Carbohydrate Polymers 87 (2012) 1933–1940

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis of xylan-*graft*-poly(L-lactide) copolymers *via* click chemistry and their thermal properties

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ARTICLE INFO

Article history:
Received 9 June 2011
Accepted 30 September 2011
Available online 6 October 2011

Keywords:
Hemicellulose
Xylan
Polylactide
Graft copolymer
Click chemistry

ABSTRACT

Di-*O*-(6-azidohexanoyl)-xylan-*graft*-poly(L-lactide)s (XylC6N_3-*g*-PLLAs) were prepared by grafting propargyl-terminated poly(L-lactide) onto di-*O*-(6-azidohexanoyl)-xylan (XylC6N_3) *via* click chemistry. Di-*O*-(6-azidohexanoyl)-xylan (XylC6N_3) was prepared *via* two steps from xylan extracted from eucalyptus kraft pulp with aqueous sodium hydroxide solution. Propargyl-terminated poly(L-lactide)s (PLLA) with three different molecular weights were synthesized *via* ring-opening polymerization of L-lactide using propargyl alcohol as initiator and tin (II) octanoate ($Sn(Oct)_2$) as catalyst. XylC6N_3 and propargyl-terminated PLLAs were treated with *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and copper(I) bromide, and the graft copolymers XylC6N_3-*g*-PLLAs were obtained. DSC measurements revealed that the glass transition temperatures (T_g) of the copolymers decreased compared to that of XylC6N_3, suggesting that the grafted PLLA side-chains act as an internal plasticizer for xylan. TGA measurements revealed that XylC6N_3-*g*-PLLAs had higher decomposition temperatures than those of XylC6N_3 or PLLA, and that the decomposition temperatures of the copolymers increased with decrease in the number of PLLA side-chains grafted to the xylan main-chain.

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1. Introduction

Hemicellulose is one of the most abundant polysaccharides in nature after cellulose and starch. The amount of hemicellulose varies according to the particular plant species. For example, annual plants or woods contain about 25–35% hemicelluloses. Hemicellulose can generally be extracted by alkaline water from plants including agricultural and forest products (Saake, Erasmy, Kruse, Schmekal, & Puls, 2004). It has a lower molecular weight than cellulose or starch, and has rather complex and branched structures with various sugar components, depending on its natural source (Janzon, Saake, & Puls, 2008; Puls, Schroder, Stein, Janzon, & Saake, 2006; Sun et al., 1999). As hemicellulose is structurally related to cellulose their reactions should be similar. However, hemicellulose has no importance in industrial applications, despite its abundance, whereas cellulose and its derivatives have major industrial applications, such as in plastics and biodegradable materials.

There have been several studies on functionalization of hemicellulose by chemical modification, and it has recently been receiving attention as a new material for functional polymers (Heinze, Koschella, & Ebringerova, 2004). For example, Sun et al. have reported preparation of a series of carboxylic esters of hemicellulose from wheat straw or sugarcane bagasse (Fang, Sun, Fowler, Tomkinson, & Hill, 1999; Sun, Fang, & Tomkinson, 2000a, 2000b; Sun, Fang, Tomkinson, & Jones, 1999; Sun, Sun, & Sun, 2004; Sun, Sun, Zhao, & Sun, 2004). Buchanan et al. (2003) have reported films of arabinoxylan esters or their blends. Daus and Heinze (2010) reported preparation of xylan-based nanoparticles for drug release systems. Hemicellulose has high potential for application as a bio-based plastic material obtained by chemical modification (Heinze et al., 2004).

Xylan is a major component of hemicellulose from straw, grasses and agricultural residues. Xylan generally has a backbone consisting of β(1→4) xylopyranose units, and usually has single arabinose units attached to some of the C3 positions of the xylan backbone as the principal substituent, and minor amounts of 4-*O*-methylglucuronic acid residues mainly linked to the C2 positions (Puls et al., 2006). In addition, two hydroxyl groups of xylan are partially substituted with acetyl groups (Glasser, Kaar, Jain, & Sealey, 2000). Xylan is currently used on an industrial scale only for conversion into furfural or xylitol (Glasser et al., 2000). Janzon et al. (2008) have reported alkali extraction of xylan from pulps. Xylan that was extracted from eucalyptus kraft pulp using 10% NaOH aqueous solution at 20:1 ratio of liquor to pulp had high xylose content (ca. 96–98%) and low mannose or arabinose content. We expected that this technique would provide homoxylan with consistent quality

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doi:10.1016/j.carbpol.2011.09.092

including chemical structure, purity, and molecular weight, for further chemical modification and for novel plastic materials.

Cellulosic derivatives such as cellulose acetate show high glass transition temperatures, which restrict their thermal processibility. Preparation of a graft copolymer is an effective method to alter physical and chemical properties of a polysaccharide as a plastic material, for example to reduce the glass transition temperature or to improve thermal stability (Teramoto & Nishio, 2003). Several researchers have studied cellulosic graft copolymers such as cellulose-*graft*-poly(lactide) or cellulose-*graft*-poly(ε-caprolactone), as biodegradable plastic materials, and reported that poly(lactide) or poly(ε-caprolactone) side-chains acted as internal plasticizers for the polysaccharide (Teramoto & Nishio, 2003; Teramoto, Yoshioka, Shiraishi, & Nishio, 2002; Vlcek et al., 2008; Yan et al., 2009). Xylan graft copolymers with side-chains of a polyester such as poly(lactide), are also expected to be novel bio-based plastic materials.

In relation to grafting methods, "click chemistry" has recently been receiving much attention as a highly efficient and stereoselective reaction. Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and terminal alkynes for transformation of 1,2,3-triazoles (Kolb, Finn, & Sharpless, 2001) is a representative click reaction. This methodology has been applied to cellulose and β-(1→3)-glucan for regioselective modification by unconventional substituents such as polymers or dendrimers *via* click chemistry (Fenn, Pohl, & Heinze, 2009; Hasegawa et al., 2006; Liebert, Hansch, & Heinze, 2006).

In the present study we have prepared xylan-*graft*-poly(lactide) copolymer as a novel xylan-based plastic material, *via* click chemistry. The synthetic scheme consists of three steps, namely preparation of (1) ω-azidoalkyl xylan esters as a backbone, and (2) terminal alkyne-containing PLLA as a side-chain; and (3) grafting PLLA chains onto the xylan backbone. The thermal properties of the synthesized graft copolymers were analyzed.

2. Experimental

2.1. General measurements

^{1}H, ^{13}C, and two-dimensional NMR spectra were recorded with a JEOL JNM-A500 FT-NMR (500 MHz) spectrometer, with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) and coupling constants (J) are reported in (ppm) and (Hz), respectively.

