

Poly(L-lactic acid)-block-poly(butylene succinate-co-butylene adipate) Multiblock Copolymers: From Synthesis to Thermo-Mechanical Properties

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ABSTRACT: Multiblock copolymers poly(L-lactic acid)-block-poly(butylene succinate-co-butylene adipate)s (abbr. P(LLA-mb-BSA)s) are synthesized via a polycondensation/chain extension/coupling method using binary chain extenders. A poly(L-lactic acid) (PLLA) prepolymer synthesized via direct melt polycondensation of L-lactic acid is rapidly chain extended with a bis (2-oxazoline) to form hydroxyl terminated dimer, and the dimer is then chain extended/coupled with a hydroxyl terminated poly(butylene succinate-co-butylene adipate) (PBSA) prepolymer by a diisocyanate. The microstructure is characterized with GPC, ¹H NMR and FTIR, and the thermo-mechanical properties are investigated with DSC, TGA, DMA, tensile, and impact testing. In the copolymers, the PLLA hard segments are crystallizable and the PBSA soft segments are amorphous, and only melting of PLLA segment was detected. Two independent glass transitions corresponding to both segments are observed, suggesting incompatibility between the two kinds of segments. The tensile modulus and strength decrease while the elongation at break and impact strength increase with increasing the weight percentage of PBSA segment ($\phi_{w,PBSA}$). The mechanical properties can be tuned in wide range by $\phi_{w,PBSA}$, from toughened thermoplastics with excellent tensile modulus, strength and impact strength to thermoplastic elastomers with high elongation at break.

1. INTRODUCTION

Poly(L-lactic acid) (PLLA) is a biobased and biodegradable aliphatic polyester commercialized in largest scale.¹ It is a typical rigid but brittle polymer. It has high modulus and strength but low impact strength, melt crystallization rate and thermal deformation temperature. In order to toughen PLLA or to prepare PLLA-based thermoplastic elastomers, many block copolymers containing PLLA hard segment and other soft segments have been reported.^{2–17} Ideal soft segment should have excellent biodegradability, incompatibility with PLLA, low glass transition temperature (T_g), and good flexibility. Poly(ϵ -caprolactone) (PCL) is such an excellent soft segment, so block copolymers based on PLLA and PCL have been extensively studied,^{4–8} in which PLLA segment provides strength and PCL segment provides elasticity and toughness. Such copolymers can be used for toughened plastics,⁸ thermoplastic elastomers,^{4,6} and even shape memory materials.¹⁷ But the high cost of PCL limits its application in bioplastics. Other reported soft segments include poly(ethylene glycol) (PEG),^{2,13} poly(ethylene succinate) (PES),¹⁶ and poly(butylene succinate) (PBS)³ etc. In comparison with PCL, poly(butylene succinate-co-butylene adipate) (PBSA) is a cheaper flexible copolyester having comparable properties.¹⁸ It is reported that PBSA is incompatible with PLLA in their blends.¹⁹ It is also reported PBSA containing 60 mol % butylene adipate unit (PBSA60) has low T_g (−53.4 °C) and is least crystallizable in the whole composition range.¹⁸ So, PBSA60 appears to be a good candidate for soft segment in multiblock copolymers.

PLLA-based block copolymers can be synthesized through ring-opening polymerization (ROP) of L-lactide using hydroxyl-terminated soft segment prepolymer as macroinitiator^{2,3,6,8,11} or by rapid chain extension/coupling of PLLA and soft segment

prepolymers synthesized from polycondensation.^{13–16} In the latter, diisocyanates are commonly used as extenders because of their high reactivity with terminal hydroxyl groups of prepolymers. In order to synthesize high-performance multiblock copolymers by diisocyanate, the PLLA prepolymer should have sufficiently high molecular weight (M_n at least ≥ 4000 g/mol) to ensure good crystallizability²⁰ and are fully hydroxyl-terminated to ensure complete reaction with diisocyanate.²¹ Direct polycondensation of L-lactic acid forms PLLA containing 50% COOH group. So, it is necessary to add a diol during polycondensation in order to synthesize fully OH-terminated PLLA.^{16,21} However, such a measure inevitably result in long reaction time in synthesizing fully OH-terminated PLLA with high enough M_n ,¹⁶ and therefore, counteract the advantage resulted from rapid chain extension/coupling reaction.

In this study, we designed and synthesized multiblock copolymers containing PLLA hard and PBSA60 soft segments with a modified chain extension/coupling method using binary extenders composed of diisocyanate and bis(2-oxazoline), in which PLLA prepolymer was rapidly chain extended by a bis(2-oxazoline) compound to form fully OH-terminated PLLA dimer with high enough M_n and therefore to facilitate subsequent chain extension/coupling with a diisocyanate. Through this method, high molecular weight poly(LLA-mb-BSA) multiblock copolymers having thermal and mechanical properties tunable from toughened thermoplastics to thermo-

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plastic elastomers were facilely synthesized. The synthesis, microstructure, thermal and mechanical properties of the copolymers were investigated and discussed in detail.

2. EXPERIMENTAL PART

2.1. Materials. L-Lactic acid aqueous solution (LLA, 90 wt %, 98%ee, Jiangxi Musashino Biochem), succinic acid (SA, LETAIHG, China), adipic acid (AA, CNPC-LH, China), 1,4-butanediol (BDO, WLHG, China), 1,5-Naphthalenedisulfonic acid (NSA, Sinopharm Chemical Reagent, China), titanium tetrabutoxide (TBT, SHMX, China), 2,2'-(1,4-Phenylene)bis-(2-oxazoline) (1,4-PBO, TCI, Japan), and hexamethylene diisocyanate (HDI, ACROS, U.S.) were all used as received.

2.2. Synthesis of Prepolymers. PLLA prepolymer was synthesized by direct polycondensation of L-lactic acid. Aqueous L-lactic acid (350 g) was added into a 500 mL four-necked round-bottom flask. In the presence of NSA (0.12 mol % based on LLA), it was first dehydrated and oligomerized at 140 °C under about 3000 Pa for 2 h and then at 160 °C under 600–800 Pa for 2 h, and finally, melt polycondensed at 180 °C under 300–500 Pa for 7 h. Thus obtained product was directly used for further reaction without purification.

