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ORIGINAL ARTICLE

# Syntheses of poly(L-lactide)-*block*-xylan butyrate-*block*-poly(L-lactide) triblock copolymers and their properties

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**Abstract** Di-hydroxyl-terminated xylan butyrate (XylBu) with two hydroxyl end groups at opposite ends of the polymer was prepared by acid hydrolysis of XylBu. L-Lactide was polymerized on to the hydroxyl groups at both ends of XylBu, by ring opening. Structural characterization of the polymerization products was carried out using GPC and NMR analyses. It was confirmed that the polymerization products were mixtures of a poly(L-lactide) (PLLA)-*b*-XylBu-*b*-poly(L-lactide) (PLLA) triblock copolymer and PLLA homopolymer. Crystallization behaviors of the polymerization products were investigated by differential scanning calorimetry measurements and polarizing optical microscopy observation to investigate the effects of the triblock copolymer on crystallization of PLLA components.

**Keywords** Hemicellulose · Xylan · PLLA · Block copolymer · Crystallizations

## Introduction

Hemicellulose, along with cellulose is one of the most abundant polysaccharides. It makes up 25–30 % of a plant cell wall and is a promising biomaterial for a variety of applications. Hemicellulose can be easily obtained from plants by an aqueous, basic extraction [1]. It has lower molecular weight than cellulose, consisting of various sugar components with branched structures that depend on its source [2–5]. In contrast to cellulose and its derivatives, hemicellulose has little importance in industrial applications, such as thermoplastic or biodegradable materials.

Xylan is a major component of hemicellulose and has a backbone consisting of $\beta(1 \rightarrow 4)$ xylopyranose units. There have been several studies on functionalization of xylan by chemical modification, and it has recently received attention as a new bio-based material [6–11]. We have reported the syntheses and characterization of xylan alkyl esters and graft copolymers for utilization of xylan as a plastic material [12–14].

While polysaccharide-based graft copolymers and glycopolymers have been widely studied, there has been less focus on polysaccharide-based block copolymers. In particular, linear copolymers consisting of polysaccharide and other polymer blocks may have potential for applications in drug delivery systems or plastic materials [15]. Block copolymers show unique properties such as self-assembly, phase separation and specific crystallization behavior, and can behave as mixing agents for multiple polymers [16–21].

Poly(lactic acid) (PLA) and poly(hydroxyalkanoate)s, such as poly(ε-caprolactone), have been studied extensively as biodegradable plastic materials. These biodegradable polyesters are expected to be suitable counterblocks with sufficiently different properties to polysaccharides. Polysaccharide–polyester graft copolymers materials have shown attractive properties, such as biodegradability, biocompatibility or thermoplasticity [22–26]. There is, however, relatively little report on the corresponding polysaccharide/polyester block copolymers. In a few reports, copolymers consisting of dextran or maltoheptaose and poly(ε-caprolactone) were prepared for the purpose of micelle formation and drug delivery [27, 28].

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In this study, we aimed to synthesize a block copolymer consisting of XylBu and PLLA for application as a bioplastic material. Di-hydroxyl-terminated XylBu, with two hydroxyl groups, one at the C1 position of the reducing end and another at the C4 position of the non-reducing end, were prepared as initiators. PLLA-*b*-XylBu-*b*-PLLA triblock copolymers were obtained by polymerization of L-lactide on the hydroxyl groups at both ends of di-hydroxyl-terminated XylBu. The products were analyzed based on their crystallization behaviors.

## Experimental

### Materials

Eucalyptus kraft pulp sheet was kindly provided by Nippon Paper Group, Inc. (Tokyo, Japan). L-Lactide was kindly provided by Musashino Chemical Laboratory Ltd. (Saitama, Japan) and crystallized from ethyl acetate before use. Lithium chloride (LiCl) was dried at 105 °C overnight. Tin (II) octanoate (Sn(Oct)$_2$) and all other reagents were commercially obtained and used without further purification.

### Xylan butyrate (**1**)

Dried xylan (0.50 g, dried at 105 °C overnight) extracted from eucalyptus kraft pulp was dispersed in dimethylacetamide (DMAc) (20 mL) and stirred at 120 °C for 2 h. The slurry was cooled to 100 °C and LiCl (0.87 g) was added to the reaction mixture. After 1.5 h, butyric anhydride (2.5 mL) and pyridine (2.5 mL) were added to the reaction mixture and stirred at 50 °C for 2 days. After completion of the reaction, the mixture was poured into ethanol (300 mL) and a precipitate formed. The precipitate was separated by filtration, washed with ethanol and distilled water, and then dried *in vacuo* to give solid, xylan butyrate (XylBu) (**1**) (0.80 g, 77.4 % yield). Number and weight average molecular weights ($M_n$ and $M_w$) and polydispersity index (PDI) ($M_w/M_n$) were $M_n = 3.15 \times 10^4$, $M_w = 5.80 \times 10^4$ and $M_w/M_n = 1.84$, respectively. The degree of substitution (DS) of the butyryl group was determined as 2.0, calculated from the ratio of the integrated butyryl group methyl and the xylan aromatic proton resonances. Thus, $DS = (I_{(CH3)}/3)/(I_{(ring\text{-}H)}/6)$, where $I_{(CH3)}$ and $I_{(ring\text{-}H)}$ are the integrated areas of the butyryl group, methyl protons (3H) and the ring protons (6H), respectively. $^1$H-NMR (CDCl$_3$): δ 0.92 (t, 3H, –C$H_3$), 1.59 (m, 2H, –C$H_2$–CH$_3$), 2.21 (br t, 2H, –CO–CH$_2$–), 3.23 (C5–H$_a$), 3.73 (C4–H), 3.86 (C5–H$_e$), 4.42 (C1–H), 4.72 (C2–H), 5.03 (C3–H), 5.65 (C1–H$_\beta$ (reducing end), $J = 8.0$), 6.22 (C1–H$_\alpha$ (reducing end), $J = 3.5$). $^{13}$C-NMR (CDCl$_3$): δ 13.6 (CH$_3$), 18.1, 18.2 (–$C$H$_2$–CH$_3$), 35.8, 35.9 (–CO–$C$H$_2$–), 62.7 (C5), 70.7 (C2), 71.7 (C3), 75.0 (C4), 100.5 (C1), 171.9, 172.4 (CO of C2 and C3, respectively).

### Perbutyryl xylosyl α-bromide (**2**)

Perbutyryl xylosyl α-bromide was prepared for characterization of the reducing end by NMR analysis. To a solution of XylBu (0.10 g) in chloroform (3 mL), 30 % hydrogen bromide (HBr) in acetic acid (0.1 mL) was added at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was poured into ethanol to form a precipitate. The precipitate was collected by centrifugation (5,000 rpm, five times), washed with ethanol, and dried *in vacuo* to give butyryl xylan α-bromide (**2**) (31.7 mg, 31.7 % yield). $M_n = 0.49 \times 10^4$, $M_w = 0.78 \times 10^4$, $M_w/M_n = 1.59$. $^1$H-NMR (CDCl$_3$): reducing end, 6.52 (C1–H$_\alpha$, $J = 4.0$).

