation of L-lactic acid with other monomers, or ring-opening copolymerization of L-lactide with cyclic monomers like glycolide, ε-caprolactone, δ-valerolactone, and trimethylene carbonate.[8,9] Although the brittleness of PLLA has been effectively improved, the products usually are expensive.

Therefore, the main aim of the work reported in this study is to synthesize novel and cheap block copolymers based on PLLA with acceptable physical properties and cost. Chain-extension, as a relatively economical and effective way to obtain high-performance block copolymers, has been successfully used to synthesize polyester-based block copolymers during previous works of Wang's group, our team, and other groups.[10–17] The research results show that toughness of PLLA or PBS has been substantially improved by the introduction of flexible segments through chain-extension reaction. Many cheap polyesters and polyethers, including poly(ε-caprolactone),[5] poly(1,2-propylene succinate),[16] poly(ethylene glycol),[18] poly(propylene glycol),[19] etc., can be employed as the flexible segments.

Unlike those works, flexible and crystallizable poly(butylene carbonate) (PBC), a very important member of the family of biodegradable aliphatic polycarbonates, is selected as the flexible
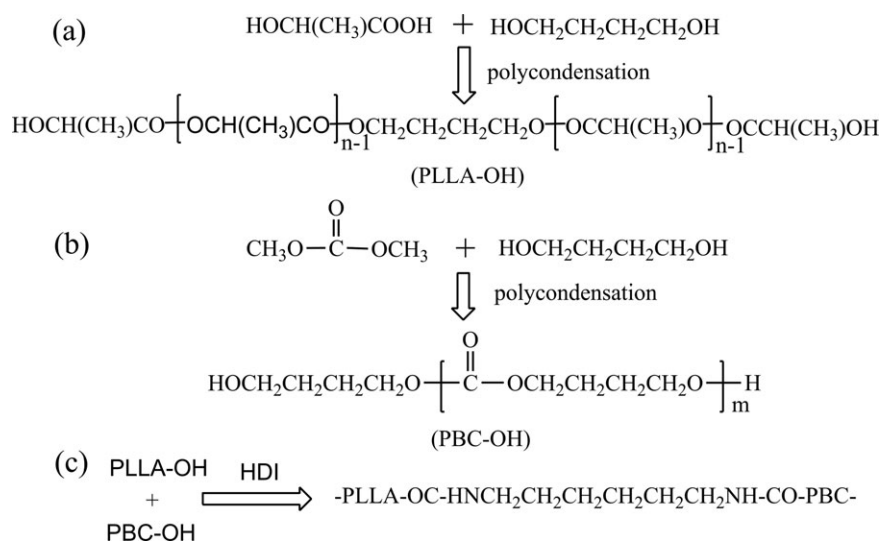
Scheme 1. Synthesis routes of PLLA-OH, PBC-OH, and PLLA-*b*-PBC copolymers.

segment to improve the toughness of PLLA in this article. PBC is a semicrystalline polymer with a clear melting point at around 60°C and a glass transition temperature at −38°C.[20–22] During previous work of our team, inexpensive PBC with high molecular weight has been successfully synthesized for the first time *via* a successive two-step polycondensation.[21] As a result of the flexibility of polymer chains and crystallizability, PBC possesses excellent impact resistance and satisfactory tensile strength. Therefore, the brittleness of PLLA is expected to be conquered by the copolymerization with PBC.

In this paper, we report a convenient route to synthesize new and inexpensive poly(ester-*co*-carbonate) multiblock copolymers, composing PLLA hard segment and PBC soft segment, by melting chain-extension with HDI as a chain-extender. The copolymers are characterized by ^{1}H nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), phase contrast optical microscopy (PCOM), and mechanical testing.

EXPERIMENTAL

Materials

Dimethyl carbonate (DMC) was a commercial product provided by Shandong Shida Shenghua Chemical (Shandong, China). 1,4-butanediol (BD) was supplied by Beijing Chemical Reagents and used without further purification. $SnCl_2 \cdot 2H_2O$ was purchased from Beijing Chemical Reagents (Beijing, China). L-Lactic acid with 85 wt% aqueous solution was bought from Sinopharm Chemical Reagent Beijing (Beijing, China), and the free water was removed by reduced pressure distillation at 80°C for 3 h. Titanium (IV) butoxide, used as a catalyst, was distilled before use. Hexamethylene diisocyanate (HDI) was purchased from Shandong Qingdao Xinyutian Chemical. All other chemicals with AR grade were used as received.

Synthesis of Dihydroxyl-Terminated Poly(L-lactic acid) Prepolymers

Poly(L-lactic acid) prepolymers (PLLA-OH) were synthesized from L-lactic acid and BD with the similar procedure proposed by Hiltunen et al.[23] One hundred and eighty grams of L-lactic acid and predetermined amount of BD were charged in a 500 mL three-necked round bottom flask, then $SnCl_2 \cdot 2H_2O$ (0.5 wt% of reactants) was added in. The polymerization temperature was first gradually increased to 160°C in 2 h and kept for 5 h in pressure of about 4000 Pa. Then the temperature was increased to 180°C, and the pressure was reduced to 150 Pa. The reaction was maintained for another 5 h. After reaction, the prepolymer was used directly without further purification.

