

# Syntheses and Physical Characterization of New Aliphatic Triblock Poly(L-lactide-*b*-butylene succinate-*b*-L-lactide)s Bearing Soft and Hard Biodegradable Building Blocks

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This study presents chemical syntheses and physical characterization of a new aliphatic poly(L-lactide-*b*-butylene succinate-*b*-L-lactide) triblock copolyester with soft and hard biodegradable building blocks. First, poly(butylene succinate) (PBS) prepolymers terminated with hydroxyl functional groups were synthesized through melt polycondensation from succinic acid and 1,4-butanediol. Further, a series of new PLLA-*b*-PBS-*b*-PLLA triblock copolyesters bearing various average PLLA block lengths were prepared via ring opening polymerization of L-lactide with the synthesized hydroxyl capped PBS prepolymer ( $M_n = 4.9$  KDa) and stannous octanoate as the macroinitiator and catalyst, respectively. By means of GPC, NMR, FTIR, DSC, TGA, and wide-angle X-ray diffractometer (WAXD), the macromolecular structures and physical properties were intensively studied for these synthesized PBS prepolymer and PLLA-*b*-PBS-*b*-PLLA triblock copolyesters.  $^{13}\text{C}$  NMR and GPC experimental results confirmed the formation of sequential block structures without any detectable transesterification under the present experimental conditions, and the molecular weights of triblock copolyesters could be readily regulated by adjusting the feeding molar ratio of L-lactide monomer to the PBS macroinitiator. DSC measurements showed all single glass transitions, and their glass transition temperatures were found to be between those of PLLA and PBS, depending on the lengths of PLLA blocks. It was noteworthy that the segmental flexibilities of the hard PLLA blocks were found to be remarkably enhanced by the more flexible PBS block partner, and the PBS and PLLA building blocks were well mixed in the amorphous regions. Results of TGA analyses indicated that thermal degradation and stabilities of the PLLA blocks strongly depended on the average PLLA block lengths of triblock copolyesters. In addition, FTIR and WAXD results showed the coexistence of the assembled PLLA and PBS crystal structures when the average PLLA block length became larger than 7.8. These results may be beneficial for this new biodegradable aliphatic triblock copolyester to be applied as a potential biomaterial.

## Introduction

In the past few decades, numerous reports have been published on the study of poly(lactide)s (PLAs), the most attractive and useful class of biodegradable polyesters, which possess many desirable properties, such as nontoxicity, low immunogenicity, and good biocompatibility, so as to be applied in biomedical and pharmaceutical fields.<sup>1–5</sup> Generally, PLAs can be found in three forms: optically pure poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA) with less or no optical activity. An optically pure PLLA is a crystalline, hard, and rather brittle material melting in a temperature range of 165–185 °C which depends on its molecular weight and the size of self-assembled crystallites.<sup>6</sup> In contrast, PDLLA having a random stereo sequence is an amorphous transparent material.<sup>7</sup>

There have been two synthetic methods available for PLA preparation, i.e., polycondensation of lactic acid and ring opening polymerization of cyclic lactide.<sup>8,9</sup> Commonly, the former method could produce PLA oligomers with average

molecular weights less than several tens of thousands despite of a few exceptions.<sup>10</sup> The latter currently provides a more general way to prepare high molecular weight PLAs mediated by several organometallic catalysts, and a so-called coordination-insertion mechanism has been proposed and generally accepted.<sup>11–17</sup>

So far, the most widely used initiator for ring opening polymerization of PLA is known as Sn(II) 2-ethylhexanoate ( $\text{SnOct}_2$ ) because it has shown very efficient for PLA synthesis. The reaction system should also include hydroxyl or amino-containing<sup>18</sup> compounds acting as co-initiator. The mechanistic studies have demonstrated that the hydroxyl capped compound can substitute at least one octanoate group of the  $\text{SnOct}_2$  molecule in a rapid equilibration, and the resultant Sn-alkoxide is then the true initiator for the polymerization process.<sup>19–21</sup> Thus, this approach allows an easy incorporation of bioactive end groups, such as vitamins and hormones,<sup>22</sup> or the syntheses of functional block or star-shaped copolymers provided that these potential co-initiators possess at least one hydroxyl or amino group.<sup>18</sup> Also, their molecular weights and distributions can be well tuned

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through adjusting the amounts of a hydroxyl capped co-initiator and SnOct<sub>2</sub> catalyst in a dry reaction system.<sup>23–26</sup>

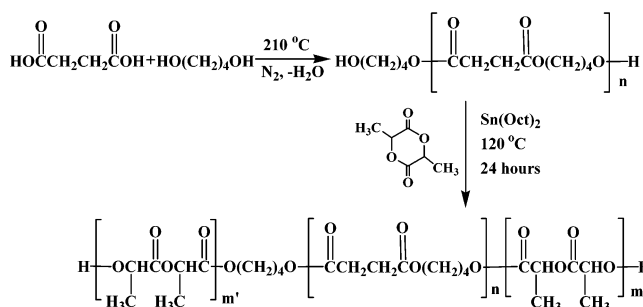
Up to date, many linear AB and ABA types of functional block copolymers have been synthesized via corresponding mono- and di-functional macroinitiators. For instance, amphiphilic poly(ethylene glycol-*b*-L-lactide) di-block copolymer, poly(L-lactide-*b*-ethylene glycol-*b*-L-lactide) tri-block copolymer,<sup>27–29</sup> poly(L-lactide-*b*-trimethylene carbonate-*b*-L-lactide),<sup>30</sup> and poly(L-lactide-*b*-[*R,S*]-3-hydroxybutyrate-*b*-L-lactide)<sup>31</sup> have been successfully prepared, and they provided a broad spectrum of mechanical and biodegradation properties to meet the demands of different ultimate applications. Interestingly, the AB or ABA type of biodegradable block copolyesters prepared from sequential ring opening polymerization of  $\epsilon$ -caprolactone and L-lactide monomers could be obtained provided that  $\epsilon$ -caprolactone was polymerized first. Otherwise, the sequential structure of resultant copolyesters would be randomized due to the presence of a rapid transesterification.<sup>32–35</sup> It was suggested that the poly(L-lactide) derived hydroxyl end groups were less reactive, thus leading to less or no transesterification.<sup>32</sup> This result provides a reasonable explanation for the formation of pure block structure of the above-mentioned block copolymers.