2.2. GPC measurement

Number and weight average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) were estimated by gel permeation chromatography (GPC) (SCL-10Avp, SIL-10A, LC-10Ai, CTO-10ACvp, 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).

2.3. FT-IR measurement

Fourier transform infrared (FT-IR) spectra were recorded with a NICOLET6700 FT-IR spectrophotometer (Thermo Scientific). Samples were mixed with KBr and pressed into disks.

2.4. DSC measurement

Differential scanning calorimetry (DSC) thermograms were recorded with a DSC8500 (Perkin-Elmer) under a nitrogen atmosphere. The samples were first heated from 25 to 220 °C (first heating scan) at 100 °C/min, then immediately quenched to −70 °C. The second heating scans were run from −70 to 220 °C at heating rate 100 °C/min. The glass transition temperature was recorded as the midpoint temperature of the heat capacity transition in the second heating scan.

2.5. TGA measurement

Thermogravimetric analysis (TGA) was carried out using a Thermo Plus TG 8120 (Rigaku) instrument under a nitrogen atmosphere. Thermograms were acquired between 30 and 450 °C at heating rate 20 °C/min.

2.6. Materials

Eucalyptus kraft pulp sheet was provided by Nippon Paper Group, Inc. (Tokyo, Japan). L-Lactide was provided by Musashino Chemical Laboratory Ltd. (Saitama, Japan), and crystallized from ethyl acetate before use. Propargyl alcohol, tin (II) octanoate (Sn(Oct)$_2$), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (Cu(I)Br), anhydrous toluene, and all other reagents were commercially obtained and used without further purification.

2.7. Xylan extraction

Prior to extraction, Eucalyptus kraft pulp sheet (50 g) was disintegrated in water using a mixer. The disintegrated pulp was dispersed in 10% sodium hydroxide (NaOH) aqueous solution (1.0 l), and allowed to stand for 2 h at 25 °C. The mixture was filtered under vacuum, and washed with water. The extract was neutralized using acetic acid to precipitate the extracted xylan, and the mixture was poured into ethanol (1.0 l) and allowed to stand overnight. The precipitated xylan was collected and washed with ethanol and water by centrifugation at 10 krpm for 10 min, and dried by lyophilization to give fine powdered xylan (2.4 g, 4.8% yield).

2.8. Di-O-(6-bromohexanoyl)-xylan

Dried xylan (1.13 g, dried at 105 °C overnight) from Eucalyptus kraft pulp was dispersed in dimethylacetamide (DMAc) (20 ml) and stirred at 120 °C for 2 h. After the slurry had been cooled to 100 °C, anhydrous LiCl (1.75 g, dried at 150 °C overnight) was added to the reaction mixture: the xylan dissolved completely after 1.5 h. Dimethylaminopyridine (DMAP) (3.7 g, 4 equiv. to anhydroxylose unit (AXU)) and 6-bromohexanoyl chloride (6.5 ml, 4 equiv. to AXU) were added to the reaction mixture, and the mixture was stirred at 70 °C for 2 days. After completion of the reaction, the mixture was poured into methanol (800 ml). The precipitate was separated by filtration, washed with methanol and distilled water, and dried *in vacuo* to give solid (3.16 g, 76.0% yield). Molar masses (g mol^{-1} in all cases) $M_n = 2.14 \times 10^4$, $M_w = 3.76 \times 10^4$, $M_w/M_n = 1.76$. ^{1}H NMR ($CDCl_3$): δ 1.44 (m, 2H, –C*H*$_2$–CH$_2$–CH$_2$–Br), 1.59 (m, 2H, –CO–CH$_2$–C*H*$_2$–), 1.77 (m, 2H, –C*H*$_2$–CH$_2$–Br), 2.26 (s, 2H, –CO–CH$_2$–), 3.23 (C5–H$_a$), 3.54 (t, 2H, J = 6.5, –CH$_2$–Br), 3.76 (C4–H), 3.89 (C5–H$_e$), 4.43 (C1–H), 4.69 (C2–H), 5.00 (C3–H). ^{13}C NMR ($CDCl_3$): δ 24.0 (–CO–CH$_2$–*C*H$_2$–), 26.3 (–*C*H$_2$–CH$_2$–CH$_2$–Br), 32.1 (–*C*H$_2$–CH$_2$–Br), 33.7 (–CO–*C*H$_2$–), 44.8 (–*C*H$_2$–Br), 62.5 (C5), 70.7 (C2), 71.7 (C3), 74.2 (C4), 99.9 (C1), 171.7, 172.2 (CO of C2 and C3, respectively).

2.9. Di-O-(6-azidohexanoyl)-xylan

To a solution of di-*O*-(6-bromohexanoyl)-xylan (3.16 g) in dimethylformamide (DMF) (20 ml), sodium azide (NaN_3) (1.69 g, 4 equiv. to AXU) was added at 60 °C. The reaction mixture was stirred for 7 days, and then cooled to room temperature,

and 20 mL of distilled water and 80 ml of chloroform added. The chloroform layer was separated and washed with brine and distilled water, and the aqueous layer was extracted with chloroform. The chloroform extracts were combined, evaporated, and dried *in vacuo* to give a solid (1.44 g, 54.1% yield). $M_n = 2.11 \times 10^4$, $M_w = 3.70 \times 10^4$, $M_w/M_n = 1.75$. ^{1}H NMR ($CDCl_3$): δ 1.37 (m, 2H, –C*H*$_2$–CH$_2$–CH$_2$–N$_3$), 1.59 (m, 4H, –CO–CH$_2$–C*H*$_2$–, –C*H*$_2$–CH$_2$–N$_3$), 2.25 (s, 2H, –CO–CH$_2$–), 3.22 (C5–H$_a$), 3.28 (t, 2H, $J = 6.5$, –CH$_2$–N$_3$), 3.76 (m, C4–H), 3.90 (C5–H$_e$), 4.43 (C1–H), 4.69 (C2–H), 5.00 (C3–H). ^{13}C NMR ($CDCl_3$): δ 24.2 (–CO–CH$_2$–*C*H$_2$–), 26.1 (–CH$_2$–CH$_2$–CH$_2$–N$_3$), 28.5 (–*C*H$_2$–CH$_2$–N$_3$), 33.7 (–CO–*C*H$_2$–), 51.2 (–CH$_2$–N$_3$), 62.5 (C5), 70.7 (C2), 71.6 (C3), 74.1 (C4), 99.8 (C1), 171.7, 172.1 (CO of C2 and C3, respectively).