### Di-hydroxyl-terminated xylan butyrate (**3**)

To a solution of XylBu (0.60 g) in chloroform (7 mL), 30 % hydrogen bromide in acetic acid (0.5 mL) was added at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was poured into a saturated aqueous solution of sodium hydrogen carbonate to neutralize the reaction and quench degradation. The resulting mixture was stirred at 40 °C for 2 days to evaporate chloroform. The compound that precipitated was filtered off, washed with water and dried *in vacuo* to give di-hydroxyl-terminated XylBu (**3**) (0.52 g, 86.6 % yield). $M_n = 0.39 \times 10^4$, $M_w = 0.81 \times 10^4$, $M_w/M_n = 2.06$. $^1$H-NMR (CDCl$_3$): the reducing end: 3.77 (C4–H$_\alpha$, overlapped), 4.61 (d, C1–H$_\beta$, $J = 7.5$), 4.77 (C2–H$_\alpha$, overlapped), 5.31 (d, C1–H$_\alpha$, $J = 3.5$), 5.43 (t, C3–H$_\alpha$, $J = 10.0$). $^{13}$C-NMR (CDCl$_3$): the reducing end: 69.4 (C3–H$_\alpha$), 90.4 (C1–H$_\alpha$), 96.1 (C1–H$_\beta$).

### PLLA-*b*-xylan butyrate-*b*-PLLA triblock copolymers

PLLA-*b*-XylBu-*b*-PLLA copolymers were synthesized by ring-opening polymerization of L-lactide in bulk with di-hydroxyl-terminated XylBu (**3**). In a typical procedure, di-hydroxyl-terminated XylBu (**3**) (0.10 g, 1 eq.) and L-lactide (0.90 g, 260 eq.) were loaded into a flask and dried in vacuo for 12 h. Subsequently, the flask was degassed and heated in an oil bath at 160 °C, without solvent. The reaction mixture turned to a transparent liquid after 1 h. The flask was purged with nitrogen and then Sn(Oct)$_2$ (15 μL) was immediately loaded under a nitrogen atmosphere. The flask was degassed again and the mixture was stirred in vacuo (3 kPa) for 1 h. The reaction mixture was dissolved in chloroform and then precipitated by addition to methanol (300 mL). The precipitated compound was filtered, washed with methanol and dried in vacuo to obtain the polymerization product (0.78 g, 78.0 % yield). Composition of XylBu and PLLA blocks in the copolymer was controlled by varying the in-feed ratio of L-lactide/XylBu. Polymerization products were found to be mixtures of PLLA-*b*-XylBu-*b*-PLLA triblock copolymer and PLLA homopolymer. Molecular weights of the copolymer and PLLA homopolymer were calculated from GPC and NMR analyses and noted as M(copolymer) and M(PLLA), respectively. $^1$H-NMR ($CDCl_3$): δ 0.92 (t, 3H, –$CH_3$), 1.49 (d, 3H, $CH_3$ (PLLA, end)), 1.48, 1.58, 1.59 ($CH_3$), 1.59 (m, 2H, –$CH_2$–$CH_3$), 2.21 (br t, 2H, –CO–$CH_2$–), 3.23 (C5–$H_a$), 3.73 (C4–H), 3.86 (C5–$H_e$), 4.36 (q, 1H, C*H (end)), 4.42 (C1–H), 4.72 (C2–H), 5.03 (C3–H), 5.17 (C*H), 5.65 (d, C1–$H_\beta$ (reducing end), $J = 8.0$), 6.22 (d, C1–$H_\alpha$ (reducing end), $J = 3.5$).

## PLLA

Poly(L-lactide)s (PLLAs) were prepared by ring-opening polymerization of L-lactide in toluene with $Sn(Oct)_2$ as catalyst. A representative procedure for PLLA ($M_n = 1.8 \times 10^4$, $M_w = 2.2 \times 10^4$, $M_w/M_n = 1.23$) is as follows. To a solution of L-lactide (1.00 g, 35 eq.) in anhydrous toluene (4 mL), $Sn(Oct)_2$ (0.07 mL, 1 eq.) was immediately added at 90 °C. The reaction mixture was stirred for 24 h under nitrogen. After polymerization the mixture was cooled to room temperature, precipitated in methanol (500 mL), collected and washed with methanol by centrifugation at 10,000 rpm and dried to give a solid (0.68 g, 67.9 % yield). PLLA ($M_n = 0.7 \times 10^4$, $M_w = 0.8 \times 10^4$, $M_w/M_n = 1.12$) was prepared in the same manner using L-lactide (1.00 g, 15 eq.) and $Sn(Oct)_2$ (0.15 mL, 1 eq.) in anhydrous toluene (20 mL) with a yield of 0.28 g (27.9 %).

## Nuclear magnetic resonance (NMR) measurement

$^1$H, $^{13}$C, double quantum filter correlation spectroscopy (DQF-COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC) and totally correlated spectroscopy (TOCSY) NMR spectra were recorded with a JEOL JNM-A500 FT-NMR (500 MHz) spectrometer, with tetramethylsilane (TMS) as internal standard. Chemical shifts ($\delta$) and coupling constants ($J$) are reported in (ppm) and (Hz), respectively.

## Gel permeation chromatography (GPC) measurement

Number and weight average molecular weights ($M_n$ and $M_w$) and PDI ($M_w/M_n$) were estimated by GPC (CBM-20A, DGU-$20A_3$, LC-6AD, SIL-$20AC_{HT}$, CTO-20A, RID-10A, Shimadzu) in chloroform at 40 °C. Shodex columns (K-806M, K-802) were used and the flow rate was 0.8 mL/min. A calibration curve was obtained using polystyrene standards (Shodex).

## Differential scanning calorimetry (DSC) measurement

DSC thermograms were recorded with a DSC8500 (Perkin-Elmer) under a nitrogen atmosphere. The samples were first heated from 30 to 200 °C (first heating scan) at 20 °C/min, then immediately quenched to −70 °C. The second heating scans were run from 50 to 200 °C at a heating rate of 20 °C/min. Glass transition temperatures were defined as the midpoint temperature of the heat capacity transition in the second heating scan. For isothermal crystallization, the samples were heated from 30 to 200 °C at 20 °C/min. The samples were then quenched to the desired crystallization temperatures (80, 90, 100, 110, 120 °C). The samples were held at the given temperature until crystallization was completed.

## Polarized optical microscopy (POM)

Samples were pressed between two glass plates and heated at 200 °C for 30 s. The spherulite morphologies of the samples were observed using Nikon E600 POL polarized microscope equipped with a hot stage. Samples were first melted on the hot stage preheated at 200 °C for 30 s and transferred immediately to the hot stage preheated at a desired crystallization temperature. The images were captured using Motic Image Plus 2.2S software. The growing rate of the spherulites was analyzed using public domain ImageJ program [29].

