

Communications

Thermoplastic Cellulose-*graft*-poly(L-lactide) Copolymers Homogeneously Synthesized in an Ionic Liquid with 4-Dimethylaminopyridine Catalyst

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An effective method for grafting L-lactide (LA) from unmodified cellulose by ring-opening polymerization (ROP) in homogeneous mild conditions is presented. By using 4-dimethylaminopyridine (DMAP) as an organic catalyst, cellulose-*graft*-poly(L-lactide) (cellulose-*g*-PLLA) copolymers with a molar substitution (MS_{PLLA}) of PLLA in a range of 0.99–12.28 were successfully synthesized in ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) at 80 °C. The amount and length of grafted PLLA in cellulose-*g*-PLLA copolymers were controlled by adjusting the molar ratios of LA monomer to cellulose. The structure and thermal properties of cellulose-*g*-PLLA copolymers were characterized by ^1H NMR, ^{13}C NMR, wide-angle X-ray powder diffraction (WAXD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and optical microscopy. The DSC results revealed that the copolymers exhibited a single glass transition temperature, T_g , which sharply decreased with the increase of MS_{PLLA} up to $MS_{\text{PLLA}} = 8.28$ ($DS_{\text{PLLA}} = 2.19$) and increased a little with a further increase of the lactyl content. When MS_{PLLA} was above 4.40, the graft copolymers exhibited thermoplastic behavior, indicating the intermolecular and intramolecular hydrogen bonds in cellulose molecules had been effectively destroyed. By using a conventional thermal processing method, fibers and disks of cellulose-*g*-PLLA copolymers were prepared.

1. Introduction

Compared with the solution processing method, the melt processing method of polymers possesses several obvious advantages such as high productivity, simplicity, and flexibility. Melt processing of cellulose is of special interest; however, it still remains a great challenge because cellulose has an extensive hydrogen-bonded and partially crystallized structure that makes it non-melt-processable. The common way to get thermoplastic products from cellulose is chemical modification, of which esterification is the primary chemistry for transformation of cellulose.¹ Some well-known cellulose esters, such as cellulose acetate and cellulose propionate, are thermoplastics. However, in their melt processing, a large amount of low-molecular-weight plasticizers, such as glycerin or polyethylene glycol, is often required, because these cellulose esters with short chain acid

show the relatively narrow processing window between the melt flow temperature and the decomposition temperature. A problem of this plasticization method is exudation or volatilization of the plasticizer, which can cause changes in long-term material performance. Esters of cellulose with long-chain carboxylic acids ($n > 6$) are materials of special interest because the long chain esters may serve as internal plasticizers and eliminate the need for admixture with small molecule plasticizers. Unfortunately, synthesis of these long-chain esters of cellulose is often difficult because of the slow acylation and competing cellulose chain cleavage catalyzed by the mineral acid.

Graft copolymerization is also a practical way to alter the physical and chemical properties of cellulose. In previous studies, various polymers have been grafted onto the cellulose or cellulose derivatives,^{2–11} among which grafting biodegradable aliphatic polyesters onto cellulose has attracted considerable research interest.^{12–17} Nishio et al.^{18–20} synthesized cellulose diacetate-*graft*-poly(lactic acid) copolymers with wide-ranging

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compositions by the ring-opening polymerization (ROP) of L-lactic acid or L-lactide (LA) using cellulose diacetate (CDA) as precursors, and found that the graft copolymers were thermoplastic. However, the limitation of using CDA as a starting material is its relatively high cost and poor mechanical properties. Moreover, the low amount of residual hydroxyl groups in CDA might result in difficulties in the synthesis of copolymers with relatively high grafting density of poly-(L-lactide) (PLLA) polymer chains. It should also be noted that the biological degradation of cellulose acetates in nature still needs further investigation. Highly substituted cellulose derivatives are highly resistant to biodegradation, even enzymatic degradation.^{21–23} Therefore, directly grafting biodegradable polymers onto the underivatized cellulose backbone will be more interesting because it is possible to create a new kind of material combining the advantages of these two groups of polymers simultaneously. As new solvents of cellulose are discovered, such as DMAc/LiCl²⁴ and ionic liquids,^{25,26} it is realized that the reaction can be carried out with unmodified cellulose in a homogeneous system, and various cellulose graft aliphatic polyester copolymers have been synthesized in different cellulose solvents.^{27–29} Mayumi et al.²⁷ and Dong et al.²⁸ synthesized cellulose-*graft*-PLLA (cellulose-*g*-PLLA) copolymers by ring-opening graft polymerization of LA onto cellulose with tin(II) 2-ethylhexanoate (Sn(oct)₂) catalyst in a *N,N*-dimethylacetamide (DMAc)/LiCl and an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl), respectively. However, the amount of grafted PLLA in synthesized copolymers was relatively low, and the graft copolymers could not be melted and were only soluble in dimethyl sulfoxide (DMSO) and water. We assume that, if the cellulose is grafted with a sufficient amount of PLLA, i.e., relatively long chain length and high grafting density of PLLA, thermoplastic cellulose-*g*-PLLA copolymers might be obtained. To this end, the highly efficient catalysis is needed for this grafting polymerization.