PBSA60 prepolymer was synthesized from SA, AA, and BDO by a two-step esterification and polycondensation process in a 500 mL four-necked round-bottom flask. The mole ratio of SA to AA was 40:60 and the alcohol/acid mole ratio of was 1.2:1. The mixture was heated to 120 °C at N₂ atmosphere and kept at this temperature until all diacids were dissolved in BDO. Then, the temperature was raised to 180 °C and kept for 4 h for esterification reaction. After that, TBT (0.1 mol % based on diacids) was added as catalyst and melt polycondensation was carried out at 190 °C under 300–500 Pa for 0.5 h. The resulting HO-PBSA60-OH prepolymer was directly used for further reaction without purification.

2.3. Synthesis of P(LLA-mb-BSA)s. PLLA prepolymer and 1,4-PBO were added into a 100 mL three-necked flask equipped with mechanical stirring and N₂ inlet. The mixture was reacted at 160 °C for 30 min. Then, PBSA prepolymer was added into the product, PLLA dimer. The total mass of the two prepolymers was 20 g. After the PBSA was melt and mixed homogeneously with the PLLA dimer, HDI (NCO/OH 1.05/1) was added and the mixture was further reacted for another 30 min. The resulting multiblock copolymer was marked as “PLSA $\phi_{w,PBSA}$ ” in which $\phi_{w,PBSA}$ means the weight percentage of PBSA60. ¹H NMR: δ_H (400 MHz, CDCl₃) 8.0 (4H,s,phenyl), 7.83 (4H,s,O=C-phenyl-C=O), 5.19 (3H,s,CH₃-), 4.35 (1H, m, -CH-OH), 4.10 (4H, s, -CH₂-O-C=O), 4.08 (4H, m, COO-CH₂-), 3.70 (4H, d, HN-CH₂-), 3.68 (2H, m, HO-CH₂-), 3.15 (4H, s, HN-CH₂-), 2.6 (4H, s, COO-CH₂-COO), 2.3 (4H, s, COO-CH₂-), 1.6–1.8 (8H, m, -CH₂-), 1.59 (1H, m, -CH-), 1.50 (4H, m, -CH₂-), 1.35 (4H, s, -CH₂-). FTIR: ν_{max} (KBr, cm⁻¹) 3500, 3520 (OH), 1620 (C=N), 3380, 1530 (N-H).

2.4. Characterization. The FTIR spectra of the prepolymers, PLLA dimer and the multiblock copolymers were recorded with a Nicolet7000 spectroscopy using a 10 mg/mL chloroform solution. The ¹H NMR spectra of the prepolymers, PLLA dimer and the multiblock copolymers were recorded with an AC-80 spectroscopy (400M, BRUKER). Deuterated chloroform was used as solvent and tetramethylsilane (TMS) as an internal reference. For PBSA prepolymer (m_s , g), styrene (n_{st} , mol) was used as additional internal standard in order to

calculate its hydroxyl value. The optical purity of PLLA prepolymer and dimer were measured as previously reported.²³

The number-average molecular weight ($M_{n,NMR}$ and $M_{n,titr}$) of the prepolymers was determined by ¹H NMR spectra and/or titration. The acid value of PLLA prepolymer, PLLA dimer and PBSA prepolymer was measured by titration. About 1 g prepolymer was dissolved in 20 mL chloroform in a 100 mL conical flask. Then bromothymol blue was added as an indicator. The mixture was titrated with 0.1 mol/L KOH ethanol solution until the solution color changed from yellow to green. The acid value ($V_{COOH,titr}$) was calculated from eq 1. The hydroxyl value (V_{OH}) of PLLA prepolymer was assumed to be equal to its V_{COOH} . The hydroxyl value (V_{OH}) of PLLA dimer was calculated from eq 2. The V_{OH} of PBSA prepolymer was calculated from its ¹H NMR data by eq 3. The $M_{n,titr}$ was calculated from eq 4. The $M_{n,NMR}$ of PLLA, PLLA dimer and PBSA prepolymers was calculated from eqs 5, 6, and 7 respectively. In eq 6, 218 (g/mol) is the molecular weight of 1,4-PBO moiety in the PLLA dimer. In eq 7, 190 g/mol and 90 g/mol are the average molecular weight of repeating unit of PBSA60 and the molecular weight of BDO.

$$V_{COOH,titr} = \frac{56.1 \times C \times (V - V_0)}{m} \quad (1)$$

$$V_{OH}(PLLA \text{ dimer}) = \frac{V_{OH}(PLLA) \times m_{PLLA}}{m_{PLLA} + m_{PBO}} \quad (2)$$

$$V_{OH}(PBSA) = \frac{A_{3.68} \times n_{st} \times 56.1 \times 1000}{2 \times A_{6.75} \times m_s} \quad (3)$$

$$M_{n,titr} = \frac{56.1 \times 2000}{V_{COOH} + V_{OH}} \quad (4)$$

$$M_{n,NMR}(PLLA) = \left(\frac{A_{5.19}}{A_{4.35}} + 1 \right) \times 72 + 18 \quad (5)$$

$$M_{n,NMR}(PLLA \text{ dimer}) = M_{n,NMR}(PLLA) \times 2 + 218 \quad (6)$$

$$M_{n,NMR}(PBSA) = 190 \times \frac{A_{4.10}}{A_{3.65}} + 90 \quad (7)$$

The molecular weight and distribution (MWD) of the multiblock copolymers were determined by GPC (PL GPC 50 plus, PL Co.) equipped with triple detectors (refractive index, light-scattering and viscosity). Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. The weight-average molecular weight (M_w) was obtained from the light-scattering detector and the MWD was obtained from the light-scattering and refractive index detectors.

The thermal transition behaviors of the prepolymers, PLLA dimer and the multiblock copolymers were recorded with differential scanning calorimetry (DSC, TA-Q200). The samples were first cooled to -80 °C and then heated to 180 °C at 10 °C/min and kept for 3 min, and then cooled to -80 °C at 10 °C/min. After kept at -80 °C for 3 min, the samples were reheated to 180 °C at 10 °C/min again.