Synthesis of Dihydroxyl Terminated Poly(butylene carbonate) Prepolymers

Poly(butylene carbonate) prepolymers (PBC-OH) was synthesized *via* a two-step polycondensation of DMC and BD with the procedure similar to that described in the literature.[21] About 1.2 mol of BD, 1 mol of DMC, and Titanium (IV) butoxide (0.5 wt% of monomer) as catalyst were charged into a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, reflux condenser, and thermometer. The reaction mixture was heated to 100°C under nitrogen and kept there for 4 h. Then the temperature was gradually increased up to 180°C in 2 h and kept there for 1 h. After that, the pressure of the reaction system was gradually reduced to 5–15 Pa, and maintained for predetermined time. The obtained polymer was used without any purification.

Synthesis of Multiblock Copolymers by Chain-Extension Reaction

The PLLA-OH and PBC-OH were put into a glass reactor that was vacuumed and purged with nitrogen for three times. Then the reactor was immersed in a 160°C silicone oil bath. Predetermined amount of HDI was injected into the reactor under mechanical stirring after the reactants were completely molten. The chain-extension reaction was finished in 1 h. The resulting copolymers were purified by dissolving in chloroform and then precipitating in excessive methanol. The obtained white powder

was dried to constant weight in vacuum oven at 40°C for further investigation.

NMR Spectroscopy

The chemical structures and compositions of the obtained polymers were characterized by a Bruker DMX-400 NMR spectrometer at ambient temperature, using CDCl₃ and tetramethylsilane as the corresponding solvent and internal chemical shift standard. The number-average molecular weights of PLLA-OH and PBC-OH were calculated from the NMR analysis.

Gel Permeation Chromatography

The molecular weight and molecular weight distribution were determined by GPC (Waters 1515, USA) at 35°C. Chloroform was used as the eluent at a flowing rate of 1.0 mL min⁻¹, and the sample concentration was 2.5 mg mL⁻¹. Molecular weights were calculated against polystyrene standards.

Differential Scanning Calorimetry

The thermal properties were measured using a Pyris Diamond DSC instrument (Perkin Elmer). All the measurements were conducted under a high-purity nitrogen atmosphere. Samples were quickly heated to 190°C and maintained there for 5 min to eliminate thermal histories, and then quenched to −70°C at a rate of 200°C min⁻¹ using liquid nitrogen as a cooling agency and held there for 5 min. After that, the samples were heated again to 190°C at 20°C min⁻¹. Both cooling and heating scans were recorded for the analysis.

Thermogravimetric Analysis

The thermal stability of the polymers was characterized using TGA with a Perkin-Elmer Pyris 7 TGA thermogravimetric analyzer. Samples of 2–3 mg were heated from 50°C to 700°C at a rate of 20°C min⁻¹ under nitrogen atmosphere with a flow rate of 20 cm³ min⁻¹.

Phase Contrast Optical Microscopy

PCOM was carried out using an Olympus optical microscope (BX51) and an Olympus camera (C-5050ZOOM). A Linkam-THMS 600 hot stage was used to control the experimental temperature. The ultrathin film was prepared on the cover glass by solution cast method. Before observation, the film was heated to 180°C and kept there for 5 min to eliminate any thermal history. Then it was cooled to 150°C at a rate of 100°C min⁻¹ and held there for phase separation.

Mechanical Properties

Tensile and flexural testing was carried out with a universal tester (Instron 1122, UK). The tensile properties of the specimens were measured according to ISO 527 at a crosshead speed of 50 mm min⁻¹; the flexural properties were determined according to ISO 178 at a crosshead speed of 2 mm min⁻¹. The impact strength was measured with an impact testing machine (CSI-137C, USA) according to ISO 180. Data were taken as the average value of at least five measurements.