# Results and discussion

## Preparation of xylan butyrate (XylBu) (**1**)

The basic synthetic strategy for the polysaccharide-based block copolymer was to modify the end group of the polysaccharide chain to allow connection of other polymers by polymerization or coupling. One approach for end group modification is acid hydrolysis of polysaccharide esters or ethers, and resulting introduction of a hydroxyl group at C1 of the reducing end or C4 of the non-reducing end [30–32]. For synthesis of xylan-PLLA block copolymer, we first prepared di-hydroxy-terminated xylan butyrate (XlyBu) (**3**) by acid hydrolysis of XlyBu (**1**), as shown in Fig. 1. XlyBu (**3**) was used as the initiator for a polymerization with L-lactide, where growth of the PLLA block occurred from the hydroxyl groups at the both ends of the XlyBu block. Acetyl and propionyl groups were found to

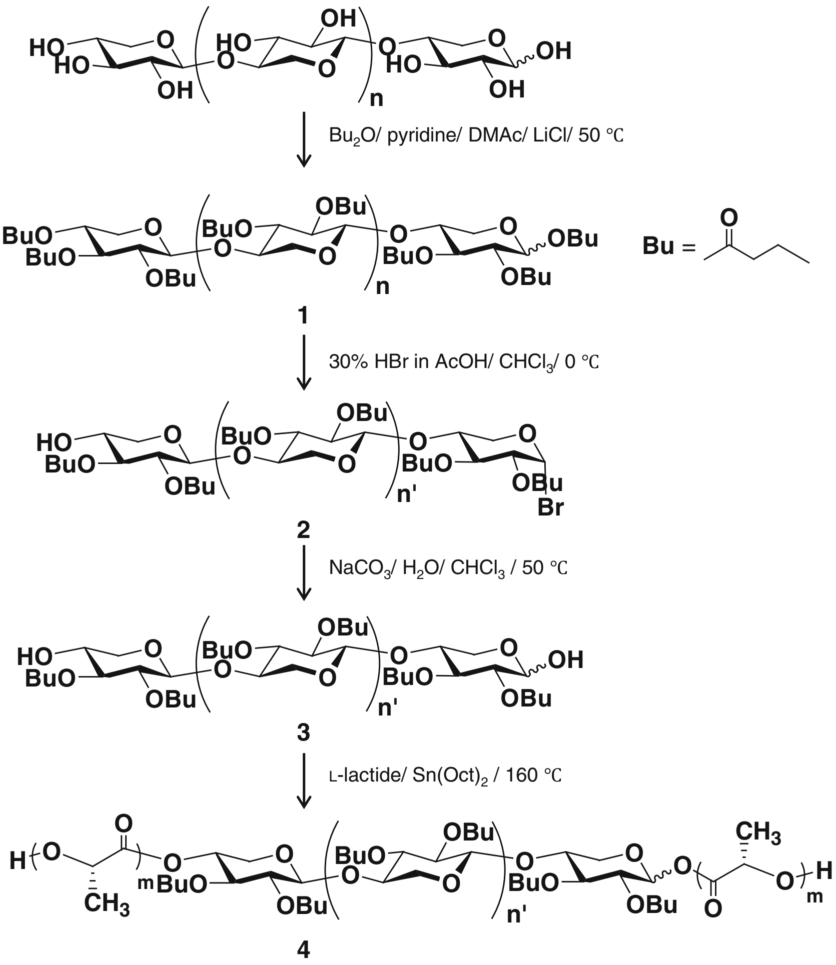

**Fig. 1** Preparation of XylBu (**1**), perbutyryl α-xylosyl bromide (**2**), di-hydroxyl-terminated XylBu (**3**) and PLLA-*b*-XylBu-*b*-PLLA triblock copolymer (**4**)

be unsatisfactory protecting groups, because the esters formed showed low solubility in chloroform and other common organic solvents, such as dimethylformamide. The butyl esters of XylBu showed much better solubility in these solvents.

The original xylan was extracted from Eucalyptus kraft pulp according to previous work [12]. XylBu (**1**) was prepared from the extract by treatment with butyric acid anhydride and pyridine in a homogeneous mixture of DMAc/LiCl [4]. The number and weight averaged molecular weights of XylBu (**1**) were estimated to be $M_n = 3.15 \times 10^4$, $M_w = 5.80 \times 10^4$ by GPC. Figure 2 shows the $^1$H-NMR spectrum of XylBu (**1**). Peaks were assigned according to reported data in the previous article [12, 13]. The degree of substitution of butyryl group (DS) was calculated to be 2.0 from the ratio of integrated areas of the alkyl group methyl and xylan aromatic protons. The two peaks at 6.22 (C1–H$_\alpha$, $J = 3.5$ Hz) and 5.65 (C1–H$_\beta$, $J = 8.0$ Hz) ppm were assigned to α and β anomeric protons at the reducing end, respectively. These assignments were in good accordance with those of cellulose triacetate [33, 34].

### Preparation of perbutyryl α-xylosyl bromide (2)

XylBu (**1**) was treated with HBr in acetic acid to obtain perbutyryl α-xylosyl bromide (**2**) via acidic hydrolysis. HBr was selected as a suitable reagent, because it did not cause cleavage of other ester groups. While the acid treatment caused some depolymerization of the main chain, the reactivity of the end groups was achieved. During the hydrolysis, a bromine group was introduced at the C1 position of the reducing end [30, 31, 34, 35]. Additionally, the C4 position of the non-reducing end was hydrolyzed to hydroxyl group. These functionalities were deemed useful for further transformations of the polymer [32, 36]. Aside from C1 position at the reducing end and C4 position at the non-reducing end, the DS of the butyryl group at the C2 and C3 positions of the xylan main chain was calculated to 2 from the peaks of butyryl protons in Fig. 2b. This indicated that no cleavage of ester groups at C2 or C3 positions occurred and that butyryl groups were not replaced by acetyl groups during this step. The C1–H proton of only the α-anomer was observed at 6.53 ppm ($J = 4.2$ Hz), indicating complete bromination at the reducing end. The