The melt flow index (MFI) of the multiblock copolymers was determined according to ASTM D1238 using a CEAST 7026 melt indexer (CEAST Co., Italy) with capillary diameter of 9.55 mm. The testing temperature was 190 °C and the load was 2.16 kg. The clipping time was 15 s.

Scheme 1. Schematic Diagram of Synthesis Rationale of P(LLA-mb-BSA) Multi-Block Copolymers

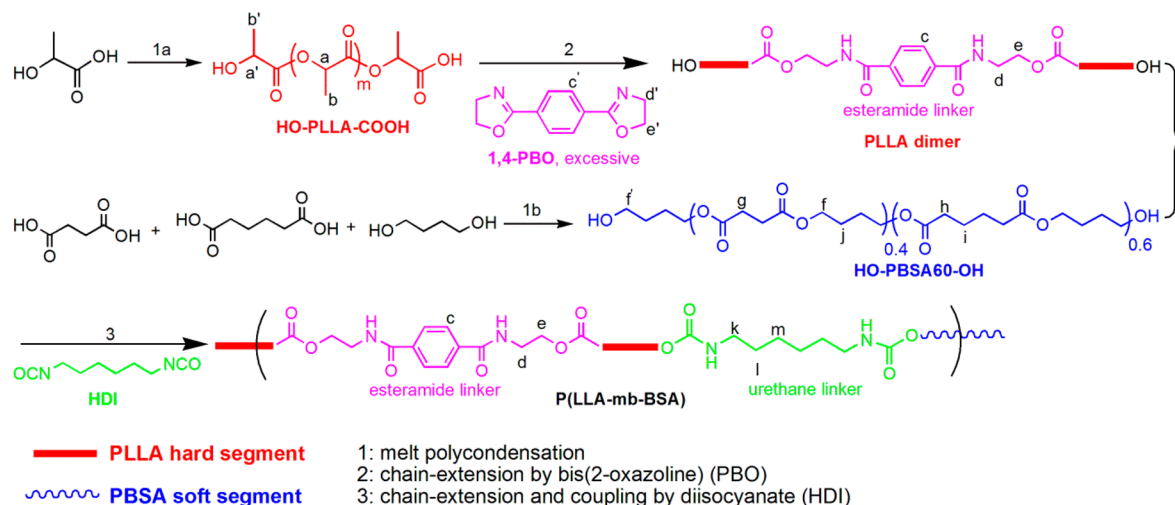


Table 1. Molecular Characteristics of PLLA Prepolymer, PLLA Dimer and PBSA Prepolymer

product	$V_{\text{COOH, titr}}$ (mgKOH g ⁻¹)	V_{OH} (mgKOH g ⁻¹)	OH% ^a	$M_{n, \text{titr}}$ ^b (g/mol)	$M_{n, \text{NMR}}$ ^c (g/mol)	S/A ^d
HO-PLLA-COOH	8.72	8.72 ^e	50	6400	6200	
PLLA dimer	0.35	8.44	96.0	12 800	12 00	
HO-PBSA-OH	1.50	57.2 ^f	97.4	1900	2000	39.6/60.4

^aHydroxyl percentage, $\text{OH}\% = V_{\text{OH}} / (V_{\text{OH}} + V_{\text{COOH}})$. ^bNumber-average molecular weight calculated from titration, see eq 4). ^cNumber-average molecular weight calculated from ¹H NMR data, see eqs 5, 6, and 7. ^dS/A means mole ratio of BS unit to BA unit from ¹H NMR. ^eThe hydroxyl value is assumed to be equal to the acid value. ^fThe hydroxyl value calculated from ¹H NMR data.

Dumbbell-shaped specimens (2 mm in thickness and 4 mm in width) were prepared using a HAAKE MiniJet II Injection molding machine and then conditioned at 25 °C and 50% humidity for over 48 h prior to testing. The tensile properties of the multiblock copolymers were measured with a Zwick Roell Z020 testing machine at 25 °C according to ASTM D638. The crosshead speed used was 20 mm/min. For each sample, at least five specimens were tested.

Rectangle-shaped specimens (80×10×4 mm) were also prepared using HAAKE MiniJet II. Then, a notch of 2 mm in depth was made with a CEAST 6591 notching machine. The notched specimens were conditioned at 25 °C and 50% humidity for over 48 h prior to testing. Izod impact testing was performed with a CEAST Resil impactor with pendulums of 1 and 4 J according to ASTM D256. For each sample, at least five specimens were tested.

DMA was performed with DMA 242C (Netzsch, Germany) with constant frequency of 1.0 Hz. The amplitude was 80 μm. The samples were first cooled to −100 °C and then heated to 120 °C at 3 °C/min.

Thermal gravimetric analysis (TGA, PerkinElmer instruments, USA) was used to characterize the thermal stability of the multiblock polymers. The samples were measured from 50 to 800 °C at 20 °C/min. All measurements were under N₂ atmosphere.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The multiblock copolymers, P(LLA-mb-BSA)s, were synthesized via chain extension and coupling of PLLA and PBSA prepolymers using 1,4-PBO and HDI as binary chain extenders. The synthesis rationale is illustrated in Scheme 1. First, a PLLA prepolymer with a terminal hydroxyl and a carboxyl group (HO-PLLA-

COOH) was synthesized via melt polycondensation of LLA, and a PBSA60 random copolymer with two terminal OH groups (HO-PBSA-OH) was synthesized via melt polycondensation of SA, AA, and BDO. Then, the PLLA prepolymer was chain extended with 1,4-PBO to give a PLLA dimer containing an esteramide linker and two terminal OH groups. Finally, the dimer and the PBSA prepolymer were chain extended and coupled by HDI via urethane chemistry to form the multiblock copolymers. The molecular characteristics of PLLA prepolymer, PLLA dimer and PBSA prepolymer were summarized in Table 1.