RESULTS AND DISCUSSION

The synthesis procedure of PLLA-*b*-PBC block copolymers is schematically described in Scheme 1. The polymerization can be divided into two stages. The first stage of the reaction is polycondensation to prepare PLLA-OH and PBC-OH. The second
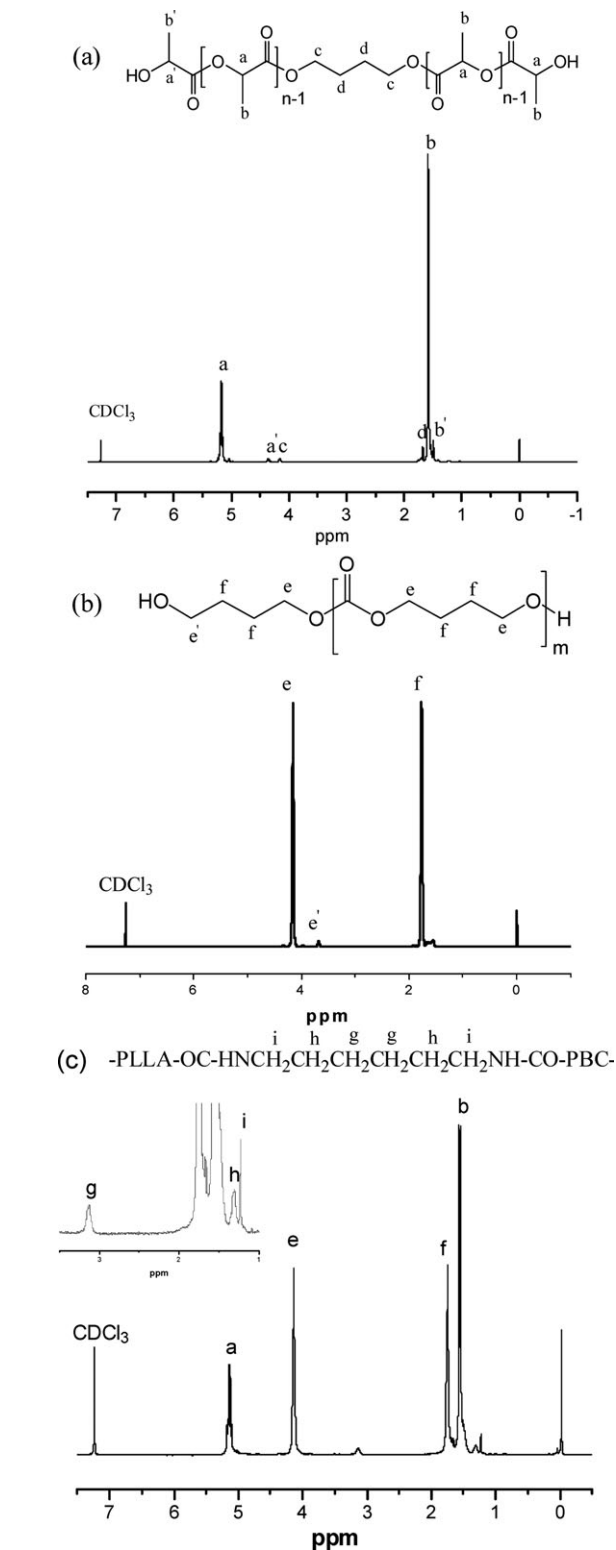
Figure 1. ¹H NMR spectrum of (a) PLLA-OH (M_n = 4800), (b) PBC-diol (M_n = 4300), and (c) PLLA-PBC3.

stage is to prepare high-molecular-weight PLLA-*b*-PBC multiblock copolymers by chain-extension of the dihydroxyl-terminated PLLA-OH and PBC-OH with HDI.

Table I. Synthetic Data for PLLA-OH

Sample	LA/BD (mol/mol)	$M_{n,NMR}$ (g/mol)	$M_{n,Thro}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI
PLLA-OH 1	50:1	2700	3690	5100	8300	1.63
PLLA-OH 2	75:1	4800	5490	9500	15000	1.58

Synthesis and Characterization of Prepolymers

Dihydroxyl-terminated PLLA-OH with different molecular weights was prepared by the condensation polymerization of L-lactic acid in the presence of BD, using $SnCl_2 \cdot 2H_2O$ as a catalyst [shown in Scheme 1 (a)]. The chemical structure and number-average molecular weights of PLLA-OH were characterized by ^1H NMR spectra [shown in Figure 1(a)]. The signals of methyl and methine protons in the repeating units of PLLA-OH prepolymers are found at 1.59 (δH^b) and 5.18 (δH^a) ppm, whereas the signals of those protons at the terminus of PLLA-OH molecular chain are found at 1.48 ($\delta H^{b'}$) and 4.36 ($\delta H^{a'}$) ppm, respectively. The signals of protons belonging to the methylene groups of $-OCH_2CH_2CH_2CH_2O-$ are observed at 1.68 (δH^d) and 4.11 (δH^c) ppm, respectively. Besides, the small peak occurring at 5.04 ppm is the signal of methine proton in lactide, suggesting that very small amount of lactide was formed during the reaction.[24] The integral area of the methine proton is used to calculate the number-average molecular weight (M_n) of PLLA-OH by the following equation:

$$M_{n,PLLAOH} = 72 \times 2 \times \frac{A_{5.18} + A_{4.36}}{A_{4.36}} + 88 + 2 \qquad (1)$$

where $A_{5.18}$ and $A_{4.36}$ represent the integral areas of internal and terminal methine proton of PLLA-OH prepolymers, respectively. The molecular weight of the repeating unit of PLLA and hydrogen at the ends of PLLA-OH molecular chain are represented by 72 and 2, respectively, and 88 is the molecular weight of $-OCH_2CH_2CH_2CH_2O-$.