In the present study, using 4-dimethylaminopyridine (DMAP) as an organic catalyst, cellulose-*g*-PLLA copolymers with a wide range of compositions were prepared by the homogeneous graft reaction of cellulose with LA in an ionic liquid AmimCl. Interestingly, some cellulose-*g*-PLLA copolymers with relatively high molar substitution of PLLA were found to be thermoplastic.

2. Experimental Section

2.1. Materials. The cellulose (microcrystalline cellulose, Vivapur 101) with a degree of polymerization (DP) of 200 was used. AmimCl was synthesized according to the literature.³⁰ LA with a purity of 99.6% was purchased from Shenzhen Bright China Industrial Co. Ltd. DMAP with a purity of 99.5% was provided by Haili Chemical Industry Co., Ltd. All of them were dried under vacuum at 70 °C for 24 h before use. PLLA with weight-average molecular weight of 50 kD was purchased from Jinan Daigang Co., Ltd. Toluene and DMSO were analytical reagents and used without further purification.

2.2. Preparation of Cellulose-*g*-PLLA Copolymers. A typical polymerization procedure was used as follows. The 4%(w/w) microcrystalline cellulose/AmimCl solution was first prepared by mechanical stirring under 80 °C for 1 h. Then LA (1.78 g) (12.30 mmol), DMAP (0.23 g) (1.85 mmol), 5.0 g of 4%(w/w) microcrystalline cellulose/AmimCl solution, and a dry magnetic stirring bar were added into a dry polymerization tube. The tube was connected to a Schlenk line and put into an oil bath at 50 °C under nitrogen atmosphere with vigorous stirring to dissolve LA and DMAP. After dissolution, the exhausting-refilling process was repeated 3 times for 1 h. Then the reaction was carried at 80 °C under nitrogen atmosphere with vigorous stirring for 12 h. After cooling to room temperature, the resultant polymer was precipitated with deionized water, and then the polymer

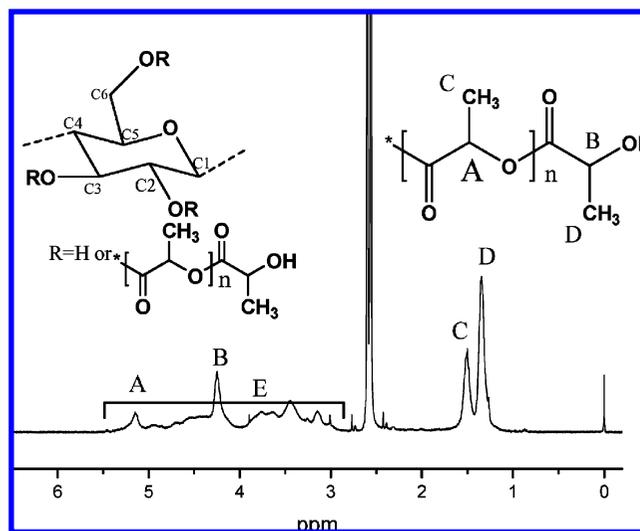
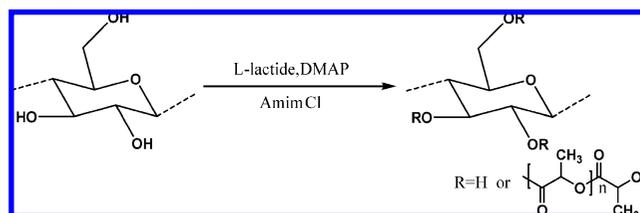


Figure 1. ¹H NMR spectrum of cellulose-*g*-PLLA copolymers ($MS_{\text{PLLA}} = 1.81$, $DS_{\text{PLLA}} = 1.17$).