In general, thermal stability of PLLA is not good enough when tin catalyst was used in melt polycondensation.²² To ensure satisfactory thermal stability of the PLLA segments in the multiblock copolymers, 1,5-naphthalenedisulfonic acid was used as nonmetallic catalyst instead of metallic catalyst stannous chloride in melt polycondensation of LLA, as previously reported.²³ The molecular weight of PLLA was controlled by polycondensation time, as previously reported.^{23,24} Its optical purity was 92.1%ee. For PBSA prepolymer synthesis, TBT was used as catalyst. The SA/AA molar ratio was 40/60 as it had been reported that PBSA60 is the least crystallizable in the whole composition range.¹⁹ The chemical and chain structures of the two prepolymers were validated by ¹H NMR (Figure 1) and FTIR (Figure 2) spectra.

Figure 3 shows the DSC curves of the PLLA prepolymer and PBSA prepolymer. The thermal transition data are summarized in Table 2. Clearly, the PLLA prepolymer is a crystalline polymer. Although no clear melt crystallization was observed but it cold-crystallized clearly at 108 °C and then melted at T_m of 156 °C with a moderate melting enthalpy (ΔH_m , 48.9 J/g) in the second heating scan at 10 °C/min. The PBSA60 prepolymer showed clear melt crystallization though it was

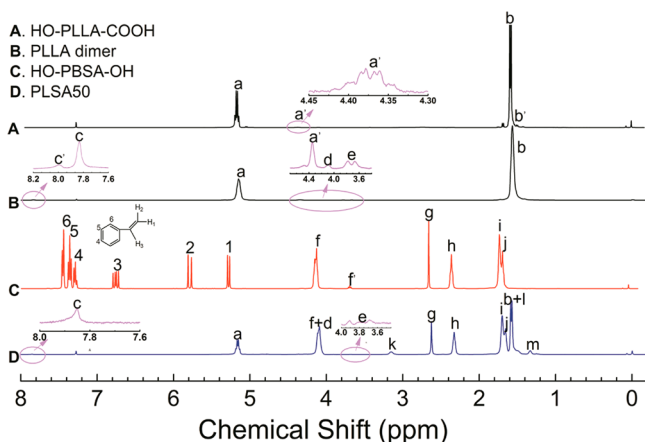


Figure 1. ^1H NMR spectra of (A) PLLA prepolymer, (B) PLLA dimer, (C) PBSA prepolymer, and (D) P(LLA-mb-BSA) multiblock copolymer (PLSA50).

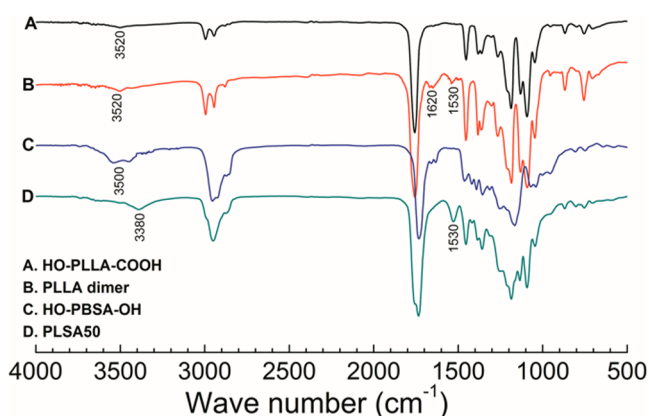


Figure 2. FTIR spectra of (A) PLLA prepolymer, (B) PLLA dimer, (C) PBSA prepolymer, and (D) P(LLA-mb-BSA) multiblock copolymer (PLSA50).

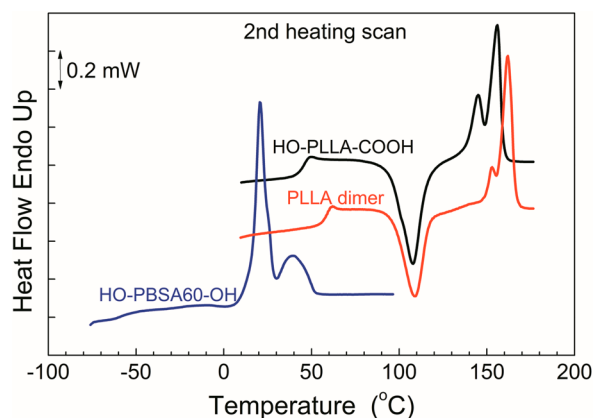


Figure 3. DSC curves of PLLA, PLLA dimer, and PBSA prepolymers.

reported to be the least crystallizable in the whole composition range.¹⁹ It has a melting enthalpy of 66.4 J/g. However, as discussed later, its crystallizability was greatly depressed when it was introduced into the multiblock copolymers. Two melting points appeared for both prepolymers, suggesting melt-recrystallization phenomenon occurred.

The molar percentage of COOH group in PLLA prepolymer was 50% COOH. So, it was first chain extended with 1,4-PBO to eliminate the COOH group to facilitate the next chain extension by diisocyanate. From the time-evolution curve of the acid value of PLLA prepolymer shown in Figure 4, it can be

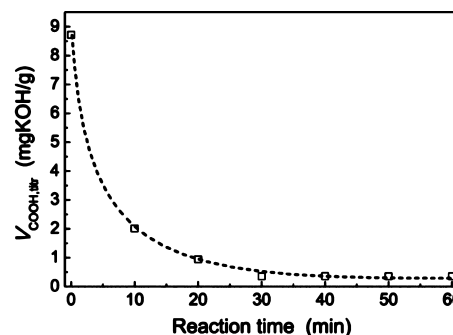


Figure 4. Time-evolution of acid value of PLLA prepolymer during its chain extension reaction with 1,4-PBO.

seen that the reaction occurred rapidly at 160 °C due to the high reactivity of oxazoline ring with COOH group. The acid value decreased sharply and reached a constant 0.354 mgKOH/g after 30 min. As a result, the percentage of COOH decreased to 4.0%, and that of OH reached 96.0%. And the optical purity became 91.9%ee.