Theoretical value of number-average molecular weight ($M_{n,Theo}$) is calculated by the feed ratio of L-lactic acid to BD, according to the following the equation:

$$M_{n,Thro} = \frac{n_{LA}}{n_{BD}} \times 72 + 88 + 2 \qquad (2)$$

where n_{LA}/n_{BD} is the feed molar ratio of L-lactic acid to BD, 72, 88, and 2 have the same meanings as those in eq. (1).

The basic data for the synthesis of PLLA-OH are listed in Table I. It can be found that number-average molecular weight calculated by ^1H NMR ($M_{n,NMR}$) is lower than the theoretical value, i.e., $M_{n,Theo}$, because of the inevitable loss of L-lactic acid during the condensation polymerization.

Dihydroxyl-terminated PBC-OH was prepared from BD and DMC with the feed molar ratio of 1.2/1 via two step reactions: transesterification and polycondensation [Scheme 1(b)]. With the excessive amount of BD, it can be expected that PBC prepolymer would predominantly be terminated with hydroxyl groups. The molecular weight of PBC was controlled by the polycondensation time. The chemical structures of PBC prepolymers were determined by ^1H NMR [Figure 1(b)]. The peaks occurring at 1.70 (δH^f) and 4.18 (δH^e) ppm are because of methylene protons of $-COOCH_2CH_2CH_2CH_2O-$ repeating unit, whereas the terminal methylene protons of PBC-OH molecules can be observed at 3.68 ($\delta H^{e'}$) ppm. M_n of PBC-OH can be calculated according to the integral areas of methylene groups at 3.68 ($A_{3.68}$) and 4.18 ($A_{4.18}$) ppm by the following equation:

$$M_{n,PBC-OH} = 90 + 116 \times \frac{A_{4.18}}{A_{3.68}} \qquad (3)$$

where 116 and 90 are the molecular weights of PBC repeating unit and PBC end chains, respectively. And the results of $M_{n,NMR}$ are listed in Table II.

Synthesis and Characterization of PLLA-b-PBC

PLLA-b-PBC block copolymers with different compositions were produced through chain-extension reaction of PLLA-OH with PBC-OH using HDI as a chain-extender. To obtain polymer with good mechanical properties, the molar ratio of $-NCO/-OH$ was fixed at 1.2/1 in this study. The reaction process is shown in Scheme 1(c) and the synthetic data of copolymers are listed in Table III.

The chain-extended products were characterized by ^1H NMR. The results are shown in Figure 1(c). If the coupling reaction proceeds as expected, some extra peak would appear in the ^1H NMR spectra of PLLA-b-PBC that differ from the prepolymer peaks, or some peaks would disappear because of the reaction of prepolymer end groups with the diisocyanate. As shown in Figure 1(c), it can be found that the peaks at 4.36 and 3.68 ppm caused by the hydroxyl end group of the PLLA-OH and PBC-OH disappear after the reaction with HDI. Furthermore, the chemical shifts of the three kinds of methylene protons arising from HDI residue in the molecular chain of PLLA-b-PBC are observed at 3.14 (δH^g), 1.32 (δH^h), and 1.23(δH^i) ppm; this also testifies that the reaction between isocyanate group of HDI

Table II. Synthetic Data for PBC-OH

Sample	Polycondensation time (min)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI
PBC-OH 1	90	2600	4800	9200	1.92
PBC-OH 2	150	4300	6100	15,200	2.49

Table III. Synthesis Data of Copolymers Containing PLLA and PBC Blocks

	M_n^a of prepolymers			
Sample	PLLA	PBC	PLLA/PBC (g/g)	[NCO]/[OH]
PLLAU	4800	–	–	1.2:1
PLLA-PBC1	4800	4300	9:1	1.2:1
PLLA-PBC2	4800	4300	8:2	1.2:1
PLLA-PBC3	4800	4300	7:3	1.2:1
PLLA-PBC4	4800	4300	6:4	1.2:1
PLLA-PBC5	4800	4300	4:6	1.2:1
PLLA-PBC6	2700	4300	7:3	1.2:1
PLLA-PBC7	4500	2600	7:3	1.2:1
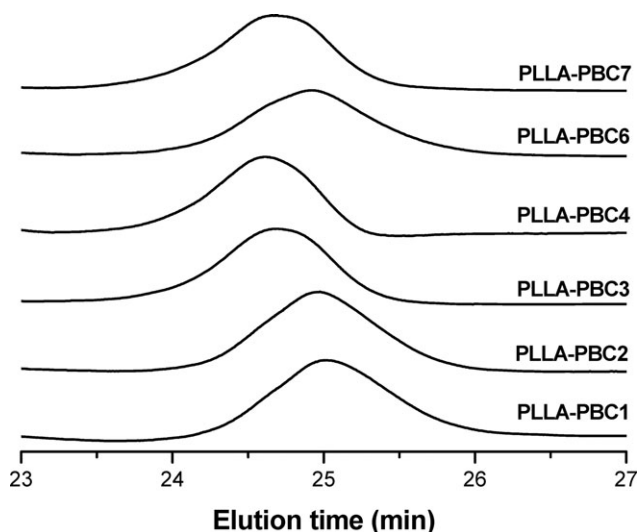
Figure 2. GPC diagrams of PLLA-*b*-PBC copolymers.