Poly(butylene succinate) (PBS) is one of the most commercially accessible biodegradable polymers. It has been extensively studied for potential applications as a feasible green polymer. PBS has been efficiently synthesized through condensation polymerization from the starting materials of succinic acid and 1,4-butanediol. High molecular weight PBS has been found to have a melting point around 114–118 °C, a glass transition temperature near –40 °C, and excellent elongation rate at break as well as the other physical properties similar to those of polyethylene.<sup>36–39</sup> In our previous studies, the catalyst dependence of PBS synthesis and its thermal stability were systematically investigated.<sup>40</sup> To develop a new biomaterial with tunable hydrophobic–hydrophilic balance, we preliminarily synthesized an optically active biodegradable poly(butylene succinate-*co*-butylene malate) P(BS-*co*-BM) with functionalizable hydroxyl pendant groups and random sequence distributions.<sup>41</sup> Moreover, on the basis of PBS macromolecular architectures, another biodegradable copolyester of poly(butylene succinate-*co*- $\epsilon$ -caprolactone) P(BS-*co*-CL) has been reported concerning its synthesis, physical characterization and biodegradation behavior.<sup>42</sup>

Considering the differences in chain flexibility, physical property, and biodegradation feature between biodegradable PLLA and PBS, Hong et al.<sup>43</sup> recently reported preparation of biodegradable polymer microspheres from the prepared PBS/PLLA blend and preliminary studies on their drug analogue releasing behavior. To share the merits of biodegradable PBS and PLLA in physical property, biocompatibility, and biodegradability, it seems interesting to prepare a new triblock poly(L-lactide-*b*-butylene succinate-*b*-L-lactide) bearing hard PLLA and soft PBS building blocks. Up to date, few related works have been reported on such a biodegradable triblock copolyester.

In this study, a series of new triblock PLLA-*b*-PBS-*b*-PLLA copolyesters were synthesized by ring opening poly-

**Scheme 1.** Schematic Preparation of Tri-Block PLLA-*b*-PBS-*b*-PLLAs



merization of L-lactide, employing a suitable bifunctional hydroxyl capped PBS prepolymer and SnOct<sub>2</sub> as the macro-initiator and catalyst. The resultant triblock copolyesters containing various average PLLA block lengths were systematically characterized by means of NMR, GPC, FTIR, WAXD, and thermal analytical instruments, and the correlation between the macromolecular structures and their physical properties will thus be discussed.

## Experimental Section

**Materials.** Succinic acid (SA, AR grade) was recrystallized twice from deionized water. 1,4-Butanediol (1, 4-BD, AR grade) was dried with CaCl<sub>2</sub> overnight and then distilled under reduced pressure prior to use. L-Lactide was generously provided by gentleman X. Pan of Synica Chemicals Ltd. (Shanghai, China), which was routinely synthesized from L-lactic acid and purified four times by recrystallization in ethyl acetate.<sup>44,45</sup> Stannous octoate from Aldrich Chemicals was distilled under reduced pressure and then dissolved in dry toluene before use. Toluene was pretreated with distillation in metallic sodium and benzophenone. All the other applied reagents were of analytical grade and used as received.

**Chemical Synthesis of PLLA-*b*-PBS-*b*-PLLA Triblock Copolyesters.** In this study, the PLLA-*b*-PBS-*b*-PLLA triblock copolyesters were prepared according to a synthetic route as seen in Scheme 1.

The bifunctional hydroxyl capped PBS macroinitiator with regulated molecular weight was prepared via a two-step procedure including esterification and subsequent polycondensation. First, 59.0 g (0.5 mol) of succinic acid and 54.0 g (0.6 mol) of 1,4-butanediol were charged into a 500 mL three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a Vigreux fractionation condenser. The esterification reaction was carried out under 210 °C and nitrogen flow for a period of 4.0 h with continuous removal of the released water. Then, the pressure of reaction system was gradually decreased, and the condensation polymerization was kept for 4 h at 210 °C under a final degree of vacuum lower than 0.5 mmHg. The viscous liquid product was cooled to the room temperature under nitrogen flow. Finally, the solid mass was dissolved in chloroform and precipitated with excess amount of cold dry methanol. The precipitate was collected by filtration and extensively washed with copious cold methanol and then dried under reduced pressure at 40 °C for 48 h.