2.10. Propargyl-terminated poly(L-lactide)

Propargyl-terminated poly(L-lactide) (PLLA) was prepared by ring-opening radical polymerization of L-lactide in toluene with $Sn(Oct)_2$ as catalyst and propargyl alcohol as initiator. A representative procedure for PLLA5300 ($M_n = 5.3 \times 10^3$) was as follows. To a solution of propargyl alcohol (51.8 μl, 1 equiv.) and $Sn(Oct)_2$ (0.3 ml, 1 equiv.) in anhydrous toluene (4 ml), L-lactide (2.0 g, 15 equiv.) in toluene (6 ml) was added dropwise 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 10krpm, and dried to give a solid (1.43 g, 71.7% yield). Propargyl-terminated poly(L-lactide)s with various molecular weights were prepared in the same manner with appropriate ratios of lactide to $Sn(Oct)_2$ and propargyl alcohol. Propargyl-terminated poly(L-lactide)s with M_n 2.9×10^3, 5.3×10^3 and 1.09×10^4 are referred to as PLLA2900, PLLA5300 and PLLA10900, respectively. ^{1}H NMR ($CDCl_3$): δ 1.48, 1.49 (d, 3H, CH$_3$ (end)), 1.58, 1.59 (CH$_3$), 2.51 (t, 1H, C≡C–H), 4.36 (q, 1H, C*H (end)), 4.73 (dd, 2H, –C*H*$_2$–C≡CH), 5.17 (C*H). ^{13}C NMR ($CDCl_3$): δ 16.6 (CH$_3$), 20.5 (CH$_3$ (end)), 52.9 (–*C*H$_2$–C≡CH), 66.7 (C* (end)), 69.0 (C*), 75.6 (–*C*≡CH), 77.0 (overlapped, –C≡*C*H), 169.6 (CO).

2.11. Di-O-(6-azidohexanoyl)-xylan-graft-poly(L-lactide)

A representative procedure for the copolymer XylC6N$_3$-*g*-PLLA5300-1 was as follows. Di-*O*-(6-azidohexanoyl)-xylan (20.0 mg), propargyl-terminated poly(L-lactide) (PLLA5300) (32.3 mg, 0.125 equiv. to AXU), and PMDETA (10.6 μl, 10 equiv. to PLLA) in chloroform/dimethylformamide (DMF) (1/1 = v/v, 2.4 ml) were weighed into a glass flask, and degassed by three freeze-pump-thaw cycles. The flask was purged with nitrogen, Cu(I)Br (8.7 mg, 10 equiv. to PLLA) was rapidly added, and the flask was degassed again and sealed. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the mixture was concentrated to remove chloroform then poured into ethanol (100 ml). The precipitate was isolated by filtration, washed with methanol and distilled water, then dried *in vacuo* to give a solid XylC6N$_3$-*g*-PLLA5300-1 (42.0 mg, 80.3% yield). The number and weight average molecular weights and polydispersity index of XylC6N$_3$-*g*-PLLA5300-1 were $M_n = 6.76 \times 10^4$, $M_w = 1.06 \times 10^5$ and $M_w/M_n = 1.56$, respectively. The copolymers XylC6N$_3$-*g*-PLLA obtained from PLLA2900, PLLA5300 and PLLA10900 are referred to as XylC6N$_3$-*g*-PLLA2900, XylC6N$_3$-*g*-PLLA5300 and XylC6N$_3$-*g*-PLLA10900, respectively. The copolymers XylC6N$_3$-*g*-PLLA obtained from initial [PLLA]/[AXU] ratios 1/8, 1/4, 1/2, 1/1 and 2/1, were numbered from 1 to 5, respectively. ^{1}H NMR ($CDCl_3$): δ 1.31 (–C*H*$_2$–CH$_2$–CH$_2$–N$_3$), 1.51 (CH$_3$ (PLLA), –CO–CH$_2$–C*H*$_2$–, –C*H*$_2$–CH$_2$–N$_3$), 2.18 (s, 2H, –CO–CH$_2$–), 3.21 (–CH$_2$–N$_3$, C5–H$_a$ (overlapped)), 3.65 (C4–H), 3.83 (C5–H$_e$), 4.28 (C*H (end)), 4.37 (C1–H), 4.62 (C2–H), 4.94 (C3–H), 5.09 (C*H (PLLA)), 7.53 (triazole). ^{13}C NMR ($CDCl_3$): δ 16.6 (*C*H$_3$ (PLLA)), 20.5 (*C*H$_3$ (PLLA, end)), 24.2 (–CO–CH$_2$–*C*H$_2$–), 26.1 (–*C*H$_2$–CH$_2$–CH$_2$–N$_3$), 28.5 (–*C*H$_2$–CH$_2$–N$_3$), 33.7 (–CO–*C*H$_2$–), 51.2 (–CH$_2$–N$_3$), 62.5 (C5), 66.7 (C* (PLLA, end)), 69.0 (C* (PLLA)), 70.7 (C2), 71.7 (C3), 74.1 (C4), 99.8 (C1), 123.6 (–N–*C*=C–), 142.1 (–N–C=*C*–), 169.6 (CO (PLLA)), 171.6, 172.1 (CO of C2 and C3, respectively).