and hydroxyl of prepolymers indeed takes place. The compositions of PLLA-*b*-PBC copolymers are calculated by the following equations:

$$F_{PLLA} = \frac{4 \times 72 \times A_{5.18}}{116 \times A_{1.70} + 4 \times 72 \times A_{5.18} + 170 \times A_{3.20}} \quad (4)$$

$$F_{PBC} = \frac{116 \times A_{1.70}}{116 \times A_{1.70} + 4 \times 72 \times A_{5.18} + 170 \times A_{3.20}} \quad (5)$$

$$F_{HDI} = 1 - F_{PLLA} - F_{PBC} \quad (6)$$

where F_{PLLA}, F_{PBC}, and F_{HDI} denote the weight fraction of the related components in the PLLA-*b*-PBC copolymer, $A_{5.18}$, $A_{1.70}$, and $A_{3.20}$ represent integral areas of the corresponding protons, and 72, 116, and 170 are the molecular weight of PLLA repeating unit, PBC repeating unit, and HDI residue in the molecular chain of the polymer, respectively. Four is a coefficient indicating the number ratio of PBC methylene protons appearing at 1.70 ppm to PLLA methine proton occurring at 5.18 ppm.

The compositions of the polymers are presented in Table IV. The weight fraction of components in the feed is *f*, whereas

F indicates weight fraction of components in resulting polymer obtained through NMR analysis. It can be found that the value of *F* is very close to that of *f*.

In addition, GPC is also important to determine the molecular weights of PLLA-OH, PBC-OH as well as PLLA-*b*-PBC block copolymers, and the results are shown in Table IV and Figure 2. Clearly, all the GPC traces of PLLA-*b*-PBC show a single elution peak, indicating that a complete reaction between prepolymers and HDI without unreacted prepolymer remaining.[25,26] Moreover, it can be found that high-molecular-weight PLLA-*b*-PBC block copolymers have been successfully synthesized. And the molecular weights of the resulting copolymers, which are more than several times higher than the prepolymers, can prove that the chain-extension reaction is very effective. In addition, the number-average molecular weight of prepolymers determined by GPC is higher than that calculated from NMR spectra. It is because of the fact that the hydrodynamic volume of polystyrene is evidently lower than that of aliphatic polyester and aliphatic polycarbonate with identical molar mass.[14] Furthermore, the number-average and weight-average molecular weight of

Table IV. Compositions and Molecular Weights of Resulting PLLA-*b*-PBC Copolymers

	PLLA		PBC		HDI		Molecular weight^a		
Sample	f_{PLLA}^b (%)	F_{PLLA}^c (%)	f_{PBC}^b (%)	F_{PBC}^c (%)	F_{HDI}^b (%)	F_{HDI}^c (%)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	PDI^a
PLLAU	96.0	94.5	0	0	4.0	5.5	2.74	4.41	1.61
PLLA-PBC1	86.3	83.9	9.6	10.7	4.1	5.4	2.91	4.90	1.68
PLLA-PBC2	76.7	74.8	19.2	21.1	4.1	4.1	3.48	6.30	1.82
PLLA-PBC3	67.1	65.6	28.6	30.0	4.3	4.4	7.07	14.1	1.99
PLLA-PBC4	57.5	55.9	38.3	39.9	4.2	4.2	7.81	18.8	2.41
PLLA-PBC5	38.3	36.3	57.4	59.6	4.3	4.1	15.2	35.8	2.35
PLLA-PBC6	65.7	63.3	28.1	30.2	6.2	6.5	3.29	6.25	1.90
PLLA-PBC7	66.4	63.9	28.4	29.7	5.2	5.4	5.95	13.2	2.22

^{a}Molecular weights were measured by GPC with PS standards. ^{b}Weight fraction in the feed ratio. ^{c}Weight fraction in copolymers determined by NMR calculating.
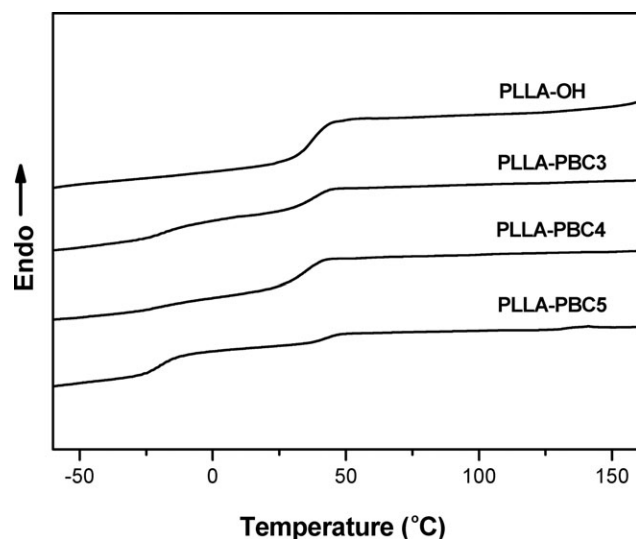
Figure 3. DSC second heating scans curves of PLLA-*b*-PBC copolymers.