**Table 1.** Chemical Syntheses of New Biodegradable Tri-Block PLLA-*b*-PBS-*b*-PLLAs

sample	L-LA/BS/Sn(Oct) <sub>2</sub> <sup>a</sup> (mol/mol/mol)	Lac/BS <sup>b</sup> (mol/mol)	L-LA monomer conversion (%)	molecular weight			
				$M_{n,NMR} \times 10^{-3}$ <sup>c</sup>	$M_w \times 10^{-3}$ <sup>d</sup>	$M_n \times 10^{-3}$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
H31	3/1/0.002	2.65/1	88.4	15.8	33.2	14.3	2.32
H21	2/1/0.002	1.74/1	86.9	12.0	28.9	12.6	2.21
H32	1.5/1/0.002	1.31/1	87.3	10.2	24.3	11.1	2.18
H11	1/1/0.002	0.82/1	82.0	8.3	22.6	10.2	2.22
H23	0.667/1/0.002	0.54/1	81.0	7.1	21.0	9.90	2.12
H12	0.5/1/0.002	0.31/1	62.0	6.2	18.7	8.95	2.09
H14	0.25/1/0.002	0.11/1	44.0	5.3	16.0	7.82	2.05
PBS				4.9	16.0	6.82	2.34

<sup>a</sup> Indicates the feeding molar ratios of L-lactide monomer, butylene succinate repeating unit BS and Sn(Oct)<sub>2</sub> catalyst. <sup>b</sup> Means the repeating unit molar ratios of  $-\text{OCH}(\text{CH}_3)\text{COOCH}(\text{CH}_3)\text{CO}-$  (Lac) and butylene succinate (BS) in the tri-block copolymers measured by <sup>1</sup>H NMR. <sup>c</sup> Number average molecular weights were calculated from <sup>1</sup>H NMR spectra. <sup>d</sup> Molecular weights were measured by GPC with PS standards.

On the basis of the prepared bifunctional hydroxyl capped PBS macroinitiator, PLLA-*b*-PBS-*b*-PLLA tri-block copolyesters were further synthesized via ring opening polymerization of L-lactide monomer with the SnOct<sub>2</sub> as the catalyst. A three-necked 50 mL flask was flamed and in turn charged with 2.0 g of the above prepared PBS, 69  $\mu\text{L}$  of the SnOct<sub>2</sub> toluene solution (SnOct<sub>2</sub> concentration: 130.0 mg/mL) and a predetermined amount of L-lactide monomer, as the feeding ratios shown in Table 1. The flask was connected to a vacuum line and heated to 50 °C for 1.0 h to eliminate toluene and the residual water. Then, the vacuum was released, and the reaction system was purged with nitrogen and elevated to 120 °C and further kept for 24 h. As a result, the crude product was attained and further dissolved in chloroform and precipitated by dry cold methanol. The precipitate was filtered and washed with abundant methanol and finally dried in vacuum oven at ambient temperature to a constant weight.

**Analytical Procedures.** *GPC Characterization.* Measurements of molecular weights were operated on a Perkin Elmer 200 Series gel permeation chromatography (GPC) equipped with a refractive index (RI) detector and a network chromatography interface NCI 900. Double PLgel 5 $\mu\text{m}$  mixed-D type of 300  $\times$  7.5 mm columns (PL Ltd., U.K.) set in series were applied with CHCl<sub>3</sub> as the eluent at a flowing rate of 1.0 mL/min under 40 °C. Polystyrene standards (Showa Denko Ltd., Japan) were employed to make a calibration curve. Hence, the molecular weights ( $M_w$ ,  $M_n$ ) and polydispersity indexes were accordingly evaluated for the PBS macroinitiators and tri-block copolyesters.

*NMR Measurement.* Macromolecular structure characterization by solution NMR was conducted under ambient temperature on a Varian VXR 300 FT-NMR spectrometer operated at 300.1 and 75.5 MHz, respectively. CDCl<sub>3</sub> and tetramethylsilane (TMS) were applied as the corresponding solvent and internal chemical shift standard.

*Fourier Transform Infrared Spectroscopy (FTIR).* FTIR spectra for the synthesized polymer samples were recorded in a manner of KBr tablet on a Bio-Rad FTS-185 FT-IR spectrometer. All FTIR spectra were collected under the room temperature over a scanning range of 400–4000 cm<sup>-1</sup> with a resolution of 4.0 cm<sup>-1</sup>.

*Wide-Angle X-ray Diffraction (WAXD).* WAXD patterns were measured under ambient temperature by a Rigaku-200

X-ray diffractometer (40 kV/40 mA). All of the samples were scanned from 5° to 40° at a rate of 8°/min, and the nickel-filtered copper K $\alpha$  X-ray beams with a pinhole graphite monochromator were applied as the incident source ( $\lambda$  = 0.154 nm).

*Thermal Analysis.* Thermal analyses of the polymer samples were implemented on a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC) and a Pyris 1 thermal gravimetric analyzer (TGA). DSC thermograms for the prepared block copolymers encapsulated in aluminum pans were recorded from the room temperature to 200 °C at a scanning rate of 20 °C/min (the first heating run). Continuously, the temperature was kept at 200 °C for 1.0 min and then rapidly quenched to –120 °C at a cooling speed faster than –450 °C/min. Then the samples were heated again from –120 to +200 °C at a rate of 20 °C/min (the second heating run). Melting point  $T_m$  and enthalpy of fusion ( $\Delta H_m$ ) were thus evaluated as the main peak top temperature and the integral of the corresponding endothermic peak recorded by the first DSC scan, respectively. Glass transition temperature ( $T_g$ ) and cold crystallization temperature ( $T_{cc}$ ) were estimated as the corresponding midpoint temperature of heat capacity change and the cold crystallization peak top temperature occurring in the recorded second DSC trace. With regard to thermal degradation behavior and thermal stability, TGA analyses were applied. Two to three milligrams of the investigated polymer samples were scanned from the room temperature to 450 °C at a heating rate of 10 °C/min under a flowing nitrogen atmosphere (45 mL/min). Peak top temperature ( $T_d$ ) of the differentiated TGA curve denoted as the dTGA trace was tentatively employed as an index to quantitatively assess thermal degradation behavior and thermal stability of the triblock copolyesters or PBS macroinitiator.