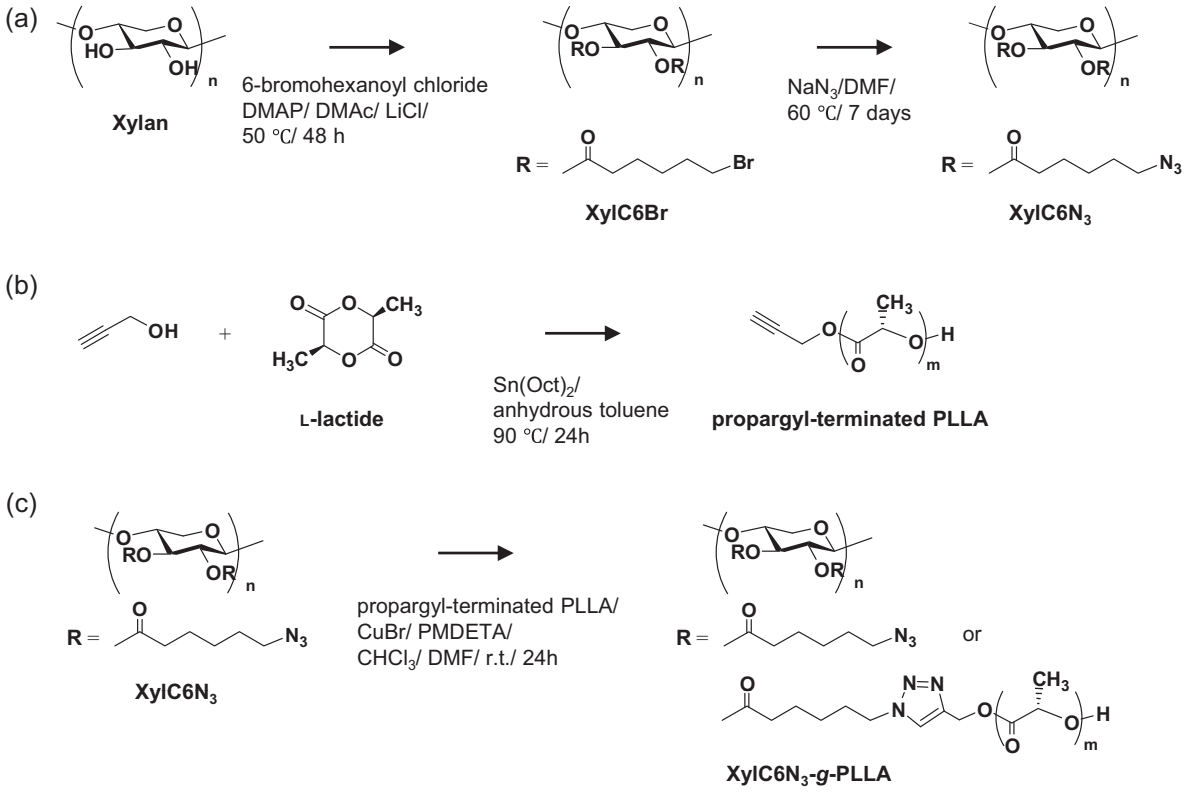
3. Results and discussion

3.1. Preparation of di-O-(6-azidohexanoyl)-xylan

Xylan ester carrying azide groups was prepared as the backbone of a graft copolymer, as shown in Scheme 1a. The original xylan was extracted from Eucalyptus kraft pulp according to previous work (Janzon et al., 2008). The ^{1}H NMR spectrum of the extracted xylan revealed that it was composed mostly of xylose units, and the hydroxyl groups of xylan were not substituted by acetyl groups or other minor sugar residues such as arabinose or glucuronic acid, as shown in Fig. 1a. The extracted homoxylan was used as starting material with uniform chemical structure for further chemical modification. The extracted xylan was esterified by treating with 6-bromohexanoyl chloride and DMAP in the DMAc/LiCl homogeneous system, which is known as a solvent system for esterification of cellulose (McCormick, Callais, & Hutchinson, 1985), to give di-*O*-(6-bromohexanoyl)-xylan (XylC6Br) as a precursor. XylC6Br was treated with NaN_3 in DMF to transform the terminal bromine group to azide group, and form di-*O*-(6-azidohexanoyl)-xylan (XylC6N$_3$). The molecular weights of xylan derivatives were determined by GPC, and are listed in the experimental section. The degrees of polymerization (DP_n) of XylC6Br and XylC6N$_3$ were 44 and 51, respectively. The molecular weight of the original homoxylan was estimated to be ca. 5.8×10^3 from DP_n of XylC6Br ($DP_n = 44$), which is similar to that of xylan (7.25×10^3) reported by Janzon et al. (2008), suggesting that drastic depolymerization of the xylan chain did not occur during esterification. Fig. 1b and c shows ^{1}H NMR spectra of XylC6Br and XylC6N$_3$ with structural assignments. Peaks assigned to the xylan starting material were not observed. The degree of substitution of 6-bromohexanoyl group (DS_{Br}) and 6-azidohexanoyl group (DS_{N_3}) was calculated from the ratio of integral areas of the methylene protons of the alkyl group and the ring protons of xylan, as follows: $DS = (I_{(CH_2)}/2)/I_{(ring\text{-}H)}$. $I_{(CH_2)}$ and $I_{(ring\text{-}H)}$ are average integral areas of methylene protons (2H) of alkyl group and ring proton (1H), respectively, and were calculated as follows. $I_{(CH_2)} = (I_{(H_a)} + I_{(H_b)} + I_{(H_c)} + I_{(H_d)} + I_{(H_e)})/5$; $I_{(ring\text{-}H)} = (I_{(C1-H)} + I_{(C2-H)} + I_{(C3-H)} + I_{(C4-H)} + I_{(C5-H_a)} + I_{(C5-H_e)})/6$. $I_{(C5-H_a)}$ and $I_{(H_a)}$ of XylC6N$_3$ were not counted because of the overlap of the peaks. DS_{Br} and DS_{N_3} were calculated as 2.4 and 2.6, respectively, indicating quantitative substitution of the two hydroxyl groups at the C2 and C3 positions. The resonance of the methylene protons (H$_a$) of the hexanoyl group shifted upfield after azidation without residual peaks, indicating quantitative substitution of bromine group by azide group. In the FT-IR spectrum, the absence of OH absorption at $\nu = 3446\ cm^{-1}$ and the absorption of N_3 at $\nu = 2100\ cm^{-1}$ are indicative of successful esterification and substitution of the Br group by the N_3 group (data shown in supplementary contents). The molecular length of XylC6N$_3$ was calculated as 25.4 nm on the assumption that the length of 3 anhydroxylose units (AXU) of the xylan chain is 1.485 nm (Nieduszynski & Marchessault, 1972).

3.2. Preparation of propargyl-terminated poly(L-lactide)

It was reported that poly(ε-caprolactone) with a terminal alkyne group acts as a building block of a block copolymer by reaction with azide-terminated poly(ethylene oxide) *via* click chemistry (He et al., 2007). In the present work, propargyl-terminated



Scheme 1. Preparation of (a) XylC6N_3, (b) propargyl-terminated PLLA, and (c) XylC6N_3-*g*-PLLA.