Figure 4. TGA curves of PLLA-*b*-PBC copolymers.

PLLA-*b*-PBC block copolymers increases steadily as the content of PLLA decreases. It can be ascribed to lower reaction activity of secondary hydroxyls on PLLA-OH as compared to that of primary hydroxyls on PBC-diol.

Thermal Behaviors of PLLA-b-PBC Copolymers

A DSC was used to study the melting behavior and thermal transition of the polymers. The relevant results are presented in Figure 3 and Table V. It can be found that all PLLA-*b*-PBC block copolymers have melting temperature corresponding to the PLLA block at 120–140°C. And the incorporation of PBC in our experimental range has little or no reduction on T_m. This phenomenon is in good agreement with the melting behavior of other block copolymers.[10–12,14–16,19] Furthermore, it can be observed that PLLA-PBC5 has the highest T_m among the copolymer samples, which may be because of the highest molecular weight.

No melting peak can be detected from the second heating scans for all the block copolymers because of their slow
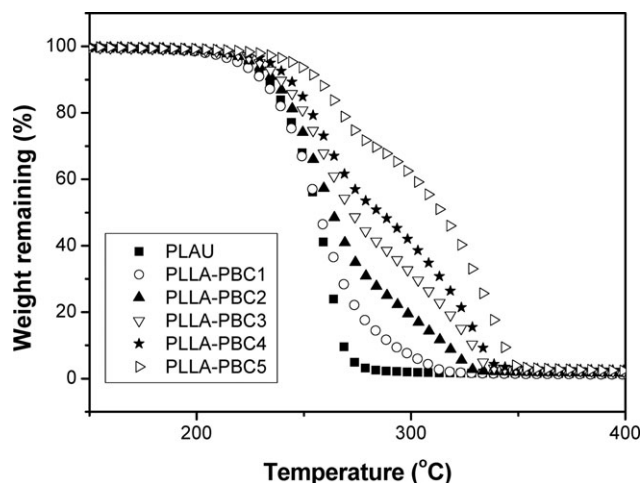
Table VI. The Thermal Degradability Data of PLLA-*b*-PBC Copolymers Determined by TGA

| Sample	$T_{5\%}$[a] (°C)	T_{max1}[b] (°C)	T_{max2}[b] (°C)
PLLAU	222.6	262.1	–
PLLA-PBC1	220.2	256.8	309.3
PLLA-PBC2	226.7	259.2	321.7
PLLA-PBC3	229.6	261.4	327.1
PLLA-PBC4	234.5	258.6	329.2
PLLA-PBC5	245.5	265.4	337.7

[a]Decomposition temperature of polymers at weight loss of 5%. [b]The maximum decomposition temperature of the polymers.

crystallization rate. What's more, it can be found that when the PBC content is more than 30%, PLLA-*b*-PBC show two glass transitions, both of which lie between the T_g of PBC (−38°C) and T_g of PLLA (around 60°C). It indicates that the PLLA hard segment and PBC soft segment are partially compatible in the amorphous region. In the case of

Table V. Thermal Parameters of PLLA-*b*-PBC Copolymers Determined by DSC

Sample	T_{m-PLLA}[a] (°C)	ΔH_{m-PLLA}[a] (J/g)	T_{m-PBC}[b] (°C)	T_{g-PLLA}[a] (°C)	T_{g-PBC}[a] (°C)
PLLA-OH	140.7	17.4	–	45.2	–
PBC-OH	–	–	61.8	–	−34
PLLAU	129.3	4.2	–	51.8	–
PLLA-PBC1	134.0	1.34	–	43.6	–
PLLA-PBC2	134.3	0.7	–	39.1	–
PLLA-PBC3	134.2	0.4	–	36.2	−15.2
PLLA-PBC4	134.2	11.2	–	39.8	−18.5
PLLA-PBC5	138.8	6.5	–	42.8	−18.1
PLLA-PBC6	120.2	0.9	–	26.4	
PLLA-PBC7	128.7	0.6	–	33.8	−7.2