Scheme 1. Synthesis of Cellulose-*g*-PLLA Using DMAP as a Catalyst in Ionic Liquid AmimCl



was dissolved in DMSO and precipitated with water and toluene to obtain a purified graft copolymer. The purified copolymer was dried in a vacuum oven at 60 °C until reaching a constant weight.

2.3. Thermal Processing of Cellulose-*g*-PLLA Copolymers. Cellulose-*g*-PLLA fibers were produced by melt spinning. Before spinning, the graft copolymer was dried in a vacuum oven at 70 °C for 12 h. The sample was placed in the barrel of Haake-SWO 556-0031 Melt Flow Speed Indicator, heated for 4 min at 140 °C, and then extruded through a capillary ($d = 2$ mm) under the load of 1.20 kg. The extruded fibers were taken up at the speed of 10 m/min at room temperature.

The graft copolymer disks with 1 mm thickness and 25 mm diameter were prepared by hot-pressing with a stainless steel mold at different temperatures. For the molding, a certain amount of copolymer was placed in the mold that was placed over a hot plate, a pressure was applied to the respective soften sample gradually to reach 5.0 MPa in vacuo, followed by keeping this pressure for 2 min at processing temperature. After the pressure was released, the samples were immediately transferred to another compressing apparatus and cold pressed at room temperature for 2 min.

2.4. Measurements. ¹H NMR spectra of cellulose-*g*-PLLA copolymers were measured with a Bruker AV 400 NMR apparatus, by using DMSO-*d*₆ as the solvent with a drop of trifluoroacetic acid-*d* to shift active hydrogen to lower field area, and tetramethylsilane (TMS) as an internal standard. Figure 1 exemplifies a ¹H NMR spectrum obtained for one cellulose-*g*-PLLA copolymer. In the spectrum, a resonance peak area derived from internal methine protons of lactyls in PLLA side-chains was designated as A, an area from terminal methine protons of lactyls in PLLA side-chains was labelled B, an area from terminal methyl protons of lactyls in PLLA side-chains was labelled C, an area from the terminal methyl protons of lactyls was labelled D, and the integral of all protons of anhydroglucose unit was labelled E. The ¹H NMR data was used for the determination of average DP of a lactyl side-chain (DP_{PLLA}) and the degree of lactyl substitution (DS_{PLLA}), defined as an average number of hydroxyls substituted for lactyls per anhydroglucose residue of cellulose. Then the values of DP_{PLLA} and

Table 1. Results of Homogeneous Graft Polymerization of PLLA on Cellulose in Ionic Liquid AmimCl

sample	LA/cellulose (mol/mol)	T^a (°C)	DMAP/OH (mol/mol)	t^b (h)	DP _{PLLA}	DS _{PLLA}	MS _{PLLA}	W _{PLLA} (%)
1	2	80	0.5	12	1.43	0.69	0.99	30.65
2	3	80	0.5	12	1.55	1.17	1.81	44.76
3	4	80	0.5	12	2.53	1.74	4.40	66.41
4	6	80	0.5	12	3.34	1.91	6.38	74.16
5	8	80	0.5	12	3.78	2.19	8.28	78.86
6	10	80	0.5	12	4.48	2.74	12.28	84.73

^a T : reaction temperature. ^b t : reaction time.