poly(L-lactide) (PLLA) was synthesized as a side-chain *via* ring-opening polymerization of lactide using propargyl alcohol as initiator and $Sn(Oct)_2$ as catalyst, as shown in Scheme 1b. Propargyl-terminated PLLAs with various molecular weights (PLLA2900 ($M_n = 0.29 \times 10^4$, $DP_n = 40$), PLLA5300 ($M_n = 0.53 \times 10^4$, $DP_n = 75$), PLLA10900 ($M_n = 1.09 \times 10^4$, $DP_n = 151$)) were synthesized at initial [L-lactide]/[initiator] ratios 5/1, 15/1 and 50/1, respectively. The characteristics of the propargyl-terminated PLLAs are given in Table 1. Their molecular weights were larger than expected from the initial [L-lactide]/[initiator] ratios, possibly due to de-activation of initiator by residual water in the polymerization system. The molecular lengths of PLLA2900, PLLA5300, and PLLA10900 were calculated as 11.1, 20.9 and 42.0 nm, respectively, on the assumption that the length of 10 lactic acid units is 2.78 nm (De Santis & Kovacs, 1968). The molecular lengths of PLLA2900, PLLA5300, and PLLA10900 relative to that of XylC6N_3 were calculated as 0.4, 0.8 and 1.7, respectively. Fig. 2 shows a ^{1}H NMR spectrum of PLLA5300 with structural assignments. The characteristic peaks of a terminal propargyl group, C≡CH (δ 2.51 ppm) and HC≡C–H_2– (δ 4·73 ppm) were observed, suggesting successful polymerization of L-lactide from the hydroxyl group of propargyl alcohol. As shown in Table 1, the peak ratio [C*H]/[C≡CH] calculated from C*H protons (δ 5.17 ppm) and C≡CH proton (δ 2.51 ppm) agreed well with DP_n values estimated by GPC analysis, indicating that the ends of PLLA chains were quantitatively substituted by propargyl groups.

3.3. Preparation of di-O-(6-azidohexanoyl)-xylan-graft-poly(L-lactide) via click chemistry (XylC6N_3-*g*-PLLA)

Propargyl-terminated PLLAs were grafted onto XylC6N_3 backbones *via* click chemistry using PMDETA and Cu(I)Br, as shown in Scheme 1c. The copolymers with PLLA2900, PLLA5300, PLLA10900 side-chains are referred to as XylC6N_3-*g*-PLLA2900, XylC6N_3-*g*-PLLA5300, and XylC6N_3-*g*-PLLA10900, respectively. The copolymers obtained from initial molecular ratios of [PLLA]/[anhydroxylose unit (AXU)] of 1/8, 1/4, 1/2, 1/1 and 2/1, were numbered XylC6N_3-*g*-PLLA-1, -2. -3, -4 and -5, respectively.

The copolymers, XylC6N_3-*g*-PLLA2900-1 to -5, were insoluble in common organic solvents such as chloroform, DMF and DMSO. The FT-IR spectra of XylC6N_3-*g*-PLLAs were difficult to normalize

Table 1
Characteristics of propargyl-terminated poly(L-lactide)s.

Propargyl-terminated PLLAs	[L-Lactide]/[propargyl alcohol]/[$Sn(Oct)_2$][a]	Yield (%)	M_n (10^{-3})[b]	M_w (10^{-3})[b]	M_w/M_n[b]	DP_n[b]	[C*H]/[C≡CH][c]	Molecular length (nm)[d]	Ratio of molecular length relative to XylC6N_3 main-chain[e]
PLLA2900	5/1/1	28.1	2.90	3.73	1.29	40	44	11.2	0.4
PLLA5300	15/1/1	71.7	5.38	7.47	1.39	75	72	20.8	0.8
PLLA10900	50/1/1	89.9	10.9	13.9	1.28	151	165	42.0	1.7

[a] Initial molar ratio. initial L-lactide = 2.0 g.
[b] Estimated by GPC using polystyrene standards.
[c] Calculated by NMR analysis from ratio of integral areas.
[d] Molecular length calculated from DP_n, on the assumption that the length of 10 lactic acid unis is 2.78 nm.
[e] Molecular length of XylC6N_3 was calculated to be 25.4 nm, on the assumption that the length of 3 AXU is 1.485 nm.

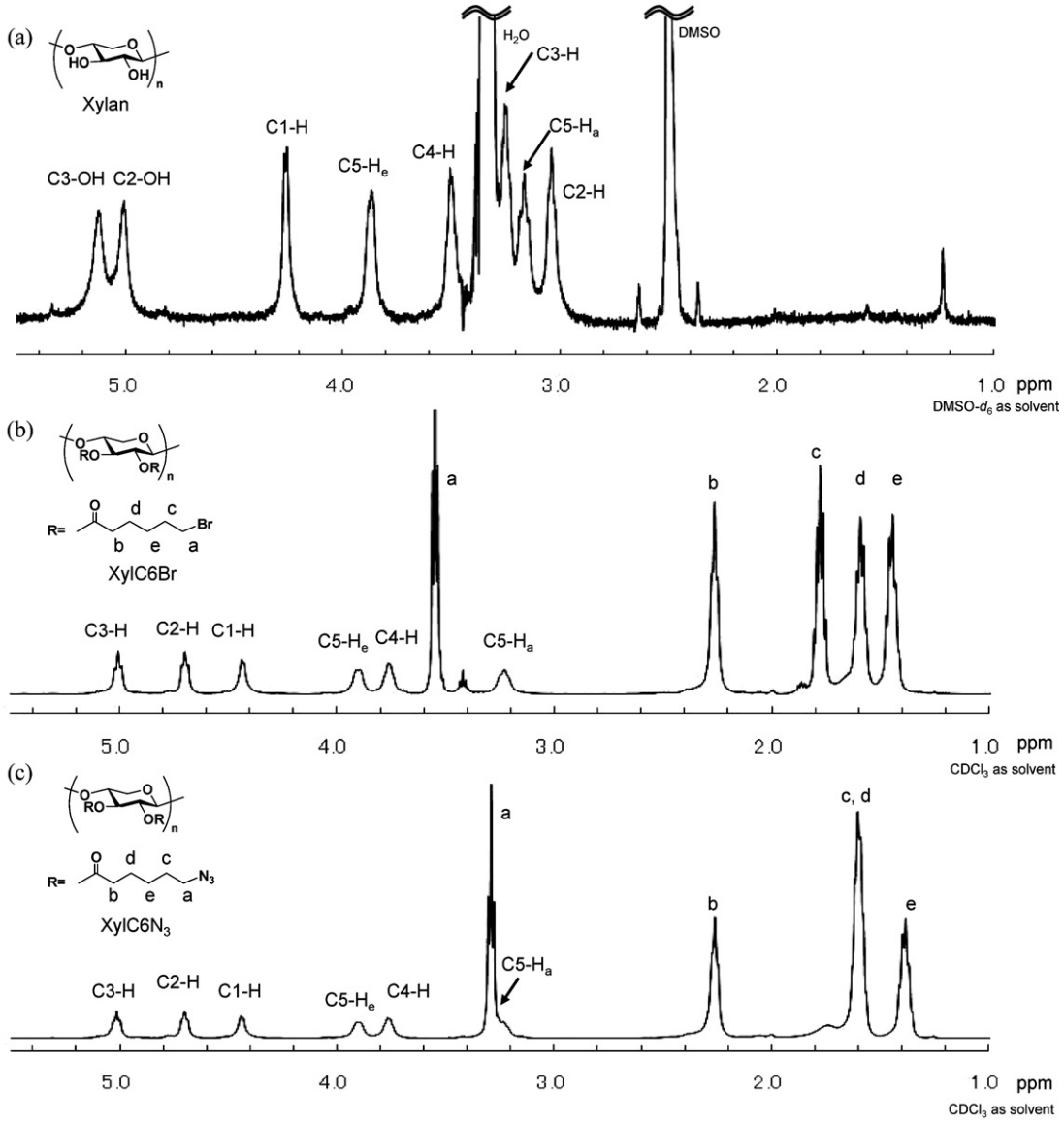


Fig. 1. ^{1}H NMR spectra of (a) xylan extracted from Eucalyptus kraft pulp, (b) XylC6Br, and (c) XylC6N_3.