## Results and Discussion

**Synthesis of Dihydroxyl Terminated PBS Prepolymer and the Tri-Block Copolymers.** To synthesize new biodegradable aliphatic PLLA-*b*-PBS-*b*-PLLA triblock copolyesters, di-functional hydroxyl capped PBS macroinitiators should be first prepared. Commonly, low molecular weight is an inherent characteristic for aliphatic polyesters prepared by melt polycondensation due to the presence of competitive



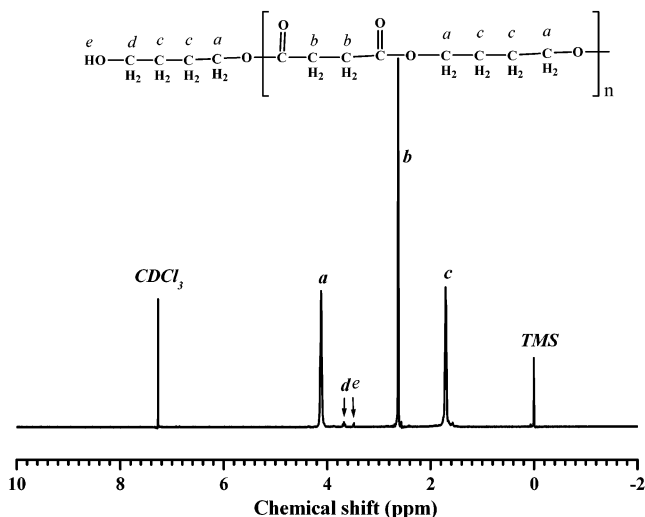


Figure 1. 300 MHz  $^1\text{H}$  NMR spectrum of the PBS prepolymer.

reactions between polycondensation and thermal degradation that will concurrently occur.<sup>46</sup> However, the molecular weight of PBS can be readily regulated in a range of  $10^3$ – $10^4$  Dalton by constantly removal of the excessive diol under vacuum. Meanwhile, the aliphatic polyester end groups can be controlled by adjusting the initial feeding molar ratio of diol to diacid. With an excessive amount of 1,4-butanediol, it can be expected that the PBS macromolecular chains will predominantly possess hydroxyl end groups, although there may still exist small amounts of carboxyl end groups stemming from the accompanying degradation reactions.<sup>46</sup> In this study, Figure 1 shows the  $^1\text{H}$  NMR spectrum of the synthesized PBS macroinitiator with the corresponding proton resonance signals assigned. The proton resonance signals occurring at 3.65 and 3.48 ppm can be reasonably assigned to the methylene proton and hydroxyl proton of  $\text{HOCH}_2\text{CH}_2$ – and no additional  $-\text{COOH}$  resonance signal could be detected within the instrumental limit. These experimental evidences prove that the synthesized linear PBS chains were terminated by hydroxyl functional end groups. Consequently, the number average molecular weight denoted as  $M_{n,\text{NMR}}$  as seen in Table 1 could be calculated from the intensity ratio of the  $-\text{OCH}_2\text{CH}_2$ – methylene proton signal and the  $\text{HOCH}_2\text{CH}_2$ – methylene proton signal occurring at 4.05 and 3.65 ppm, respectively.

As to the syntheses of PLLA-*b*-PBS-*b*-PLLA triblock copolyesters, ring opening polymerization of the L-lactide monomer was carried out in bulk with a prepared PBS prepolymer with  $M_n$  equal to 4.9 KDa as a suitable macroinitiator and  $\text{SnOct}_2$  as catalyst under 120 °C. It has been reported that less or no transesterification reactions occurred under such reaction conditions.<sup>27</sup> Table 1 summarizes the synthetic results with various feeding amounts of L-lactide monomer. Figure 2 shows the typical  $^1\text{H}$  NMR spectrum of the copolymerization product. It can be seen that the  $\text{HOCH}_2\text{CH}_2$ – methylene proton signal belonging to PBS ( $\delta = 3.65$  ppm) entirely disappeared. Furthermore, a new proton NMR signal at  $\delta = 4.35$  ppm attributed to the  $\text{HOCH}$  methine proton was present.<sup>32</sup> This result clearly demonstrated that the PBS derived hydroxyl group had initiated the ring opening polymerization of L-lactide and

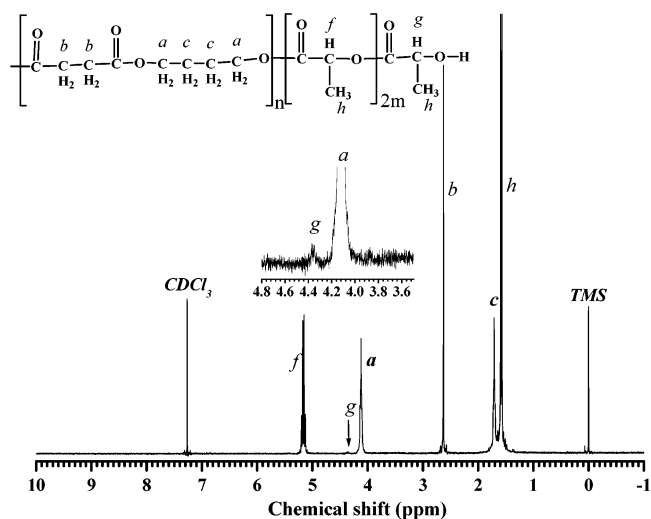


Figure 2. 300 MHz  $^1\text{H}$  NMR spectrum of the tri-block copolymer (H21).