DS_{PLLA} were estimated by eqs 1 and 2, respectively. Accordingly, the molar substitution (MS_{PLLA}), which was defined as the average number of introduced lactyl units per anhydroglucose residue of cellulose can be calculated with the eq 3, and a PLLA weight content (W_{PLLA}) in the graft product was calculated with a molecular weight (162) of anhydroglucose unit and that (72) of lactyl unit, as the eq 4.

$$DP_{PLLA} = \frac{I_C + I_D}{I_D} \quad (1)$$

$$DS_{PLLA} = \frac{I_D}{I_E - (I_C + I_D)/3} \times \frac{7}{3} \quad (2)$$

$$MS_{PLLA} = DP_{PLLA} \times DS_{PLLA} \quad (3)$$

$$W_{PLLA} = \frac{72MS_{PLLA}}{162 - DS_{PLLA} + 72MS_{PLLA}} \times 100\% \quad (4)$$

¹³C NMR spectra were recorded on Bruker AV 300 NMR apparatus at 100 °C by using TMS as the internal standard and DMSO-*d*₆ as solvent.

Wide-angle X-ray powder diffraction (WAXD) was performed by XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Ni-filtered Cu K α radiation (40 kV, 30 mA) with 4°/min scanning rate at room temperature. Diffraction intensity was measured in a range of $2\theta = 3$ –60°.

Differential scanning calorimetry (DSC) analysis of the cellulose, cellulose-*g*-PLLA copolymers and PLLA was conducted on a Perkin-Elmer (PE) DSC-7. In order to provide the same thermal history before the measurement, each sample was heated from –20 to 220 °C at a scanning rate of 20 °C/min and kept at 220 °C for 5 min and quenched to room temperature. All the reported T_g 's were observed in the second scan.

Thermogravimetric analysis (TGA) was carried on a PE Pyris 1 thermogravimetric analyzer with a heating rate of 20 °C/min from 50 to 600 °C under nitrogen atmosphere.

Thermal flow behavior of cellulose-*g*-PLLA was observed by an Olympus BX5.1 optical microscope equipped with a Linkam THMS 600 hot-stage device. A small piece of cellulose-*g*-PLLA was sandwiched between two cover glasses, and heated from 30 to 100 °C at a rate of 20 °C/min, holding 1 min, and then heated from 100 °C to soften and flow completely at a heating rate of 5 °C/min. The whole process was recorded by taking photos at desired interval of temperature.

3. Results and Discussion

3.1. Synthesis and Characterization of Cellulose-*g*-PLLA Copolymers. Hedrick et al. reported that nucleophilic organic compounds such as DMAP and 4-pyrrolidinopyridine (PPY) could be used as a kind of highly efficient catalyst for the controlled synthesis of PLLA.³¹ In our experiments, cellulose, LA, DMAP, and cellulose-*g*-PLLA were dissolved in ionic liquid AmimCl, and a homogeneous ROP reaction of LA with

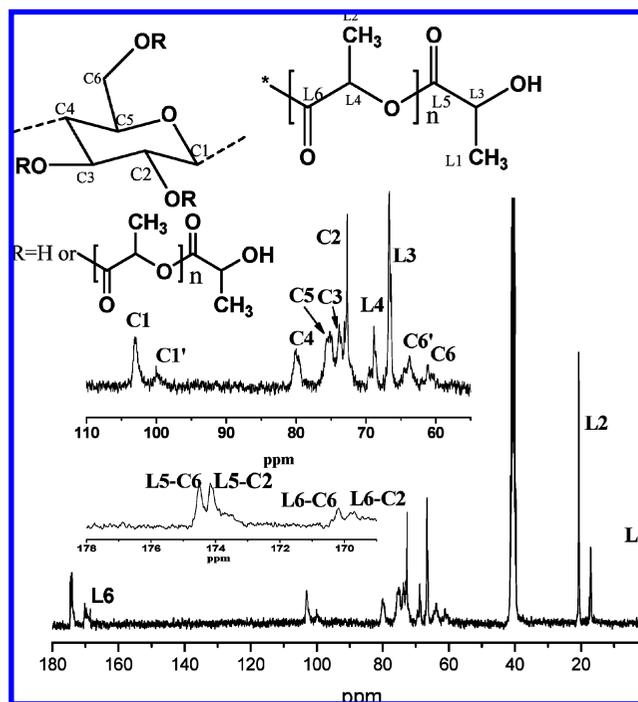


Figure 2. ¹³C NMR spectrum of cellulose-*g*-PLLA (MS_{PLLA} = 1.81, DS_{PLLA} = 1.17) copolymers.