The ^1H NMR and FTIR spectra of the PLLA dimer are illustrated in Figures 1B and 2B, too. In Figure 1B, in addition to the chemical shifts of CH_3 at 5.19 ppm (a) and CH at 1.59 ppm (b) in PLLA chain, some new signals appear at 7.83 ppm (c), 3.78 ppm (d) and 4.35 ppm (e, overlapped with a'). They are attributed to the benzene ring CH and the two CH_2 groups in the formed esteramide linker. The new signals at 8.0 ppm (c'), 4.09 ppm (d') and 4.48 ppm (e') are attributed to unreacted 1,4-PBO. In Figure 2B, the absorption of N-H vibration in the formed amide bond appears at 1530 cm^{-1} . The peak at 1620 cm^{-1} is attributed to the C=N absorption of unreacted 1,4-PBO. All these results indicate the reaction between the COOH group and 1,4-PBO occurred. Thus obtained PLLA dimer has lower crystallization and melt enthalpies but higher T_g as compared with the PLLA prepolymer because of molecular weight growth, see Table 2.

Finally, the P(LLA-mb-BSA) multiblock copolymers were synthesized via chain extension and coupling of the PLLA dimer and PBSA prepolymer by HDI at 160 °C for 30 min, without catalyst. It is found from the ^1H NMR spectrum of PLSA50 (Figure 1D) that the characteristic chemical shifts

Table 2. Thermal Transition Properties of PLLA, PLLA Dimer and PBSA Prepolymers

intermediate product	cooling scan		second heating scan				
	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)
HO-PLLA-COOH	nd	nd	46.0	108	145/156	43.9	48.9
PLLA dimer	nd	nd	59.3	108	153/161	35.1	35.4
HO-PBSA-OH		55.8	−60.6	nd	20.7/41.0	nd	66.4

belonging to PLLA segments (5.19 ppm (a), 1.59 ppm (b)), benzene ring in esteramide linker (7.86 ppm (c)) and PBSA segments (4.08 ppm (f), 2.6 ppm (g), 2.3 ppm (h), 1.6–1.8 ppm (i+j)) still exist. But the signals belong to end hydroxyl groups of PLLA and PBSA prepolymers (4.35 ppm (a') and 3.68 ppm (f')) disappeared because of molecular weight growth, and three new signals appeared at 3.15 ppm (k), 1.50 ppm (l), and 1.35 ppm (m) because of chain extension and coupling. They are attributed to the chemical shifts of three kinds of methylene protons in the formed urethane linker in the multiblock copolymer. These results indicate that chain extension occurred as expected.

It can also be seen from the FTIR spectrum of PLSA50 (Figure 2D) that the absorption of NCO groups in HDI is not observed at 2200 cm^{-1} ,²⁶ the absorption of terminal hydroxyl vibration at 3520 cm^{-1} disappeared and the absorptions of N–H vibration in urethane bond at 3380 cm^{-1} and 1530 cm^{-1} are obviously observed. The results also indicate that the NCO groups had been completely reacted with the terminal hydroxyl groups of PLLA dimer and PBSA prepolymer and a multiblock poly(esterurethane) copolymer was formed.

The copolymers reached high molecular weight in short time because of the high hydroxyl content of the prepolymers and high reactivity of the chain extension/coupling reaction. As shown in Table 3, the weight average molecular weight (M_w)

Table 3. Molecular Weight Distribution and Melt Flow Index (MFI) of Chain-Extended PLLA (PLSA0), Multi-Block Copolymers (PLSA10-PLSA90) and Chain-Extended PBSA (PLSA100)

sample	M_n (10^3 g mol^{-1})	M_w (10^3 g mol^{-1})	PDI	MFI (g 1 min^{-1})
PLSA0	nd ^a	nd	nd	8.4
PLSA10	nd	nd	nd	14.8
PLSA20	nd	nd	nd	13.0
PLSA30	nd	nd	nd	15.6
PLSA40	nd	nd	nd	13.0
PLSA50	37.9	122	3.2	14.4
PLSA60	36.9	153	4.2	11.2
PLSA70	50.3	176	3.5	8.5
PLSA80	50.4	165	3.3	8.0
PLSA90	59.4	141	2.4	11.4
PLSA100	54.9	102	1.8	10.5

^aThe copolymers containing $\leq 40\%$ PBSA segment were insoluble in THF because of good crystallization of PLLA segments²⁵ and therefore the GPC characterization was not performed.

ranges from to 102 000 to 176 000 g/mol, and the melt flow index ranges from 8.0 to 15.6 g/10 min. All the products have unimodal molecular weight distribution. The polydispersity ranges from 1.8 to 4.2.

3.2. Thermal Transition Behaviors. The DSC curves of the chain-extended PLLA (PLSA0) and PBSA (PLSA100) and the multiblock copolymers (PLSA10-PLSA90) are shown in Figure 5, and the thermal transition data are summarized in Table 4. In comparison with the respective prepolymers, PLSA0 and PLSA100 exhibited similar thermal transitions, but their melt enthalpies both decreased because of weakened crystallization after chain extension. For the multiblock copolymers, the respective glass transitions of PLLA and PBSA segments were observed, indicating the hard and soft segments are incompatible with each other. The PLLA hard segments hardly crystallized from melt due to its poor melt-crystallization ability,²⁷ but cold-crystallized easily at heating rate of $10\text{ }^\circ\text{C/min}$ and then melted when $\phi_{w,\text{PBSA}}$ is less than 70%. The crystallization and melting enthalpies both decreased with $\phi_{w,\text{PBSA}}$. But the melting temperature did not show clear dependence on $\phi_{w,\text{PBSA}}$, validating the block structure of the copolymers. Although the PBSA prepolymer itself showed good crystallization ability as discussed above, the PBSA soft segments hardly melt- and cold-crystallized when $\phi_{w,\text{PBSA}}$ was less than 70%. These results suggest that the crystallization of hard and soft segments were depressed to certain extent. When $\phi_{w,\text{PBSA}}$ was over 70%, the PBSA segments still exhibited certain cold-crystallization and melting in the first heating scan. The PLLA segments also exhibited weak cold-crystallization and melting in the first scan.