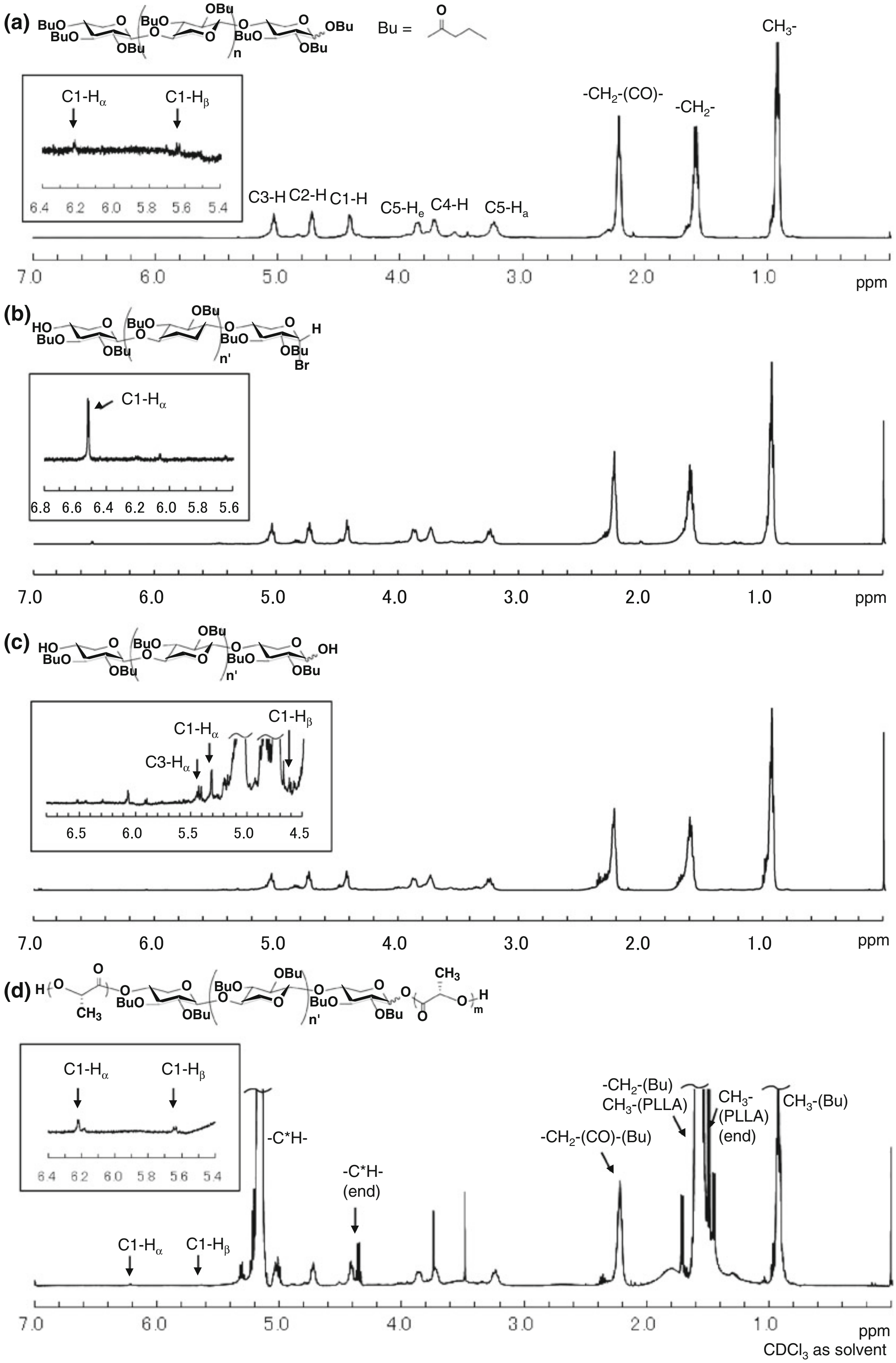

**Fig. 2** $^1$H-NMR spectra of **a** XylBu (**1**), **b** perbutyryl α-xylosyl bromide (**2**), **c** di-hydroxyl-terminated XylBu (**3**) and **d** polymerization product **4-1**

molecular weight of the xylan derivative decreased from $3.16 \times 10^4$ to $0.49 \times 10^4$ after the HBr treatment suggesting depolymerization of the xylan main chain.

### Preparation of di-hydroxyl-terminated XylBu (3)

Perbutyryl α-xylosyl bromide (**2**) was treated with water to convert the bromine group to a hydroxyl group and obtain di-hydroxyl-terminated XylBu (**3**), with two hydroxyl groups, one at the C1 position of the reducing end and another at the C4 position of the non-reducing end. In the $^1$H-NMR spectrum of XylBu (**3**) shown in Fig. 2c, the α-anomeric proton resonance at 6.53 ppm (C1–$H_\alpha$, $J = 4.2$ Hz) of α-xylosyl bromide (**2**) disappeared. These were replaced by anomeric proton resonances observed at 4.61 (d, C1–$H_\beta$, $J = 7.5$) and 5.31 (d, C1–$H_\alpha$, $J = 3.5$) ppm, which were assigned by $^{13}$C-, HSQC-, H–H TOCSY-NMR analysis. The terminal hydroxyl groups were found to be present in both α and β anomeric forms. The NMR data indicated that the bromine group at the C1 position of the reducing end was substituted by the hydroxyl group. These assignments were in good accordance with those for cellulose esters having a hydroxyl group at the C1 position of the reducing end [30, 33], which supported the chemical structure determination of the XylBu end group (**3**). The $M_n$ of di-hydroxyl-terminated XylBu (**3**) was $0.39 \times 10^4$, and showed no substantial differences with that of perbutyryl α-xylosyl bromide (**2**).

### Polymerization of L-lactide with XylBu (3)

L-Lactide was polymerized via ring opening in bulk using XylBu (**3**) as the initiator and $Sn(Oct)_2$ as the catalyst. Two hydroxyl groups at both ends of XylBu (**3**) were considered as initiation sites. Polymerization products **4-1**, **4-2** and **4-3** were obtained after polymerization at initial [L-lactide]/[XylBu (**3**)] ratios 100/1, 260/1 and 560/1, respectively, as shown in Fig. 1 and Table 1. The ratio of L-lactide to one hydroxyl group of XylBu (**3**) for products **4-1**, **4-2** and **4-3**, was 50/1, 130/1 and 280/1, respectively. GPC data for products **4-1**, **4-2** and **4-3** are shown in Fig. 3, and their $M_n$ and $M_w/M_n$ are listed in Table 1. Chromatograms of the products showed a peak at higher molecular weight region than XylBu (**3**) with a small shoulder peak at lower elution time. No peaks corresponding to remaining XylBu (**3**) were observed. This indicated that XylBu (**3**) worked as an initiator and was incorporated into the block polymer. A representative $^1$H-NMR spectrum of product **4-1** is shown in Fig. 2d. Peaks of both XylBu and PLLA components were observed and assigned according to our previous works [13, 14]. In addition, protons signals of C1–H of the reducing end group with α- and β-configurations appeared at 6.24 ppm ($J = 3.3$ Hz) and 5.64 ppm ($J = 8.7$ Hz), respectively. These chemical shifts were identical to those of XylBu (**1**), which has an ester group at the C1 position of the reducing end. This indicated that the C1 position of the reducing end of XylBu (**3**) was re-esterified by PLLA and that the desired block copolymers were successfully obtained.