due to overlapping peaks and to the small XylC6N_3 content in the compounds (data shown in supplementary contents). Consequently, conversion of the azide group to the triazole ring could not be determined by the absorbance of N_3 groups. Considering the fact that both XylC6N_3 and PLLA2900 are soluble in chloroform, it is possible that the insoluble compounds are the desired graft copolymers XylC6N_3-*g*-PLLA2900. It is suggested that PLLA2900 had high reactivity for click reaction with XylC6N_3 and that the solubility of XylC6N_3-*g*-PLLA2900s with many PLLA side-chains decreased in chloroform because of their high molecular weights.

GPC data for XylC6N_3-*g*-PLLA5300 and XylC6N_3-*g*-PLLA10900 are shown in Fig. 3. The chromatograms of XylC6N_3-*g*-PLLA10900-1

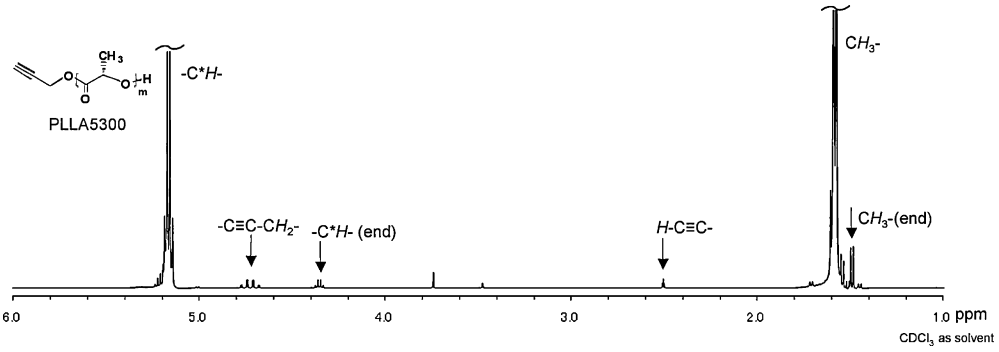


Fig. 2. ^{1}H NMR spectrum of PLLA5300.

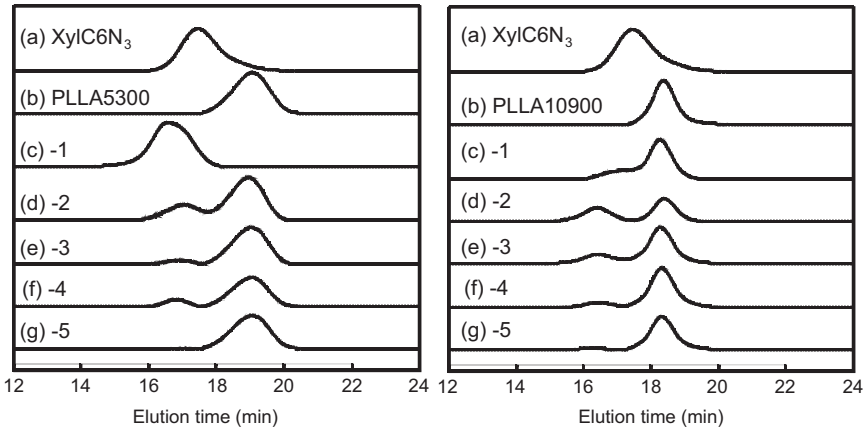


Fig. 3. GPC data for (a) XylC6N$_3$, (b) PLLA, and XylC6N$_3$-*g*-PLLAs (c) -1, (d) -2, (e) -3, (f) -4, and (g) -5. Left: PLLA5300 and right: PLLA10900.

to -5 show small peaks associated with the high molecular weight fractions, but most of the original PLLA still remained, as shown in Fig. 3c–g (right). The low reactivity of PLLA10900 is likely to be due to the low concentration of the terminal alkyne group of PLLA chains. It was difficult to purify the high molecular weight fraction, which is considered to be the copolymer, by re-precipitation or column chromatography.

In the case of XylC6N$_3$-*g*-PLLA5300-2 to -5, small peaks of the high molecular weight fractions were also observed in their chromatograms, but a large amount of original PLLA still remained, as shown in Fig. 3c–g (left). This is likely to be due to the low alkyne group content of the polymer chain. However, in the case of XylC6N$_3$-*g*-PLLA5300-1 with initial molecular ratio [PLLA]/[AXU] = 1/8, the peaks of original XylC6N$_3$ and PLLA5300 were not observed, and a new single peak corresponding to higher molecular weight appeared, as shown in Fig. 3c (left). This indicates that PLLA chains were quantitatively grafted onto the xylan backbone, and that the copolymer XylC6N$_3$-*g*-PLLA5300-1 could be obtained without the need for purification procedures. The number and weight average molecular weights and polydispersity index of XylC6N$_3$-*g*-PLLA5300-1 were calculated as $M_n = 6.76 \times 10^4$, $M_w = 1.06 \times 10^5$ and $M_w/M_n = 1.56$, respectively. M_n and DP_n of XylC6N$_3$ were determined as 2.11×10^4 and 51, respectively, as discussed in the previous section. The number of PLLA side-chains (N) per xylan main-chain was determined as 8.8 according to the equation:

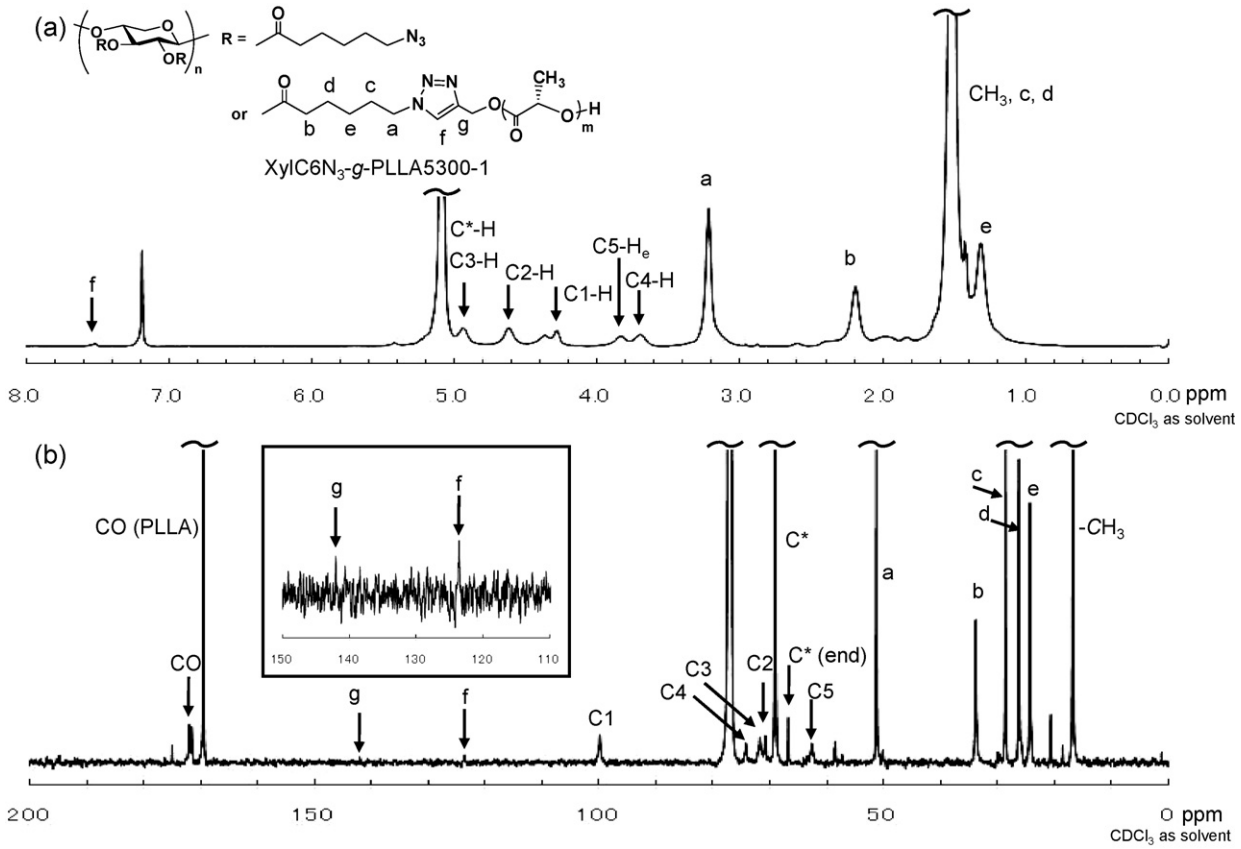


Fig. 4. (a) ^{1}H, and (b) ^{13}C NMR spectra of XylC6N$_3$-*g*-PLLA5300-1.

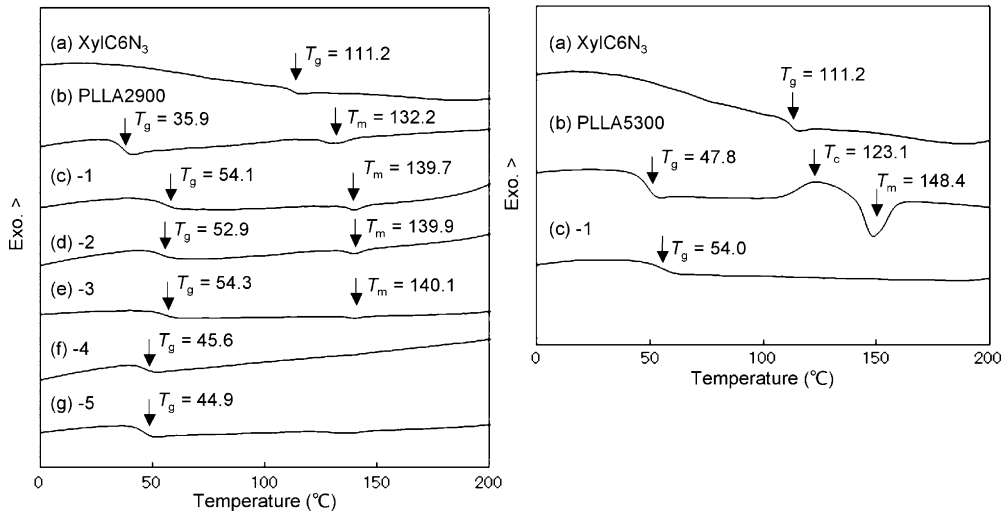


Fig. 5. DSC thermograms of (a) XylC6N$_3$, (b) PLLA; and XylC6N$_3$-*g*-PLLAs (c) -1, (d) -2, (e) -3, (f) -4, and (g) -5. Left: PLLA2900 and right: PLLA5300.

$N = (M_n(\text{XylC6N}_3\text{-}g\text{-PLLA5300-1}) - M_n(\text{XylC6N}_3))/M_n(\text{PLLA5300})$. The PLLA chain content of the copolymer molecule was calculated as 68.8% according to the equation:

$wt(\%) = \{(M_n(\text{XylC6N}_3\text{-}g\text{-PLLA5300-1}) - M_n(\text{XylC6N}_3))/M_n(\text{XylC6N}_3\text{-}g\text{-PLLA5300-1})\} \times 100$. According to these values, it was estimated that PLLA chains were grafted every 5.8 AXU at interchain distance 2.9 nm. The solubility of XylC6N$_3$-*g*-PLLA5300-1 in chloroform was higher than that of XylC6N$_3$-*g*-PLLA2900-1. The longer PLLA5300 chains, which have higher solubility than that of XylC6N$_3$ main-chains, might improve the solubility of the copolymer, but the details are not known. ^{1}H and ^{13}C NMR spectra of XylC6N$_3$-*g*-PLLA are shown in Fig. 4. Peaks assigned to both xylan and PLLA were observed in both spectra. In the ^{1}H NMR spectrum, the proton signal of triazole was observed at 7.53 ppm. In the ^{13}C NMR spectrum, signals assigned to the 1,2,3-triazole ring were observed at 123.6 and 142.1 ppm, indicating successful grafting of PLLA chains.