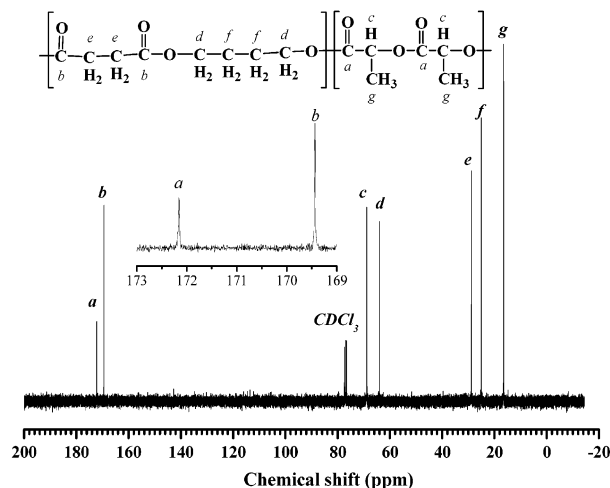
the copolymer chains were terminated by L-lactide derived hydroxyl groups. From the  $^1\text{H}$  NMR spectra, molar ratios of the  $-\text{OCH}(\text{CH}_3)\text{CO}-\text{OCH}(\text{CH}_3)\text{CO}-$  (Lac) to butylene succinate repeating unit (BS) (Lac/BS, Table 1) were determined from the corresponding intensities of the  $-\text{OCH}(\text{CH}_3)\text{CO}-\text{OCH}(\text{CH}_3)\text{CO}-$  (Lac unit) methine proton signals at 5.15 ppm and the  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{COCH}_2\text{CH}_2\text{CO}-$  (BS unit) methylene proton signals at 4.05 ppm. The conversions of the L-LA monomer were calculated by the comparison of Lac/BS ratios in the resultant copolymers and L-LA/BS ratios in the feeds. It indicates that the conversions of L-lactide monomer were over 80% when the feeding molar ratio of L-lactide monomer to the BS repeating unit became greater than 2/3. Otherwise, the value of the L-lactide monomer conversion rapidly decreased as seen for samples H12 and H14 in Table 1. This phenomenon may be attributed to either the partial sublimation of the L-lactide monomer during the process of copolymerization or the reversibility of lactide polymerization which results in a relatively high concentration of the unreacted monomer at equilibrium,<sup>47</sup> or both. The  $M_{n,\text{NMR}}$  values of the copolymers (Table 1) were calculated from the sum of the  $M_{n,\text{NMR}}$  value of the PBS prepolymer and the number average molecular weight of the corresponding poly(L-lactide) part of the copolymers determining from the intensity ratios of the  $\text{OCH}$  methine proton signals ( $\delta = 5.15$  ppm) and the  $\text{HOCH}$  terminal methine proton signals ( $\delta = 4.35$  ppm). Clearly, the  $M_{n,\text{NMR}}$  values of the copolymers increased along with the increasing of the contents of Lac repeating unit in the copolymers. The segment lengths of each block, in other words degree of polymerization (DP, Table 2) of each part, can thus be estimated from the corresponding  $M_{n,\text{NMR}}$  values.

Figure 3 presents a typical  $^{13}\text{C}$  NMR spectrum for the prepared copolyester (H21) with Lac/BS repeating unit molar ratio equal to 1.74. From the inset of Figure 3, it can be clearly observed that only two distinct carbonyl  $^{13}\text{C}$  signals occurring at 172.2 and 169.5 ppm could be detected, which were attributed to corresponding carbonyl  $^{13}\text{C}$  resonances of the PBS and PLLA segments. The absence of any intermediate signals between the two carbonyl  $^{13}\text{C}$  resonance signals

**Table 2.** Thermal Properties of Biodegradable Tri-Block PLLA-*b*-PBS-*b*-PLLAs

sample	$T_g$ (°C) <sup>a</sup>	$T_{cc}$ (°C) <sup>a</sup>	PLLA block				PBS block			
			$T_m$ (°C) <sup>b</sup>	$\Delta H_m$ (J/g) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>	DP <sup>d</sup>	$T_m$ (°C) <sup>b</sup>	$\Delta H_m$ (J/g) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>	DP <sup>d</sup>
H31	13.4	68.0	163.5	45.2	291.9	37.8	105.6	19.2	367.1	28.5
H21	-0.94	63.8	162.4	37.7	280.3	24.8	106.6	28.2	381.5	28.5
H32	-1.69	59.2	157.0	35.2	267.2	18.7	108.1	36.2	381.9	28.5
H11	-17.0	51.6	156.5	25.6	254.8	11.7	108.4	49.5	371.6	28.5
H23	-23.7	30.4	150.1	8.55	250.5	7.8	109.2	62.5	380.6	28.5
H12	-29.7	21.2	e	e	237.0	4.4	110.0	74.3	376.6	28.5
H14	-29.4	5.40	e	e	232.0	1.6	110.8	87.9	375.6	28.5
PBS	-29.5	e	e	e	e	0	115.1	93.2	402.2	28.5