DMAP catalyst was successfully performed, as shown in Scheme 1. Cellulose-*g*-PLLA copolymers with various grafting lengths were synthesized by adjusting the molar ratios of LA monomer to cellulose, and the experimental results are shown in Table 1. It can be seen that the grafting content of PLLA in copolymers increased with the increase of molar ratio of LA to cellulose in feed. When the molar ratio of LA to cellulose was 10, the molar substitution (MS_{PLLA}) of PLLA in the graft product was up to 12.28, which was greatly higher than that reported in the DMAc/LiCl system²⁷ and that in AmimCl with Sn(oct)₂ as a catalyst.²⁸

¹³C NMR spectra of cellulose-*g*-PLLA copolymers (MS_{PLLA} = 1.81, DS_{PLLA} = 1.17) are shown in Figure 2. The peaks at chemical shifts of 17.1, 20.7, 66.4, and 68.8 ppm were ascribed to L1, L2, L3 and L4 carbons (indexed in Figure 2), respectively, of ring opened LA positions. Carbonyl carbons from L5 and L6 appeared at 174.1 and 170.1 ppm, respectively. The peaks at 60.6, 80.0, 103.0, and 71.2–77.4 ppm were assigned to C6, C4, C1, and C2, C3, and C5 carbons of cellulose origin, respectively. The C6' peak and C1' peak, which were due to the C6 carbons and C2 carbons of LA-substituted hydroxyl groups of cellulose, appeared at around 63.9 and 99.9 ppm, respectively. These results indicated that the LA molecule not only combined at the C6 position but also combined at C2 position. Moreover, in the magnified scale of 170–180 ppm, there were two peaks (174.5 and 174.1 ppm) for carbonyl carbons of L5, which also demonstrated that the LA molecule

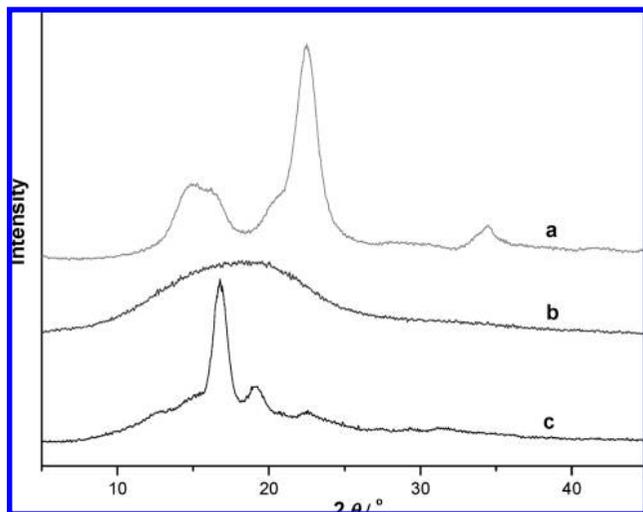


Figure 3. WAXD spectra of cellulose (a), cellulose-*g*-PLLA ($MS_{\text{PLLA}} = 12.28$, $DS_{\text{PLLA}} = 2.74$) (b), and PLLA (c).

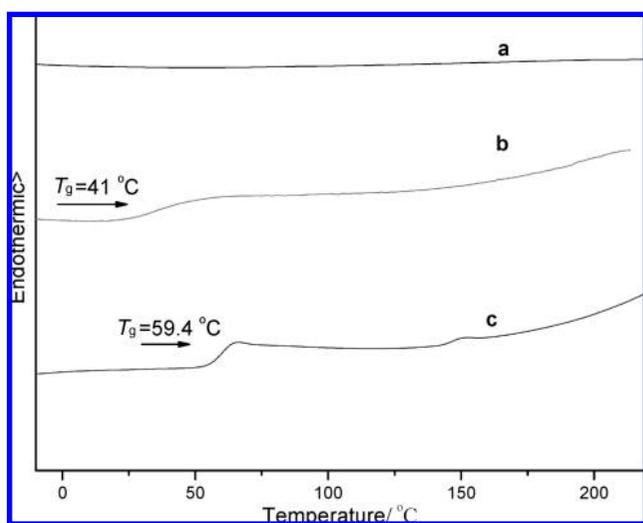


Figure 4. DSC curves of cellulose (a), cellulose-*g*-PLLA ($MS_{\text{PLLA}} = 8.28$, $DS_{\text{PLLA}} = 2.19$) (b), and PLLA (c).