3.3. Tensile and Izod Impact Properties. All the samples were injected in melt to prepare specimens for mechanical testing. For the samples having weak crystallizability, the specimens were cooled long enough to facilitate demolding. The results are shown in Figure 6 and Table 5.

The composition dependences of tensile modulus (E), strength (σ_b), and elongation at break (ϵ_b) as well as izod impact strength (σ_{imp}) are illustrated in Figure 7. Clearly, the chain-extended PLLA is a typical rigid thermoplastics characterized by high tensile modulus (3.03 GPa) and strength (65.1 MPa) but very low elongation at break (2.6%) and poor izod impact strength (2.2 kJ/m^2). The high modulus and strength validate its high molecular weight. In contrast, the chain-extended PBSA is a typical flexible polymer having weak tensile modulus (6 MPa) and strength (6.5 MPa) but very high elongation at break (1100%). For the multiblock copolymers, the mechanical properties exhibit obvious composition depend-

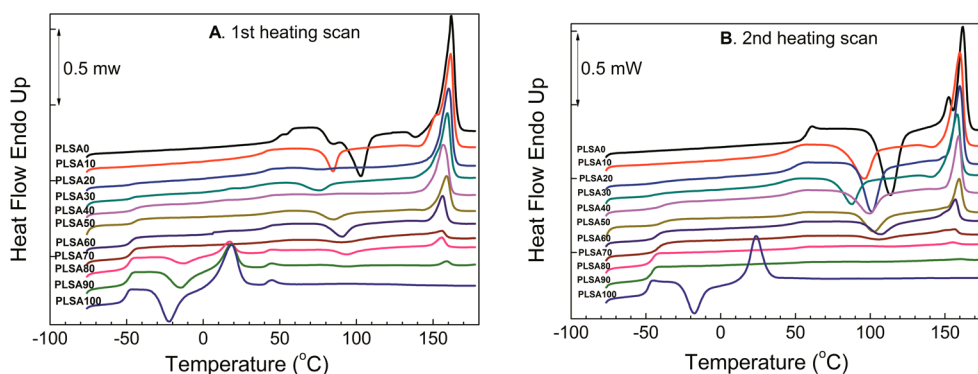
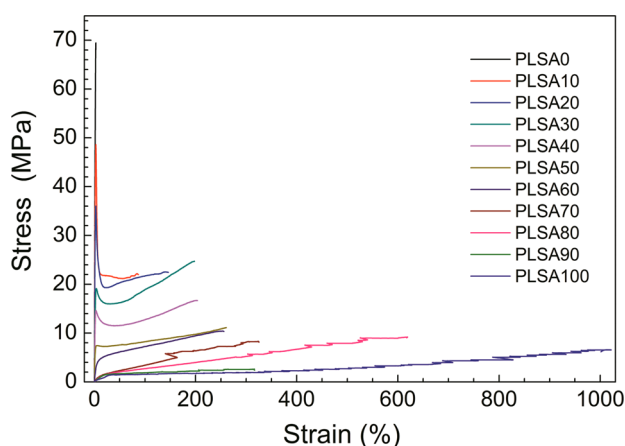


Figure 5. DSC curves of chain-extended PLLA (PLSA0), multiblock copolymers (PLSA10-PLSA90) and chain-extended PBSA (PLSA100).

Table 4. Thermal Transition Properties of Chain-Extended PLLA (PLSA0), Multi-Block Copolymers (PLSA10-PLSA90) and Chain-Extended PBSA (PLSA100)^a

PLSA	first heating scan						second heating scan					
	T_{g1} (°C)	T_{g2} (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J g ⁻¹)	ΔH_m (J g ⁻¹)	T_{g1} (°C)	T_{g2} (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J g ⁻¹)	ΔH_m (J g ⁻¹)
PLSA0		56.0	102.7	161.8	28.8	38.9	/	58.3	113.5	161.7	34.2	35.0
PLSA10	nd	40.3	84.7	161.4	7.5	34.2	nd	48.2	95.6	159.8	19.5	30.8
PLSA20	-47.0	41.0	77.2	159.9	0.9	27.0	-41.8	48.4	101.1	159.6	22.8	25.7
PLSA30	-47.2	33.9	75.8	159.3	4.5	23.6	-45.4	43.0	87.8	158.1	12.6	20.9
PLSA40	-45.6	40.1	76.0	156.8	0.2	18.3	-39.4	44.6	99.7	159.2	12.5	13.5
PLSA50	-44.4	44.7	84.9	158.8	4.0	11.0	-38.3	49.9	102.4	159.3	10.8	9.6
PLSA60	-47.4	41.2	90.9	156.6	6.2	7.2	-43.2	49.9	104.9	157.1	7.2	6.5
PLSA70	-46.7	43.4	89.7	156.2	1.3	3.1	-42.6	43.4	106.0	156.8	2.7	3.1
PLSA80	-48.1	41.4	94.3	156.1	2.5	2.6	-45.0	50.4	114.4	155.1	0.3	0.7
			-12.1*	16.8*	3.3*	4.6*						
PLSA90	-48.4	41.5	93.1	157.5	0.6	1.0	-45.6	52.1	98.0	155.0	0.1	0.2
			-14.7*	18.1*	8.0*	10.9*						
PLSA100	-49.9		-22.9	18.4	13.8	22.8	-48.0		-18.1	23.3	11.9	20.1

^a T_{g1} and T_{g2} : glass transition temperature of PBSA and PLLA segment respectively; T_{cc} : cold crystallization temperature; T_m : melt temperature; ΔH_{cc} : cold crystallization enthalpy; ΔH_m : melt enthalpy. *: data for PBSA segment.