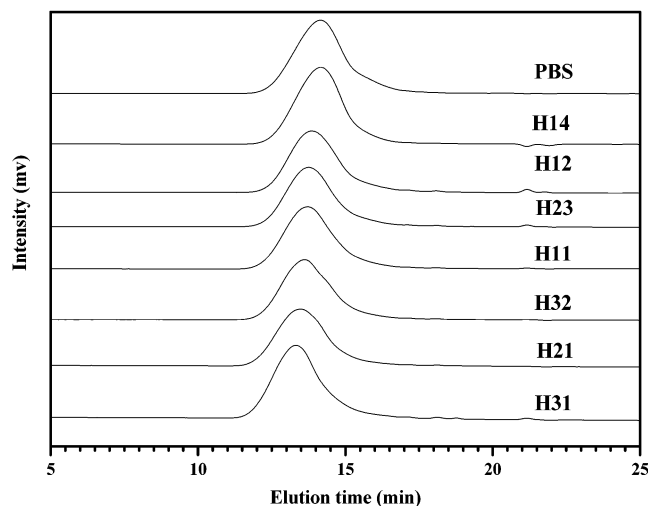
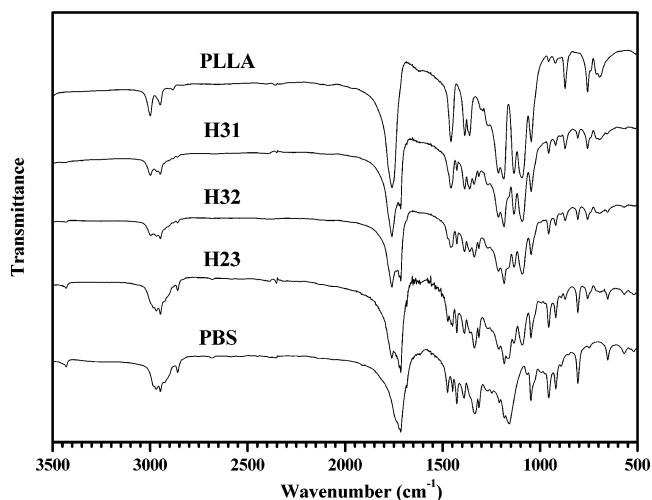
<sup>a</sup>  $T_g$  and  $T_{cc}$  (cold crystallization temperature) were estimated from the second DSC heating run at 20 °C/min after a rapid quenching. <sup>b</sup>  $T_m$  and  $\Delta H_m$  were measured from the first DSC scan at a heating rate of 20 °C/min. <sup>c</sup> The peak top temperatures ( $T_d$ ) in the dTG traces were measured by TGA with a scanning rate of 10 °C/min. <sup>d</sup> The average degree of polymerization of each block was calculated from  $M_{n,NMR}$  (Table 1). <sup>e</sup> Not detected.

**Figure 3.** 75.5 MHz  $^{13}\text{C}$  NMR spectrum of the tri-block copolymer (H21).

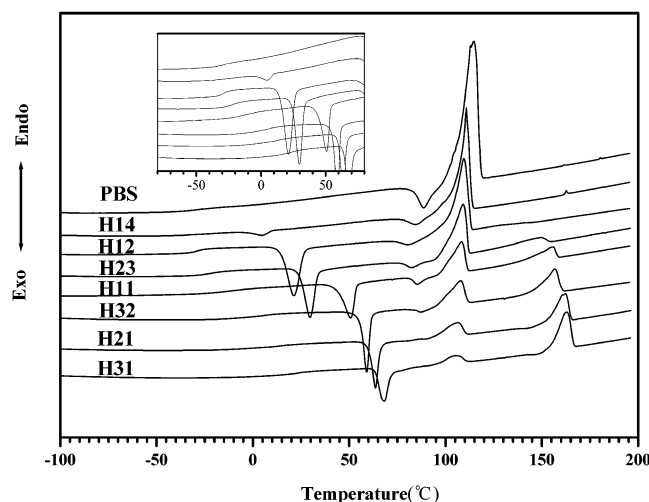
demonstrates that no transesterification happened during the ring opening polymerization process under such reaction conditions. The formation of the pure triblock structure can thus be confirmed. In contrast, according to the literature, poly(butylene succinate-*co*-lactide) with randomized sequence distribution was found to show 4~6  $^{13}\text{C}$  NMR signals in the carbonyl region, which reflected the presence of different sequential microstructures.<sup>48</sup> Therefore, it can be concluded that the PLLA-*b*-PBS-*b*-PLLA triblock copolyesters bearing various PLLA block lengths were successfully synthesized.

Figure 4 depicts the GPC traces of the prepared copolyesters as well as the PBS prepolymer, all of which show unimodal elution traces. With increasing Lac repeating unit content, the GPC elution trace was found to gradually shift toward a higher molecular weight region, which was in good agreement with the results from  $^1\text{H}$  NMR analysis (Table 1). Moreover, their molecular weight distributions are of 2.0~2.4, with little broadening compared with the original PBS. There is an approximately linear correlation between molecular weights of  $M_n$  and  $M_w$  and the molar ratios of Lac/BS unit in the triblock copolyesters. These results demonstrate that the molecular weight as well as average block length of PLLA could be well regulated by adjusting the initial feeding molar ratio of L-lactide monomer to the PBS macroinitiator.