[a]Measured from the second DSC heating scan. [b]Measured from the first DSC heating scan.
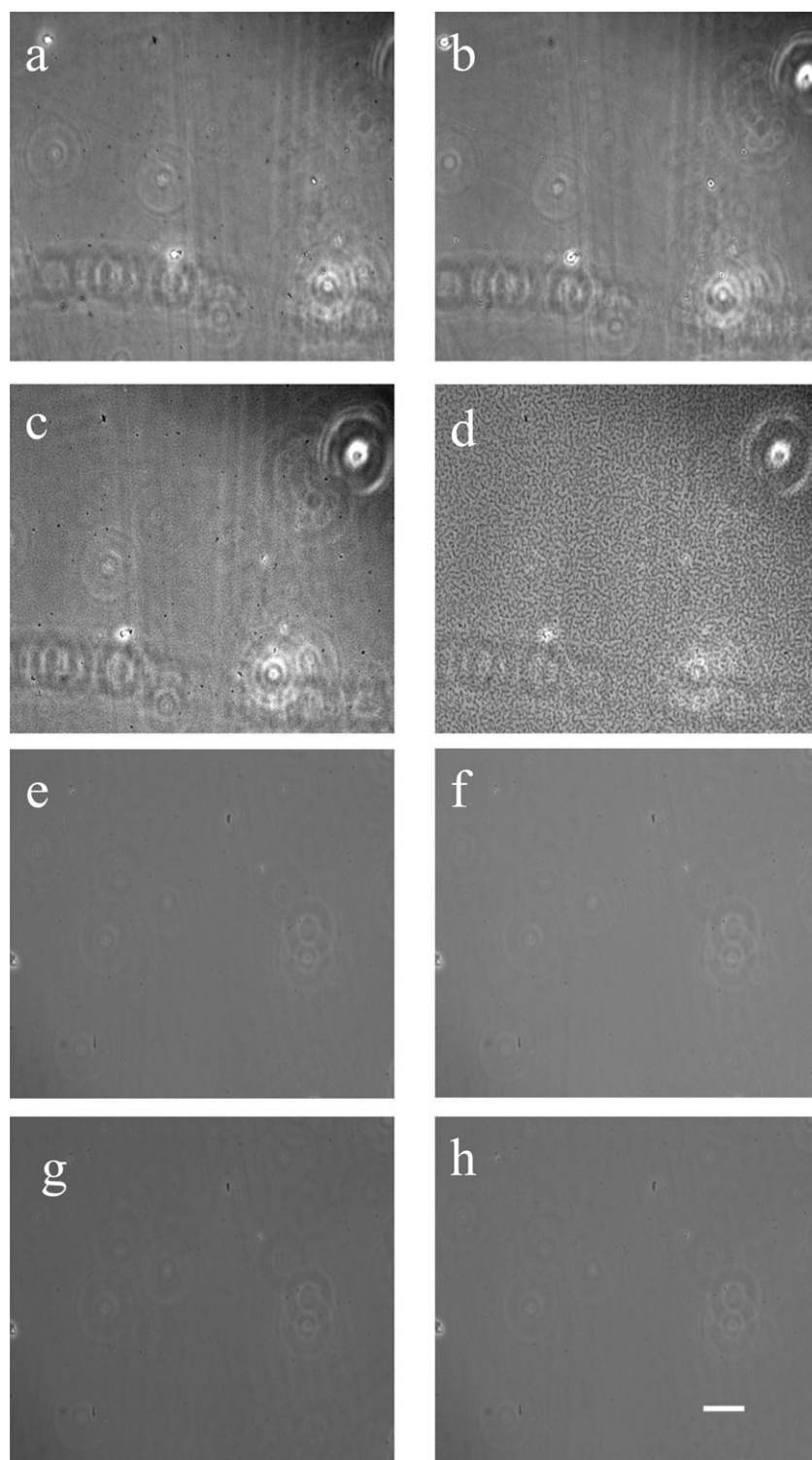
Figure 5. Phase contrast optical micrographs annealed at 150°C for PLLA-PBC3 (a) 5 min; (b) 30 min; (c) 120 min; (d) 180 min; PLLA-PBC6 (e) 5 min; (f) 30 min; (g) 120 min; (h)180 min. The scale bar in (h) corresponds to 10 μm and also applies to (a)–(g).

PLLA-PBC6 based on shorter PBC segment, only one glass transition temperature can be detected, suggesting that the two segments are compatible. When the PBC block content is less than 20%, the T_g of PBC segment cannot be detected by DSC because of its low content. And the T_g of the PLLA block shifts to lower temperature region with increasing PBC content. It is well known that T_g is related to the flexibility of polymer chains. Therefore, the lower T_g indicates that the flexibility of PLLA is improved by the copolymerization with PBC.

Table VII. Mechanical Properties of PLLA-*b*-PBC Copolymers

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ m^{-2})
PLLAU	49 ± 5.3	1384 ± 80	3.1 ± 1.1	34 ± 2.1	3400 ± 120	1.6 ± 0.1
PLLA-PBC1	31 ± 0.5	1080 ± 90	8.1 ± 0.2	32 ± 1.3	3000 ± 54	1.6 ± 0.2
PLLA-PBC2	27 ± 1.2	819 ± 54	50 ± 5	43 ± 2.4	2200 ± 65	2.1 ± 0.2
PLLA-PBC3	25 ± 0.8	538 ± 40	180 ± 18	34 ± 0.6	1200 ± 12	3.9 ± 0.3
PLLA-PBC4	19 ± 1.2	436 ± 34	190 ± 16	25 ± 0.2	880 ± 20	66 ± 6.3
PLLA-PBC5	21 ± 2.5	160 ± 43	270 ± 24	18 ± 0.7	530 ± 21	77 ± 3.2
PLLA-PBC6	17 ± 0.9	215 ± 32	430 ± 31	7 ± 0.9	370 ± 32	4.9 ± 0.5
PLLA-PBC7	25 ± 2.0	452 ± 19	330 ± 21	21 ± 3.2	770 ± 35	5.3 ± 0.3