**Figure 6.** Tensile stress–strain curves of chain-extended PLLA (PLSA0), multiblock copolymers (PLSA10-PLSA90) and chain-extended PBSA (PLSA100).

ences. With increasing $\phi_{w,PBSA}$, the tensile modulus and strength decrease, while the elongation at break and impact strength increase. When 10% PBSA segment was incorporated, the elongation at break increased significantly from 2.6% to

91% and the izod impact strength increases a little. At $\phi_{w,PBSA}$ of 30–40%, the impact strength increases rapidly and reaches 10.8–45.7 kJ/m². At $\phi_{w,PBSA} \geq 50\%$, the elongation at break exceeds 230% and the specimens were not broken in impact testing. These results indicate that the copolymers with $\phi_{w,PBSA} \leq 40\%$ behave like toughened PLLA thermoplastics, while the copolymers with $\phi_{w,PBSA} \geq 50\%$ appears like thermoplastic elastomers.

3.4. Dynamic Mechanical Behaviors. The dynamic mechanical behaviors were further investigated. The storage modulus and $\tan\delta$ of three typical samples, PLSA30, PLSA50, and PLSA70, are shown in Figure 8. Clear decrease of storage modulus and $\tan\delta$ peak appear at the glass transition temperature range of PBSA and PLLA segments. The glass transition temperatures agree with the results from DSC. The existence of two independent T_g s further indicates the incompatibility between PLLA and PBSA segments. The storage modulus decreases with $\phi_{w,PBSA}$. For PLSA50 and PLSA70, rubber plateau appears between the two glass transitions in the Figure 8A, suggesting their elastomeric properties.

3.5. Thermal Stability. Finally, the thermal stability of the copolymers and the chain-extended PLLA and PBSA was

Table 5. Mechanical Properties and Characteristic Decomposition Temperatures ($T_{d,5}$ and $T_{d,max}$) of Chain-Extended PLLA (PLSA0), Multi-Block Copolymers (PLSA10-PLSA90) and Chain-Extended PBSA (PLSA100)

sample	E^a (GPa)	σ_b^b (MPa)	ϵ_b^c (%)	σ_{imp}^d (kJ m ⁻²)	$T_{d,5}^f$ (°C)	$T_{d,max1}^f$ (°C)	$T_{d,max2}^f$ (°C)
PLSA-0	3.03 ± 0.17	65.1 ± 7.1	2.6 ± 1.2	2.2 ± 0.3	335	380	nd
PLSA-10	1.35 ± 0.06	49.9 ± 2.3	91 ± 40	2.8 ± 0.4	321	380	nd
PLSA-20	1.00 ± 0.03	37.7 ± 2.6	123 ± 62	4.0 ± 0.1	318	375	410
PLSA-30	0.53 ± 0.03	24.1 ± 0.7	171 ± 69	10.8 ± 0.4	311	345	410
PLSA-40	0.39 ± 0.01	18.8 ± 2.5	200 ± 7.4	45.7 ± 1.0	305	340	410
PLSA-50	0.26 ± 0.02	15.2 ± 3.2	228 ± 44	nb ^e	302	325	410
PLSA-60	0.09 ± 0.003	11.0 ± 1.5	246 ± 14	nb	296	315	410
PLSA-70	0.012 ± 0.003	10.4 ± 2.0	417 ± 113		291	305	410
PLSA-80	0.01 ± 0.004	9.4 ± 2.7	503 ± 114		290	300	410
PLSA-90	0.007 ± 0.003	4.0 ± 0.5	340 ± 12		296	290	415
PLSA-100	0.006 ± 0.001	6.5 ± 1.3	1094 ± 93		318	385	415

^aTensile modulus. ^bTensile strength. ^cElongation at break. ^dIzod impact strength. ^eNot broken. ^fDetermined from TGA at 20 °C/min, N₂ atmosphere.

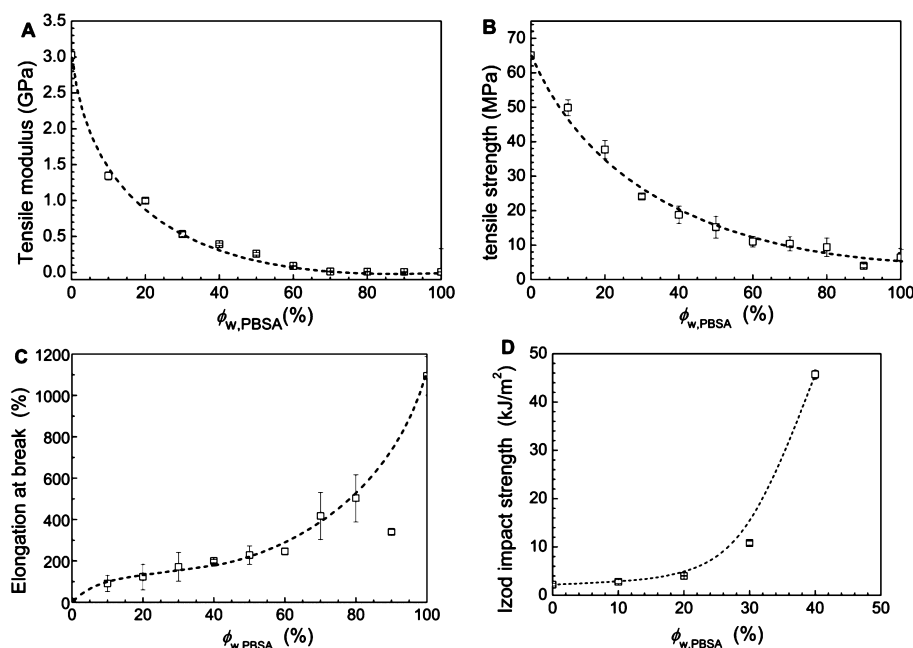


Figure 7. Mechanical properties of the chain-extended PLLA (PLSA0), multiblock copolymers (PLSA10-PLSA90) and chain-extended PBSA (PLSA100). A: tensile modulus; B: tensile strength; C: elongation at break; D: impact strength.