Figure 5 shows FTIR spectra of some synthesized triblock copolyesters as well as the PBS, PLLA homopolymers. For

**Figure 4.** GPC elution traces of the tri-block copolymers and PBS macroinitiator.**Figure 5.** FTIR spectra of the block copolymers and PBS/PLLA homopolymers.

the PLLA-*b*-PBS-*b*-PLLA triblock copolyesters, two strong absorption bands could be obviously detected at 1760 and 1715  $\text{cm}^{-1}$  which were originated from the bond vibration of ester carbonyl groups of the PLLA and PBS blocks, respectively. When the PLLA average block length increased from 0 for the PBS prepolymer to 37.8 for PLLA-*b*-PBS-*b*-PLLA tri-block sample H31, the intensity of carbonyl IR absorption of the PLLA segment at 1760  $\text{cm}^{-1}$  increased as compared with that of the PBS part at 1715  $\text{cm}^{-1}$ . A similar

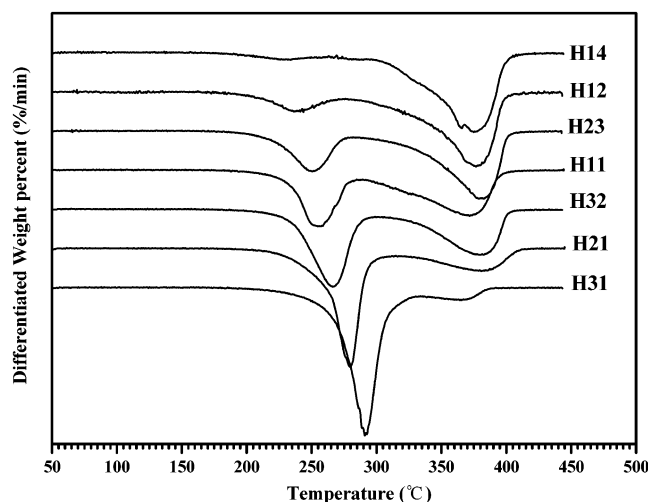


**Figure 6.** DSC traces of tri-block copolymers with various PLLA block lengths (the second run).

phenomenon can be seen for the PLLA-*b*-PCL-*b*-PLLA tri-block copolyesters, whereas their random copolyesters only exhibited one ester carbonyl FT-IR absorption.<sup>34</sup> These FT-IR experimental results provide new proofs for the formation of triblock copolymers.

**Thermal Properties of the Copolymers.** In this study, thermal properties of the copolymers were characterized by means of DSC and TGA, and the results are summarized in Table 2. Figure 6 shows the typical DSC curves of the PLLA-*b*-PBS-*b*-PLLA triblock copolymers bearing various average PLLA block length on the identical PBS block. All samples were subjected to the second heating run after rapid quenching in liquid nitrogen from 200 °C. These curves indicate the presence of a few characteristic transitions, such as glass transition, cold crystallization, and melting, which are typical for semicrystallization polyesters. As more clearly shown in the inset of Figure 6, each sample exhibits a single glass transition step, and the corresponding glass transition temperature spans between −36 °C for PBS and 56 °C for PLLA homopolymers (Table 2).<sup>49</sup> The occurrence of a single glass transition step indicates that the amorphous chain/segments attributed to the PBS and PLLA blocks were well mixed, thus leading to formation of a miscible amorphous phase. Because the glass transition temperature of the PLLA homopolymer is more than 90 °C higher than that of the PBS homopolymer, much lower chain/segmental flexibility was found for the PLLA block. As seen in Table 2, the glass transition temperatures show a strong dependence on the comonomer content in these triblock copolyesters, and the segmental flexibility and mobility of PLLA block were remarkably enhanced through mixing with a more flexible PBS block.

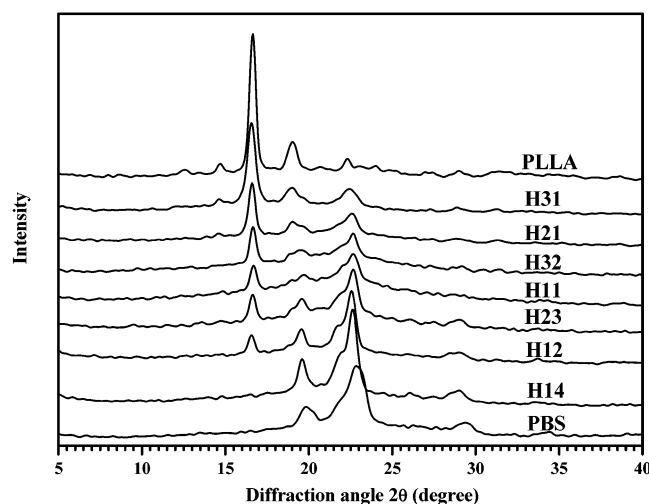
With respect to cold crystallization phase transition for the PLLA-*b*-PBS-*b*-PLLA triblock copolyesters, there only exists one cold crystallization transition peak in each thermal scanning trace. From sample H14 to H31 with PLLA average block length changing from 1.6 to 37.8, the cold crystallization transition peaks seem to shift monotonically toward high temperatures. This result may be suggested by the reason that the segmental flexibility and chain crystallizability of the PBS and PLLA blocks were tuned and moved toward



**Figure 7.** dTGA traces of the tri-block copolymers with various PLLA block lengths.

each other. It has been reported that the cold crystallization temperatures of the individual PBS and PLLA were −2.9<sup>42</sup> and 106 °C<sup>49,50</sup> respectively. The increased  $T_{cc}$  for the PBS block and the decreased  $T_{cc}$  for the PLLA block shifted toward each other and approached similar temperature when the PLLA average block length increased to a certain extent. On the basis of  $\Delta H_m$  and  $T_m$  results estimated from the first heating scan as seen in Table 2, only PBS block could assembly crystal structure for sample H14 and H12 with  $T_m$  near 110 °C. For PLLA-*b*-PBS-*b*-PLLA triblock copolyesters with a PLLA average block length more than 7.8, both PBS and PLLA crystal structures seemed to be concurrently assembled. Two distinct melting points could be observed around 110 and 160 °C corresponding to the  $T_m$  of the PBS and PLLA block, which is in close agreement with the melting behavior of their relative homopolymers.<sup>40,48,49</sup> These results provide a clear evidence for the phase separated morphology of the assembled crystals in the triblock PLLA-*b*-PBS-*b*-PLLA. It can also be seen that the apparent melting peak of the crystallizable PLLA block tends to shift toward a high temperature with an increased heat of fusion when the average PLLA block length in the triblock copolyester increased. This result can be suggested because these different PBS and PLLA blocks in the triblock macromolecular chains would act as impurities to disturb crystallization of the block partners and finally reduce their crystallite sizes, increase the surface free energy of crystallites, and decrease the thickness of lamellae, thus leading to generate less perfect crystals. In addition, DSC analysis indicates that a critical block length larger than 7.8 is necessary for crystallization of PLLA block.<sup>46</sup>