### Structural characterization of the polymerization products

At this point, it was not clear whether the polymerization products **4-1**, **4-2** and **4-3** were "pure" block copolymer or "mixtures" of the copolymer and a PLLA homopolymer. Therefore, molecular weights of the copolymers were estimated from NMR and GPC analysis. The degree of polymerization (DP) of the PLLA block in the polymerization products was calculated from integration of C*H protons (δ 5.17 ppm) and C*H (end) proton (δ 4.36 ppm), as follows: DP (PLLA) = ((C*H) + (C*H(end))/(C*H(end)). Molecular weights (M) of the PLLA block were calculated as follows: M (PLLA) = DP (PLLA) × M(lactide)/2, where M(lactide) = 144.13. These values are listed in Table 1.

**Table 1** Characterization of the polymerization products

| Polymerization products | Lactide (eq)[a] | Lactide (g)[b] | Yield (%) | $M_n$ ($10^4$)[c] | $M_w/M_n^c$ | DP (PLLA)[d] | M (PLLA) ($10^4$)[d] | M (copolymer) ($10^4$)[e] | Estimated composition of the copolymer in the product (wt%)[f] |
|---|---|---|---|---|---|---|---|---|---|
| **4-1** | 100 | 0.4 | 51 | 1.1 | 1.8 | 36 | 0.3 | 0.9 | 79.3 |
| **4-2** | 260 | 0.9 | 78 | 1.9 | 1.8 | 72 | 0.5 | 1.4 | 42.4 |
| **4-3** | 560 | 2.0 | 85 | 4.6 | 1.6 | 176 | 1.3 | 2.9 | 40.3 |

[a] Initial molar ratio of lactid equivarent to XylBu (**3**)

[b] Initial amount of XylBu (**3**): 0.1 g, $M_n$[XylBu(**3**)] = $0.39 \times 10^4$

[c] Molecular weight and PDI of the products

[d] Calculated by NMR analysis

[e] M (copolymer) = $M_n$ [XylBu (**3**)] + M (PLLA) × 2

[f] Estimated from GPC and NMR analyses

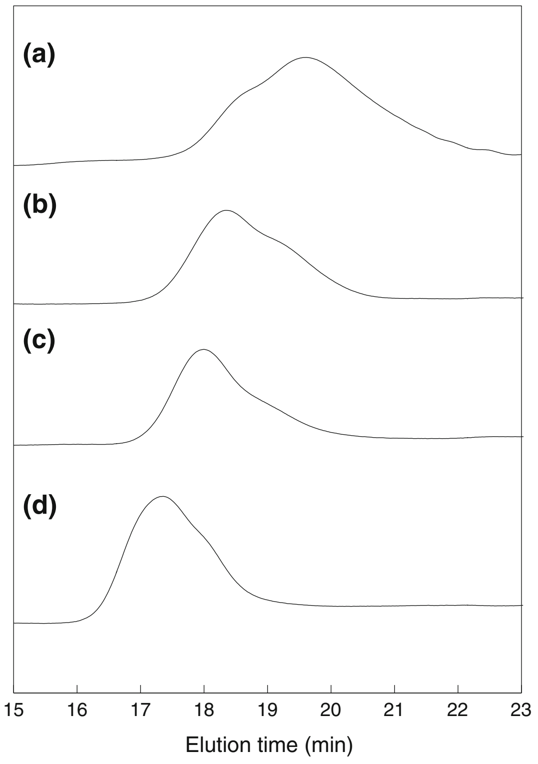

**Fig. 3** GPC data of **a** XylBu (**3**) and products, **b 4-1**, **c 4-2** and **d 4-3**

Molecular weights (M) of the copolymers were estimated as follows: M (copolymer) = $M_n$ [XylBu (**3**)] + 2 × M (PLLA) on the assumption that PLLA was polymerized from both the ends of XylBu (**3**). The M (copolymer) values tended to increase at higher proportions of the initial lactide. These values showed good agreement with $M_n$s of the polymerization products. M (PLLA) values or sums of M (PLLA) and $M_n$ [XylBu (**3**)] ($0.39 \times 10^4$) were not high enough to give $M_n$ value of the products. It was suggested that the obtained polymer was PLLA-*b*-XylBu-*b*-PLLA “triblock” copolymer and not PLLA homopolymer or diblock copolymers.

Compositions (wt%) of the copolymers in the polymerization products were estimated as follows: M (copolymer)/$M_{theor.}$ (copolymer), based on GPC and NMR data. Theoretical molecular weights of the block copolymers [$M_{theor.}$ (copolymer)] were estimated on the assumption that weight losses in their yield were because of L-lactide, as follows: $M_{theor.}$ (copolymer) = $M_n$ [XylBu (**3**)] + 2 × $M_{theor.}$ (PLLA) × yield (%). Theoretical molecular weights of PLLA blocks ($M_{theor.}$ (PLLA)) were also calculated, as follows: $M_{theor.}$ (PLLA) = M (lactide) × initial [lactide]/[XylBu (**3**)]/2. The composition values are listed in Table 1. These values suggested that PLLA homopolymers were produced during polymerization as a bi-product. It was therefore likely that the polymerization products **4-1 4-2** and **4-3** consisted of mixtures of triblock copolymers **4** and PLLA homopolymers. The shoulder peak in GPC elution curves might be attributed to PLLA homopolymer. However, it proved difficult to purify the block copolymers by gel permeation chromatography or re-precipitation.

## DSC measurements

Polymerization products **4-1 4-2** and **4-3**, namely mixtures of the triblock copolymers and PLLA homopolymer, were analyzed by DSC measurements. Molecular weights of the triblock copolymers and PLLA homopolymer are listed in Table 1. Their DSC thermograms are shown in Fig. 4. All samples showed a glass transition peak ($T_g$) at 48–53 °C and a melting peak ($T_m$) at 146–163 °C. Products **4-2** and **4-3** showed a crystallization peak ($T_c$) at 94 and 95 °C, respectively. PLLA homopolymers with $M_n$ of $0.7 \times 10^4$ and $1.8 \times 10^4$, corresponding to those PLLA included in products **4-2** and **4-3**, respectively, were analyzed for comparison. The PLLAs exhibited $T_g$ and $T_m$ at ca. 50 and ca. 150 °C. It has been reported that xylan butyrate has neither $T_g$, $T_c$ nor $T_m$ [13]. These data suggested that $T_g$, $T_c$ and $T_m$ of the polymerization products were derived from PLLA