combined at different positions. From the appearance of the C6' peak and the C1' peak, we assigned these two peaks to *O*-lactyl carbonyl carbons in the C6 and C2 positions with reference to the assignment of chemical shift of carbonyl carbons.³²

The crystalline structure of cellulose, cellulose-*g*-PLLA, and PLLA was examined by WAXD measurements (Figure 3). PLLA shows the strongest diffraction peak at $2\theta = 16.76^\circ$ and three diffraction peaks at $2\theta = 14.99$, 19.22 , and 22.56° , whereas cellulose shows three peaks at $2\theta = 15.2$, 22.5 , and 34.5° . However, neither the crystallization peak of PLLA nor that of cellulose was observed for cellulose-*g*-PLLA copolymers, only a dispersive broad peak around $2\theta = 18.22^\circ$ was obtained, indicating copolymers synthesized in the present study were amorphous. In a study by Teramoto et al.,¹⁸ it was shown that CDA-*g*-PLLA copolymers had a crystalline diffraction pattern when $MS_{\text{PLLA}} \geq 14.0$, which should be caused by the relatively long PLLA side-chains.

3.2. Thermal Properties of Cellulose-*g*-PLLA Copolymers. The thermal behavior of cellulose-*g*-PLLA copolymers was measured by DSC. Figure 4 displays thermograms of unmodified cellulose, cellulose-*g*-PLLA ($MS_{\text{PLLA}} = 8.28$, $DS_{\text{PLLA}} = 2.19$), and neat PLLA in the second heating scan. In

Table 2. Thermal Properties of Cellulose-*g*-PLLA Copolymers

sample	T_g	$T_{\text{onset}}(^{\circ}\text{C})$	$T_{\text{max}}(^{\circ}\text{C})$	soften	$T_{\text{initial flowing}}(^{\circ}\text{C})$
cellulose		351.7	372.0	–	
1	142.5	280.9	304.8	–	
2	155.2	310.2	347.9	–	
3	60.5	286.4	328.7	+	147
4	43.8	263.3	323.3	+	110
5	41.0	261.7	303.4 323.3	+	105
6	49.6	257.5	300.8 327.4	+	100
PLLA	59.4	349.1	381.6	+	150

conventional DSC, a reversing event like the glass transition may be hidden by a nonreversing event, such as enthalpic relaxation, so the neat unmodified cellulose did not show a glass transition temperature (T_g) in the standard heating scan. However, using a more sensitive method, Batzer and Kreibich reported a T_g of 230°C for dry cellulose.³³ In the present study, PLLA homopolymer exhibited a glass transition temperature at 59.4°C , which is consistent with previous literature.³⁴ From this figure, it is clearly seen that a T_g of 41°C was observed for cellulose-*g*-PLLA copolymer. This may have resulted from the expansion of intermolecular distance and the enhancement of chain mobility due to the introduction of side PLLA chains.³⁵ It should be noted here that no melting peak was observed in DSC curves of all the copolymer products, suggesting that the synthesized cellulose-*g*-PLLA copolymers were amorphous. This conclusion is in accordance with that obtained by WAXD measurement.

The data collected from DSC for all the samples were summarized in Table 2. It can be seen that with the increase of MS_{PLLA} , the T_g of cellulose-*g*-PLLA copolymers sharply decreases first and then increases slightly after reaching a minimum point of 41.0°C at $MS_{\text{PLLA}} = 8.28$. Compared to the unmodified cellulose, the remarkable decrease in T_g for cellulose-*g*-PLLA copolymers suggested the grafted PLLA side chains played an effective role as “internal” plasticizer to the originally semirigid cellulose material. The increase of T_g observed in the sample with $MS_{\text{PLLA}} = 12.28$ might be attributed to the restricted molecular motion of cellulose-*g*-PLLA by the increased number of PLLA, even if the chain length of each PLLA chain was relatively short. Similar phenomena was also observed for CDA-*g*-PLLA copolymers.¹⁸