On the other hand, thermal degradation behavior and stability are of great importance for application of biodegradable aliphatic polyester. Here, to make a quantitative assay of thermal stabilities of the synthesized copolymers, peak top temperatures ( $T_d$ ) of the corresponding differentiated TGA traces (dTGA) were applied as shown in Figure 7 and Table 2. Clearly, two thermal degradation steps are presented for all copolymer samples containing different Lac/BS unit molar ratios. The PBS block exhibits a higher  $T_d$  of 380 °C as previously reported<sup>40</sup> although the applied sample had a



**Figure 8.** WAXD patterns of the tri-block copolymers as well as PBS and PLLA.

low molecular weight about several thousands, and the peak at a lower temperature side belongs to thermal degradation of the PLLA block. It is interesting to note that  $T_d$ 's of the PLLA block increased along with extending the average PLLA block length, whereas those of the PBS block were not remarkably changed in most cases. Hence, the average block length was found to play a very important role in both crystallization behavior and thermal stability for the PLLA block in the PLLA-*b*-PBS-*b*-PLLA copolymers. According to the literature, the end functional groups significantly affected thermal degradation and stabilities for polyesters, and the high molecular weight samples containing less hydroxyl and/or carboxylic acid end groups were expected to have higher thermal stabilities.<sup>51,52</sup> So, the tri-block PLLA-*b*-PBS-*b*-PLLA samples with higher molecular weight contain longer PLLA block lengths and less hydroxyl end groups, thus exhibit higher thermal stabilities.

**Wide Angle X-ray Diffraction and Crystal Structures of the Tri-Block Copolymers.** Figure 8 shows the wide angle X-ray diffraction patterns at ambient temperature for the semicrystalline PLLA-*b*-PBS-*b*-PLLA triblock copolymers with various Lac/BS repeating unit molar ratios as well as PBS and PLLA. It can be observed that the PBS and PLLA showed distinct WAXD patterns. The semicrystalline PBS sample exhibited characteristic X-ray diffraction peaks at  $2\theta = 19.6$  and  $22.6^\circ$ , whereas those of the PLLA homopolymer were detected at  $2\theta = 16.6$  and  $19.0^\circ$ . Regarding crystal structures of the triblock copolymers, there is no detectable PLLA crystalline peak when the PLLA block content is lower than 10% (sample H14), which is well consistent with the DSC result. However, all of the samples with a longer block length of PLLA clearly showed the X-ray diffraction peaks at  $16.6$ ,  $19.0$ ,  $19.6$ , and  $22.6^\circ$ , the characteristic of PBS and PLLA crystallites. This result unambiguously demonstrated that the PBS and PLLA blocks formed well self-assembled corresponding PBS and PLLA type of crystal structures. In addition, the diffraction intensities varied concurrently with the average PLLA block lengths, and a similar tendency can be detected by the DSC analysis.

## Conclusions

In summary, a series of new biodegradable aliphatic PLLA-*b*-PBS-*b*-PLLA triblock copolyesters with soft PBS and hard PLLA building blocks were synthesized via ring opening polymerization of L-lactide under  $120^\circ\text{C}$  in bulk, employing the hydroxyl capped PBS prepolymer and  $\text{SnOct}_2$  as the macroinitiator and catalyst. Varying the feeding molar ratio of L-lactide monomer to the PBS macroinitiator, the syntheses of triblock copolyesters were well regulated with tunable average PLLA block lengths and molecular weights. Based on the NMR characterization, the PBS prepolymer was confirmed to be terminated by reactive hydroxyl groups, and two distinct carbonyl  $^{13}\text{C}$  resonance peaks occurring at 172.2 and 169.5 ppm demonstrated their block structures of the synthesized triblock copolyesters without any detectable transesterification. GPC elution traces of all of the samples showed unimodal signals and gradually shifted to the high molecular weight region when the average PLLA block length increased. Moreover, FTIR characterization of the triblock copolyesters indicated two intrinsic strong and sharp absorption bands at  $1760$  and  $1715\text{ cm}^{-1}$  attributed to ester carbonyl bond vibrations of the PLLA and PBS blocks as referred to those of the PLLA and PBS. With regard to thermal properties, only one glass transition temperature could be detected for all block copolymers, indicating good miscibility of the PBS and PLLA blocks in the amorphous regions, and the chain and/or segmental mobilities of PLLA blocks were remarkably enhanced by a more flexible PBS block partner. In addition, DSC analyses and WAXD patterns confirmed the coexistence of individual crystalline structures of the PLLA and PBS blocks when the PLLA block length became larger than 7.8. Additionally, all triblock copolyesters exhibited two thermal degradation steps regardless of their average PLLA block lengths, and thermal stabilities of the PLLA blocks were found to strongly depend on the average PLLA block length. These results may be beneficial for this new biodegradable aliphatic triblock copolyester to be applied as a potential biomaterial.

Further studies are now under investigation on biocompatibility and biodegradation behavior of microspheres and biomaterials prepared from corresponding low and high molecular weight triblock copolyesters.

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