Thermal Stabilities of PLLA-*b*-PBC

It is well regarded that pure PLLA is not stable against heat during thermal processing, which would restrict its application. The thermal stability of PLLA-*b*-PBC block copolymers was investigated by TGA and the results are shown in Figure 4. The data of thermal decomposition are summarized in Table VI. The PLLA-*b*-PBC copolymers undergo a two-stage thermal degradation. The first stage with a maximum decomposition temperature of around 260°C is the degradation of PLLA segment, and the second stage with a maximum decomposition temperature higher than 300°C is the thermal degradation of PBC block. From Table VI, it can be seen that that $T_{5\%}$ of PLLA-*b*-PBC tends to increase with the increase of PBC component in copolymers, indicating that the thermal stabilities of PLLA-*b*-PBC increase with the increase of PBC content.

Compatibility between PLLA and PBC Blocks in the Copolymers

It is known that many properties of block copolymers, especially the mechanical properties, are affected by the segmental compatibility. The aforementioned thermal results show that PLLA and PBC segments of the copolymers have certain compatibility. In order to thoroughly discuss the compatibility of the blocks in the copolymers, the phase morphology of PLLA-*b*-PBC was investigated by phase contrast optical microscopy.

Figure 5 shows phase contrast optical micrographs of PLLA-PBC3 and PLLA-PBC6 melted at 190°C for 5 min and then isothermally annealed at 150°C for predetermined times. For the block copolymer PLLA-PBC3, phase separation has not been observed until isothermally annealed at 150°C for 120 min. PLLA-rich (dark part) and PBC-rich (light part) phase coarsen with time, and form bicontinuous structure [Figure 5(a–d)] finally. These features show that phase separation of PLLA segment and PBC segment in PLLA-PBC3 is a spinodal decomposition.[27] However, for the block copolymer PLLA-PBC6 [Figure 5(e–h)] based on shorter PLLA segment, the two-phase structure cannot be observed at 150°C even after isothermally annealed for 180 min. The results indicate that PLLA block is compatible with PBC block in PLLA-PBC6 copolymer. It is consistent with the aforementioned results of DSC. It is regarded that the compatibility of blocks in the copolymers is affected by the molecular weight of the blocks, and the lower molecular

weight, the better compatibility.[27] Because of the low molecular weight of PLLA block (Table III), PLLA and PBC blocks in PLLA-PBC6 copolymer have good compatibility.

Mechanical Properties of PLLA-*b*-PBC

Mechanical properties of polymers are more important than any other properties with respect to practical applications. The mechanical properties of PLLA-*b*-PBC are summarized in Table VII. As PBC ratio is raised, the tensile and flexural strengths of PLLA-*b*-PBC decrease, but the elongation at break improves greatly. At the same time, the notched impact strength increases from 1.6 kJ m^{-2} for PLLAU (chain-extended PLLA) to 77 kJ m^{-2} for PLLA-PBC5. It is because of the fact that PBC soft block remarkably increases the flexibility of the copolymer, thus causes great improvement of elongation at break and impact strength, but slight drop of tensile strength. In the cases of PLLA-PBC3 and PLLA-PBC6 with similar weight content of PLLA, it can be found that the tensile strength and flexural strength of PLLA-PBC3 with longer PLLA segment are significantly higher than that of PLLA-PBC6 with shorter PLLA segment. It should be ascribed to the evident higher molecular weight of PLLA-PBC3 as compared to that of PLLA-PBC6, as shown in Table IV. Previous studies of our research and Wang et al. have testified that the propolymers with M_n of 4000–5000 have the highest reactivity and lead to highest M_n of chain-extended polymers. And the M_n of PLLA prepolymer for the synthesis of PLLA-PBC3 just lies in this range.

CONCLUSIONS

A series of novel PLLA-*b*-PBC block copolymers have been successfully synthesized by chain-extension of PLLA-OH and PBC-OH with HDI as a chain-extender. The structures of PLLA-*b*-PBC copolymers are confirmed by means of ^{1}H NMR and GPC analysis. The results testify that chain-extension reaction is a very effective method to synthesize PLLA and PBC-based block copolymers with high molecular weights. PBC soft segment is effective in enhancing the impact strength, whereas hardly decreases the T_m of the copolymers. In addition, PBC improves thermal stability of PLLA. The structures and properties of copolymers are controllable by conveniently varying the molecular weights and feed ratio of prepolymers.

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