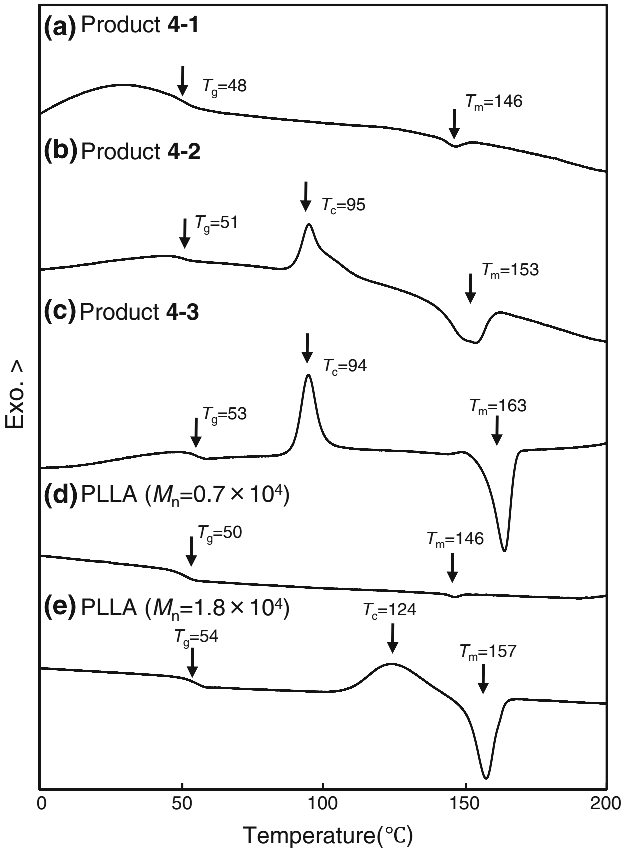

**Fig. 4** DSC thermograms of products **a 4-1**, **b 4-2**, **c 4-3**, **d** PLLA ($M_n = 0.7 \times 10^4$) and **e** PLLA ($M_n = 1.8 \times 10^4$)

components. The $T_g$ of products **4-1**, **4-2** and **4-3** did not show substantial differences from PLLA homopolymers.

Interestingly, product **4-3** showed a crystallization peak at 94 °C, shifted to a markedly low temperature compared with 124 °C of PLLA ($M_n = 1.8 \times 10^4$). Product **4-2** also showed a clear exothermic peak owing to crystallization at 95 °C, while PLLA ($M_n = 0.7 \times 10^4$) showed no crystallization peak. Product **4-1** showed no crystallization peak, likely because of its low molecular weight. These results indicated that crystallization of PLLA was enhanced by the presence of the block copolymers and that the copolymers behaved as nucleating agents for PLLA components.

## Isothermal crystallization

Isothermal crystallization behaviors of the polymerization products **4-2** and **4-3** were analyzed to investigate the effects of the triblock copolymer on crystallization behavior of PLLA components. Products **4-2** and **4-3** were melted at 200 °C, followed by isothermal crystallization at 80, 90, 100, 110 and 120 °C. Figure 5 shows the plots of the crystallization half-time ($t_{1/2}$) of the PLLA homopolymer ($M_n = 1.8 \times 10^4$) and products **4-1** and **4-3**. Product **4-1** and PLLA ($M_n = 0.7 \times 10^4$) showed no crystallization owing to their low molecular weight and were not analyzed. Crystallization half-time ($t_{1/2}$) is defined as the time taken to reach 50 % of maximum crystallization. The $t_{1/2}$ was strongly dependent on crystallization temperature. Product **4-2** and **4-3** showed shortest $t_{1/2}$ at 90 °C. The $t_{1/2}$s of products **4-2** and **4-3** at 90 °C were 3.5 min and 1.7 min, respectively. These values were shorter than that of PLLA ($M_n = 1.8 \times 10^4$) with $t_{1/2}$ of 5.4 min. The same trend was observed at 80 °C. The $t_{1/2}$ of PLLA with low molecular weight ($M_n = 0.7 \times 10^4$) could not be measured because of its low crystallinity. These observations indicated that copolymers enhanced the crystallization of PLLA during isothermal crystallization at 80 and 90 °C. These results agreed well with the results of non-isothermal crystallization in Fig. 4.

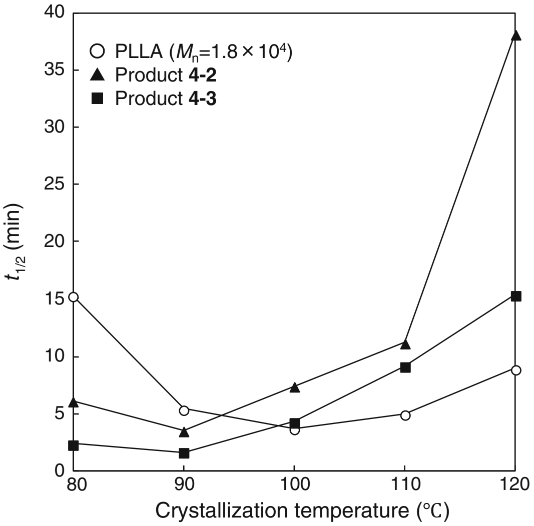

**Fig. 5** Plots of $t_{1/2}$ of PLLA ($M_n = 1.8 \times 10^4$) (*circles*), products **4-2** (*triangles*) and **4-3** (*squares*), isothermally crystallized at different temperatures from melt at 200 °C

To further understand the effect of the copolymers on crystallization behavior of PLLA components, products **4-2** and **4-3** were isothermally crystallized at 90 °C and analyzed by polarized optical microscopy observation. The images of their spherulites are shown in Fig. 6. The images show spherulites grown at 90 °C, which were observed 90 s after the samples were set to a given temperature from melt. The spherulite growth rate could not be analyzed at 90 °C because of fast growth of small crystals. As can be seen in the images in Fig. 6b, c, the number and growth rate of spherulites of products **4-2** and **4-3** were higher compared with PLLA. Few small spherulites of PLLA were observed at the same observation time (Fig. 6a). Crystallization of PLLA block within the copolymer should be retarded because of covalent bonding to the XylBu block, according to the previous report [20]. Meanwhile, we have recently demonstrated that xylan butyrate works as nuclei for PLLA [37]. It was suggested

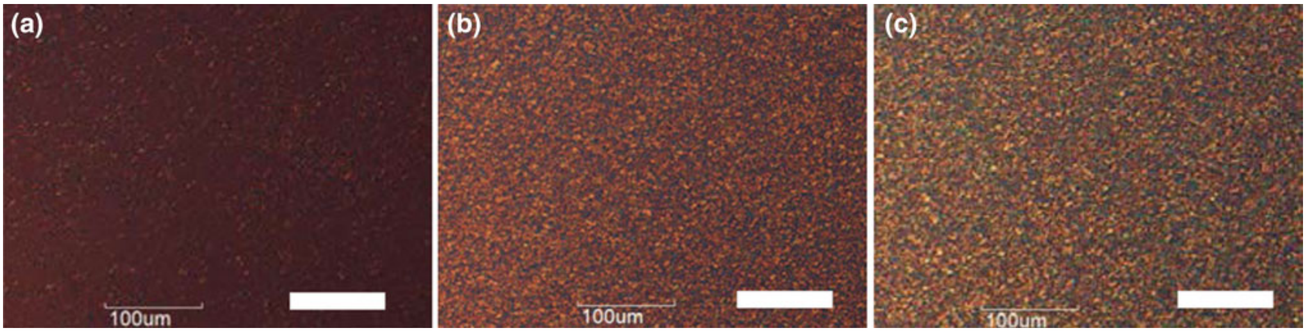

**Fig. 6** Spherulite images of **a** PLLA ($M_n = 1.8 \times 10^4$) and products, **b** **4-2** and **c** **4-3** isothermally crystallized at 90 °C after melting. Observation time is 90 s for all samples. *Scale bar* 100 μm