3.4. Thermal properties of XylC6N$_3$-*g*-PLLAs

The thermal behavior of XylC6N$_3$-*g*-PLLA2900-1 to -5 and XylC6N$_3$-*g*-PLLA5300-1 was analyzed by DSC and TGA measurements. Fig. 5 shows DSC thermograms of XylC6N$_3$, PLLAs, XylC6N$_3$-*g*-PLLA2900-1 to -5, and XylC6N$_3$-*g*-PLLA5300-1 as the second heating cycles. The heating rate was set to 100 °C/min, because no glass transition was observed at the usual heating rate of 10 or 20 °C/min. This fact suggests that molecular motion of the copolymers is quite restricted. PLLA5300 showed peaks due to the glass transition (T_g) (47.8 °C), cold crystallization (T_c) (123.1 °C) and melting (T_m) (148.4 °C), but PLLA2900 showed T_g (35.9 °C) and a small peak corresponding to T_m (132.2 °C), most likely due to the short chain length. A remarkable decrease in the T_g values compared to that of XylC6N$_3$ (111.2 °C) was observed for all of the XylC6N$_3$-*g*-PLLA copolymers, suggesting that the grafted PLLA side-chains played an effective role as an internal plasticizer for the XylC6N$_3$ and xylan starting material.

The T_g values of XylC6N$_3$-*g*-PLLA2900-1 to -5 and XylC6N$_3$-*g*-PLLA5300-1 were higher than those of PLLA2900 or PLLA5300. These results may be attributed to the restricted molecular motion of PLLA side-chains by grafting onto the xylan main-chain. The data confirm that XylC6N$_3$-*g*-PLLA2900-1 to -5 were the desired graft copolymers, although their molecular weights could not be determined by GPC due to low solubility.

XylC6N$_3$-*g*-PLLA2900-1 to -3 showed an endothermic peak due to melting (T_m) of PLLA side-chains, suggesting that PLLA2900 side-chains were crystallized. Peaks due to melting were not observed in the case of XylC6N$_3$-*g*-PLLA2900-4 to -5, indicating that the PLLA side-chains of XylC6N$_3$-*g*-PLLA2900-4 to -5 were not crystallized. On the other hand, XylC6N$_3$-*g*-PLLA5300-1 showed only T_g (54.0 °C) and no melting transition. It is known that PLLA crystal (unit cell dimensions: $a = 1.07$ nm, $b = 0.645$ nm, c (fiber axis) = 2.78 nm) comprises anti-parallel chains at the distance of 0.625 nm (De Santis & Kovacs, 1968), and that it has a lamella structure by chain-folding with thickness 9–12 nm, consisting of 32–43 lactic acid monomer units (Kalb & Pennings, 1980). It is likely that the PLLA chains of XylC6N$_3$-*g*-PLLA2900-1 to -3 can form an anti-parallel conformation by interdigitation of extended PLLA2900 ($DP_n = 40$) side-chains of the different copolymer molecules, and that the density of the

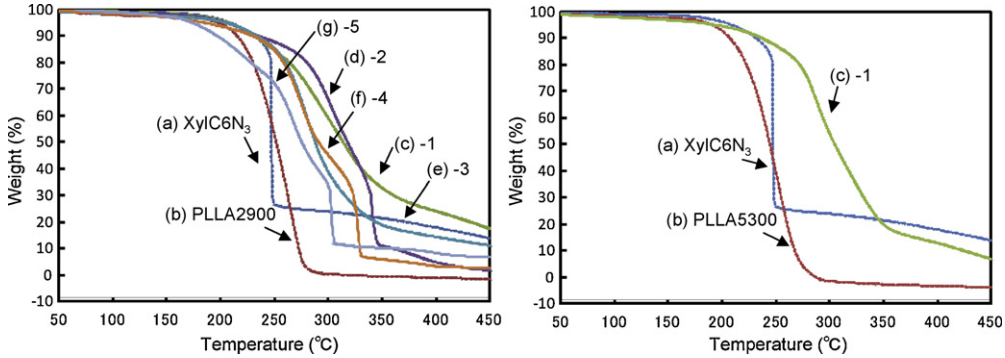


Fig. 6. TGA thermograms of (a) XylC6N$_3$, (b) PLLA; and XylC6N$_3$-*g*-PLLAs (c) -1, (d) -2, (e) -3, (f) -4, and (g) -5. Left: PLLA2900 and right: PLLA5300.

PLLA side-chains of XylC6N_3-*g*-PLLA2900-4 and -5 was too high for interdigitation and prevented its crystallization. It is thought that the PLLA5300 (DP_n = 75) side-chains of XylC6N_3-*g*-PLLA5300-1 are too long to form an anti-parallel structure with extended chains between the different copolymer molecules, but too short to form a chain-folding structure by PLLA chains on the same copolymer molecule.

The TGA measurements shown in Fig. 6 revealed that the decomposition temperature of the copolymers increased compared to that of XylC6N_3 and PLLA2900 or PLLA5300, suggesting that the thermal stability of the copolymers was substantially increased by grafting PLLA onto the xylan ester main-chain. In relation to the effect of the chemical structure of the copolymer, the decomposition temperature increased with decrease in the number of PLLA side-chains per xylan main-chain. In addition, the decomposition temperature of XylC6N_3-*g*-PLLA5300-1 (266.3 °C) with longer PLLA side-chains was higher than that of XylC6N_3-*g*-PLLA2900-1 (250.9 °C). The thermal stability of the copolymer was increased by a small number of PLLA chains with appropriate molecular weight.

4. Conclusions

As novel xylan-based plastic materials, di-*O*-(6-azidohexanoyl)-xylan-*graft*-poly(L-lactide)s (XylC6N_3-*g*-PLLAs) were prepared by grafting propargyl-terminated PLLA (PLLA2900 and PLLA5300) onto di-*O*-(6-azidohexanoyl)-xylan (XylC6N_3) *via* click chemistry. The XylC6N_3-*g*-PLLA2900-1 to -5 copolymers that were obtained quantitatively with initial molecular ratios [PLLA]/[AXU] = 1/8, 1/4, 1/2, 1/1 and 2/1, respectively, were insoluble in chloroform. The copolymer XylC6N_3-*g*-PLLA5300-1, which was soluble in chloroform, was successfully obtained without purification by quantitative grafting of PLLA5300 chains on XylC6N_3 at initial molecular ratio [PLLA]/[AXU] = 1/8.

According to DSC measurements, the grafted PLLA side-chains played an effective role as an internal plasticizer for the original XylC6N_3 and native xylan. TGA scans revealed that a small number of PLLA chains with appropriate molecular weight could effectively increase the thermal stability of the copolymer.

Acknowledgements

This study was supported in part by a Grant-in-Aid for Scientific Research (A) (No. 22245026) (to T.I.) from the Japan Society for the Promotion of Science (JSPS), and in part by JX Nippon Oil & Energy Corporation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.09.092.

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