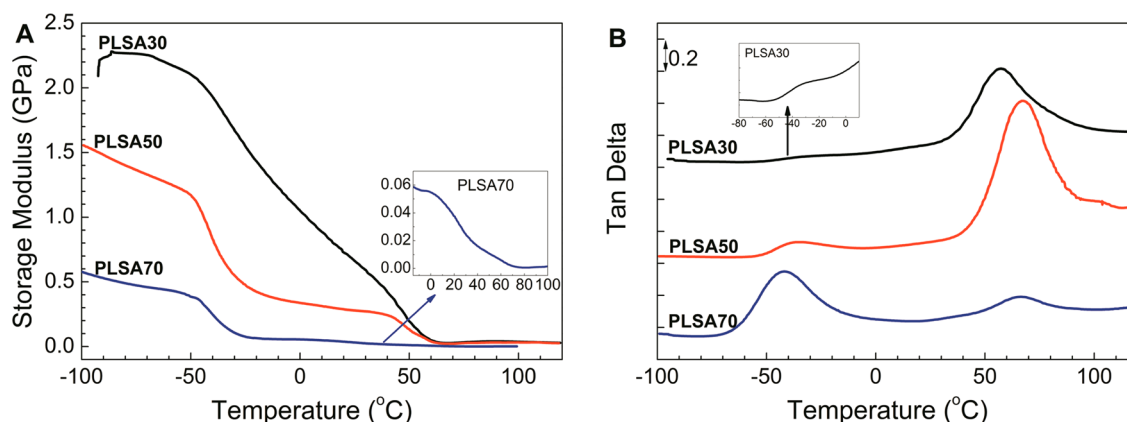


Figure 8. Temperature dependences of storage modulus (A) and $\tan\delta$ (B) of three typical multiblock copolymers (PLSA30, PLSA50, and PLSA70).

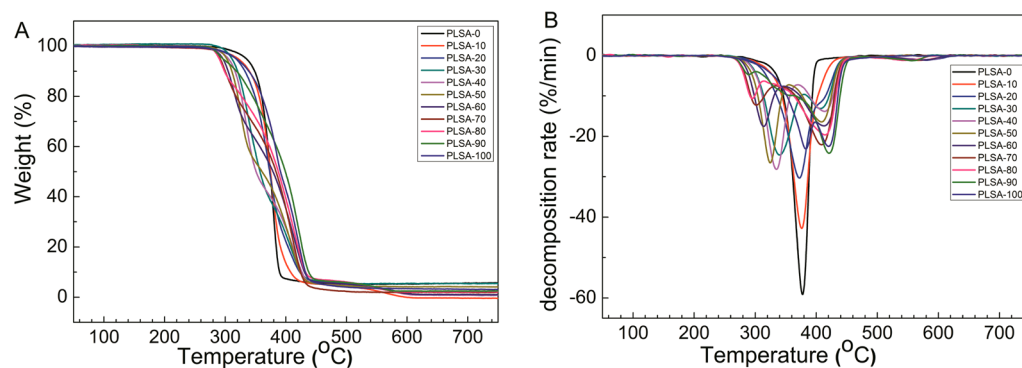


Figure 9. TGA (A) and differential TGA (B) curves of chain-extended PLLA (PLSA0), multiblock copolymers (PLSA10-PLSA90) and chain-extended PBSA (PLSA100).

assessed. Figure 9 shows the TGA curves. The results are listed in Table 5. All the products have good thermal stability. They did not decompose until 270 °C and the decomposition temperature at 5% weight loss ($T_{d,5}$) were all over 290 °C. The thermal stability of PLSA100 is similar to that of PBSA

copolymer previously reported.²⁸ For PLLA prepared via melt polycondensation, its thermal stability is often not good enough due to residual tin-based catalyst.²² In our previous study, we found that the thermal stability can be greatly improved using disulfonic acids as catalyst.²³ In this study, 1,5-naphthalenedi-

sulfonic acid was also used as catalyst, as a result, the chain-extended PLLA and all the multiblock copolymers have good thermal stability.

The thermal decomposition behavior shows clear composition dependence. PLSA0 has higher $T_{d,5}$ (335 °C), narrower T_d range (270 °C–395 °C) and unimodal differential TGA curve ($T_{d,max}$ 380 °C). In comparison, PLSA100 has lower $T_{d,5}$ (318 °C), broader T_d range (270 °C–445 °C) and undergoes two-stage thermal degradation. Its differential TGA curve is bimodal with $T_{d,max1}$ of 385 °C and $T_{d,max2}$ of 415 °C. All the multiblock copolymers undergo two-stage composition-dependent thermal degradation except PLSA10. And it is interesting that the $T_{d,max1}$ decreases with PBSA segment content but the $T_{d,max2}$ keeps almost constant. The cause is not clear yet at present and need further study. In addition, the biodegradability of the P(LLA-*mb*-BSA)s also needs to be assessed though they are reasoned to be biodegradable because PLLA- and PBSA-based poly(esterurethane)s are reported to be biodegradable^{29,30}

4. CONCLUSIONS

Novel high molecular weight multiblock copolymers poly(LLA-*mb*-BSA)s were successfully synthesized via a modified chain extension/coupling method using binary chain extenders. The PLLA hard segment retains its crystallizability but the PBSA soft segment becomes amorphous though the PBSA prepolymer is crystallizable. The two segments are incompatible with each other and therefore, the copolymers exhibit two independent glass transitions. The melting temperature of PLLA segment keeps unchanged but the melting enthalpy decreases with increasing $\phi_{w,PBSA}$. The chain extended PLLA has excellent tensile modulus (3.0 GPa) and strength (65 MPa), but very low elongation at break (2.6%) and impact strength (2.2 kJ/m²). The tensile modulus and strength of the copolymers decrease while the elongation at break and impact strength increase with increasing $\phi_{w,PBSA}$. The mechanical properties can be continuously tuned in wide range by copolymer composition. At $\phi_{w,PBSA}$ of 30–40%, the copolymers have impact strength as high as 10–46 kJ/m². At $\phi_{w,PBSA} \geq 50\%$, the copolymers have large elongation at break and behave like thermoplastic elastomers. With these advantages, the multiblock copolymers may find applications as toughened thermoplastics as well as thermoplastic elastomers. Further modifications in improving crystallization of PLLA segment and adopting more flexible soft segment is under way and will be reported later.

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Notes

The authors declare no competing financial interest.

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