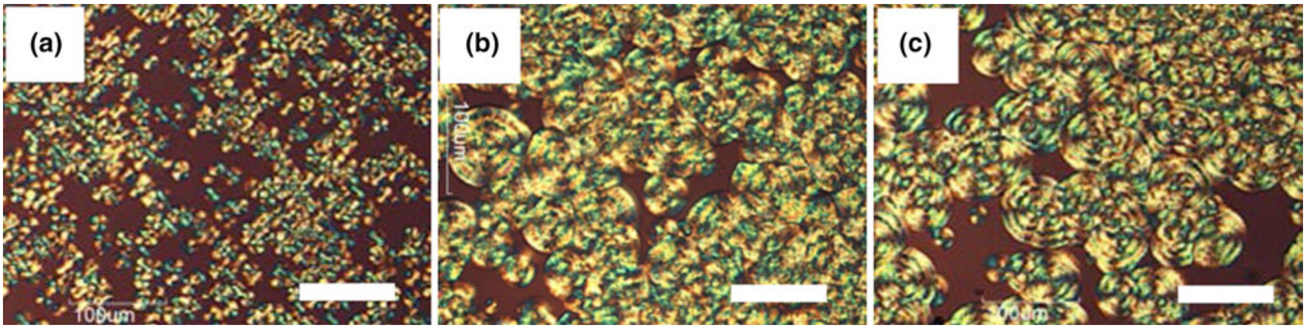

**Fig. 7** Spherulite images of **a** PLLA ($M_n = 1.8 \times 10^4$) and products, **b** **4-2** and **c** **4-3** isothermally crystallized at 110 °C after melting. Observation time for PLLA, products **4-2** and **4-3** were 45 s, 9 min and 9 min, respectively. *Scale bar* 100 μm

that crystallization of PLLA components in products **4-2** and **4-3**, namely, free PLLA homopolymer and PLLA block within the copolymer, were enhanced by the nucleating effect of XylBu block in spite of the anchored structure.

## Spherulite morphology

Figure 7 shows images of spherulites of PLLA ($M_n = 1.8 \times 10^4$) and products **4-2** and **4-3** grown at 110 °C after melting. The observation time for PLLA and products **4-2** and **4-3** were 45 s, 9 min and 9 min, respectively, after set to the crystallization temperature. The spherulite growth rates for PLLA and products **4-2** and **4-3** were 32.6, 5.7 and 4.0 μm/min, respectively. In the case of the products **4-2** and **4-3**, crystallization of PLLA components was inhibited. The numbers of spherulites of products **4-2** and **4-3** were smaller at 110 °C compared with that of PLLA homopolymer. These results agreed well with $t_{1/2}$ data in Fig. 5. The $t_{1/2}$s of products **4-2** and **4-3** at 110 °C were 11.1 min and 9.2 min, respectively. These values were longer than that of PLLA ($M_n = 1.8 \times 10^4$) with $t_{1/2}$ of 5.0 min.

Interestingly, banded extinction rings were observed for products **4-2** and **4-3**, but not for PLLA. It has been reported that miscible or partially miscible polymer blends exhibit extinction rings [38]. Cellulosic graft copolymers containing PLLA or poly(ε-caprolactone) (PCL) [25, 39] have also been reported to exhibit extinction rings. Poly(ε-caprolactone)-polybutadiene [19], poly styrene-PLLA [21] and poly(p-dioxanone)-poly(ε-caprolactone) [20] diblock copolymers are examples of a diblock copolymer that exhibits extinction bands. The appearance of an extinction band has been attributed to lamellar twisting caused by crystallization with specific interactions between polymer components. It is supposed that crystallization of PLLA or PCL was inhibited by countercomponents, which operated as impurities in the crystallizable polymers. In the present study, XylBu was considered as an impurity for crystallization of PLLA components. It was suggested that the PLLA block in the copolymer was incorporated in the crystallization of PLLA chains to form a mixed crystal composed of PLLA homopolymer and PLLA block of the copolymer. The XylBu block of the copolymer might have been excluded from the lamella composed of PLLA components, but remained as an impurity in the amorphous layer because of its chemical bond to PLLA. This may have resulted in lamellar twisting of PLLA.

Further investigations into the crystalline structure of copolymer/PLLA mixed systems, by small-angle X-ray scattering and electron microscopic analysis, may aid in the further characterization of these systems. These results demonstrate the occurrence of specific, temperature-dependent interactions between the block copolymers and PLLA components.

## Conclusion

Di-hydroxyl-terminated XylBu, which has two hydroxyl groups, one at the C1 position of the reducing end and another at the C4 position of the non-reducing end, was prepared. PLLA-*b*-XylBu-*b*-PLLA block copolymers were obtained by ring-opening polymerizations of L-lactide using di-hydroxyl-terminated XylBu as an initiator. The polymerization products were mixtures of PLLA-*b*-XylBu-*b*-PLLA triblock copolymer and PLLA homopolymer. DSC measurements and polarizing optical microscopy observation of the polymerization products revealed that crystallization of PLLA components was enhanced at 90 °C, and that the triblock copolymers worked as nuclei for PLLA components. Banded extinction rings were observed when crystallized at 110 °C for polymerization products suggesting lamellar twisting of PLLA components in the copolymer/PLLA mixed system.

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## References

1. Saake B, Erasmy N, Kruse T, Schmekal E, Puls J (2004) Isolation and characterization of arabinoxylan from oat spelts. In: Hemicelluloses: science and technology, ACS symposium series. American Chemical Society, Washington, DC, pp 52–65
2. Janzon R, Saake B, Puls J (2008) Upgrading of paper-grade pulps to dissolving pulps by nitren extraction: properties of nitren extracted xylans in comparison to NaOH and KOH extracted xylans. Cellulose 15:161–175
3. Puls J, Schroder N, Stein A, Janzon R, Saake B (2006) Xylans from oat spelts and birch kraft pulp. Macromol Symposia 232:85–92
4. Sun RC, Fang JM, Tomkinson J, Jones GL (1999) Acetylation of wheat straw hemicelluloses in *N*,*N*-dimethylacetamide/LiCl solvent system. Ind Crops Prod 10:209–218
5. Ebringerova A, Heinze T (2000) Xylan and xylan derivatives—biopolymers with valuable properties, 1—naturally occurring xylans structures, procedures and properties. Macromol Rapid Commun 21:542–556
6. Heinze T, Koschella A, Ebringerova A (2004) Chemical functionalization of xylan: a short review. In: Hemicelluloses: science and technology, ACS symposium series. Washington, DC; American Chemical Society, pp 312–325
7. Buchanan CM, Buchanan NL, Debenham JS, Gatenholm P, Jacobsson M, Shelton MC, Watterson TL, Wood MD (2003) Preparation and characterization of arabinoxylan esters and arabinoxylan ester/cellulose ester polymer blends. Carbohydr Polym 52:345–357
8. Ren JL, Sun RC, Liu CF (2007) Etherification of hemicelluloses from sugarcane bagasse. J Appl Polym Sci 105:3301–3308
9. Fang JM, Sun RC, Fowler P, Tomkinson J, Hill CAS (1999) Esterification of wheat straw hemicelluloses in the *N*,*N*-dimethylformamide/lithium chloride homogeneous system. J Appl Polym Sci 74:2301–2311
10. Ebringerova A (2006) Structural diversity and application potential of hemicelluloses. Macromol Symposia 232:1–12
11. Sun RC, Sun XF, Tomkinson I (2004) Hemicelluloses and their derivatives. In: Hemicelluloses: science and technology, ACS symposium series. American Chemical Society, Washington, DC, pp 2–22
12. Fundador NGV, Enomoto-Rogers Y, Takemura A, Iwata T (2012) Acetylation and characterization of xylan from hardwood kraft pulp. Carbohydrate Polymers 87:170–176
13. Fundador NGV, Enomoto-Rogers Y, Takemura A, Iwata T (2012) Syntheses and characterization of xylan esters. Polymer 53:3885–3893
14. Enomoto-Rogers Y, Iwata T (2012) Synthesis of xylan-*graft*-poly(L-lactide) copolymers *via* click chemistry and their thermal properties. Carbohydr Polym 87:1933–1940
15. Schatz C, Lecommandoux S (2010) Polysaccharide-containing block copolymers: synthesis, properties and applications of an emerging family of glycoconjugates. Macromol Rapid Commun 31:1664–1684
16. Forster S, Antonietti M (1998) Amphiphilic block copolymers in structure-controlled nanomaterial hybrids. Adv Mater 10:195–217
17. Segalman RA (2005) Patterning with block copolymer thin films. Mater Sci Eng R-Rep 48:191–226
18. Cigana P, Favis BD, Jerome R (1996) Diblock copolymers as emulsifying agents in polymer blends: influence of molecular weight, architecture, and chemical composition. J Polym Sci Part B-Polym Phys 34:1691–1700
19. Nojima S, Wang DJ, Ashida T (1991) Ringed spherulite in binary blends of poly(epsilon-caprolactone) and epsilon-caprolactone butadiene diblock copolymer. Polym J 23:1473–1482
20. Albuerne J, Marquez L, Muller AJ, Raquez JM, Degee P, Dubois P, Castelletto V, Hamley IW (2003) Nucleation and crystallization in double crystalline poly(p-dioxanone)-*b*-poly(epsilon-caprolactone) diblock copolymers. Macromolecules 36:1633–1644
21. Chao CC, Chen CK, Chiang YW, Ho RM (2008) Banded spherulites in PS-PLLA chiral block copolymers. Macromolecules 41:3949–3956
22. Simon J, Muller HP, Koch R, Muller V (1998) Thermoplastic and biodegradable polymers of cellulose. Polym Degrad Stab 59:107–115
23. Teramoto Y, Nishio Y (2003) Cellulose diacetate-graft-poly(lactic acid)s: synthesis of wide-ranging compositions and their thermal and mechanical properties. Polymer 44:2701–2709
24. Teramoto Y, Nishio Y (2004) Biodegradable cellulose diacetate-graft-poly(L-lactide)s: enzymatic hydrolysis behavior and surface morphological characterization. Biomacromolecules 5:407–414
25. Kusumi R, Teramoto Y, Nishio Y (2008) Crystallization behavior of poly(epsilon-caprolactone) grafted onto cellulose alkyl esters: effects of copolymer composition miscibility. Macromol Chem Phys 209:2135–2146
26. Kusumi R, Lee SH, Teramoto Y, Nishio Y (2009) Cellulose ester-*graft*-poly(epsilon-caprolactone): effects of copolymer composition and intercomponent miscibility on the enzymatic hydrolysis behavior. Biomacromolecules 10:2830–2838
27. Li B-G, Zhang L-M (2008) Synthesis and characterization of novel amphiphilic block copolymers based on maltoheptaose and poly(epsilon-caprolactone). Carbohydr Polym 74:390–395
28. Liu J-Y, Zhang L-M (2007) Preparation of a polysaccharide–polyester diblock copolymer and its micellar characteristics. Carbohydr Polym 69:196–201
29. Rasband WS, US National Institutes of Health, Bethesda, MD, USA, http://rsb.info.nih.gov/ij/, 1997–2009
30. Mezger T, Cantow HJ (1983) Cellulose containing block copolymers. 4 Cellulose triester macroinitiators. Angew Makromol Chem 116:13–27
31. de Oliveira W, Glasser WG (1994) Novel cellulose derivatives. 2. Synthesis and characteristics of mono-functional cellulose propionate segments. Cellulose 1:77–86
32. Bemiller JN, Wing RE (1968) Methyl terminal-4-*O*-methylmalto-oligosaccharides. Carbohydr Res 6:197–206
33. Einfeldt L, Gunther W, Klemm D, Heublein B (2005) Peracetylated cellulose: end group modification and structural analysis by means of $H^1$-NMR spectroscopy. Cellulose 12:15–24
34. Kamitakahara H, Enomoto Y, Hasegawa C, Nakatsubo F (2005) Synthesis of diblock copolymers with cellulose derivatives. 2. Characterization and thermal properties of cellulose triacetate-*block*-oligoamide-15. Cellulose 12:527–541
35. Mezger T, Cantow HJ (1984) Cellulose-containing triblock copolymers—syntheses via cellulosic dithiodiaryl photoinitiators. Polym Photochem 5:49–56
36. Enomoto-Rogers Y, Kamitakahara H, Yoshinaga A, Takano T (2010) Radially oriented cellulose triacetate chains on gold nanoparticles. Cellulose 17:923–936
37. Fundador NGV, Enomoto-Rogers Y, Takemura A, Iwata T (2013) Xylan esters as bio-based nucleating agents for poly (L-lactic acid). Polym Degrad Stab 98:1064–1071
38. Keith HD, Padden FJ, Russell TP (1989) Morphological-changes in polyesters and polyamides induced by blending with small concentrations of polymer diluents. Macromolecules 22:666–675
39. Teramoto Y, Nishio Y (2004) Biodegradable cellulose diacetate-*graft*-poly(L-lactide)s: thermal treatment effect on the development of supramolecular structures. Biomacromolecules 5:397–406