The thermal stability of graft copolymers was also evaluated by TGA measurement, as shown in Table 2 and Figure 5. Obviously, the onset decomposition temperature (T_{onset}) and the maximum decomposition temperature (T_{max}) of cellulose-*g*-PLLA copolymers were lower than those of both cellulose and PLLA homopolymer. The decreased thermal stability of copolymers should be attributed to the introduction of PLLA side chains onto the cellulose backbone, which destroyed the crystalline structure of cellulose to some extent. This was also confirmed by WAXD and DSC results. In addition, at $MS_{\text{PLLA}} \leq 6.38$, the graft copolymers decomposed in one step. In contrast, at $MS_{\text{PLLA}} \geq 8.28$, the thermal degradation of cellulose-*g*-PLLA copolymers proceeded in two steps, indicated by two derivative thermogravimetry (DTG) peaks, which should be attributed to the different decomposition temperatures of PLLA and cellulose chains. For cellulose-*g*-PLLA copolymer with $MS_{\text{PLLA}} = 12.28$, the degradation occurring at around 300°C should be caused by the PLLA chains, and that at around 320°C should be caused by the cellulose chain, which is similar to that observed in cellulose-*g*-PCL copolymers.³⁵

3.5. Thermal Flow Characteristics and Thermal Processing of Cellulose-*g*-PLLA Copolymers. Thermal flow behavior of cellulose-*g*-PLLA copolymers was observed by

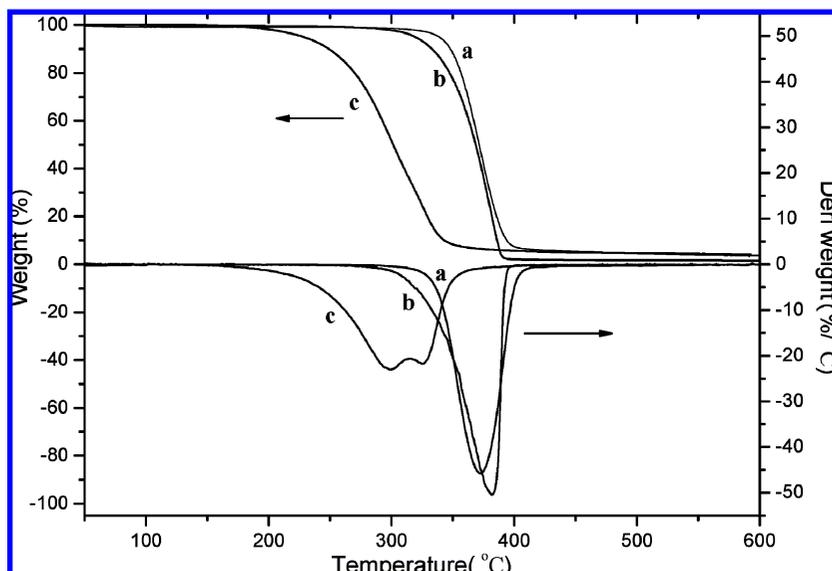


Figure 5. TG and DTG curves of cellulose (a), PLLA (b), and cellulose-g-PLLA ($MS_{PLLA} = 12.28$, $DS_{PLLA} = 2.74$) (c).

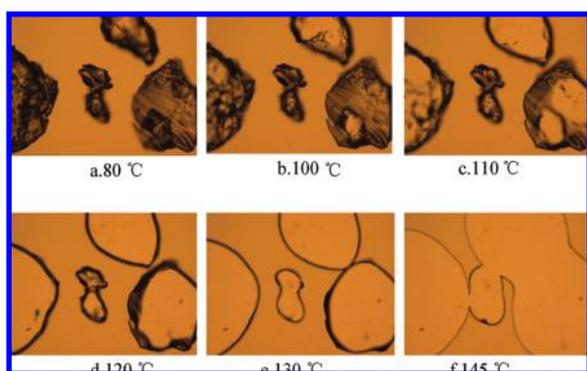


Figure 6. Optical micrographs of cellulose-g-PLLA copolymers ($MS_{PLLA} = 12.28$, $DS_{PLLA} = 2.74$) obtained at different temperatures.

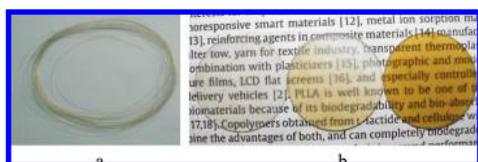


Figure 7. Photographs of Cellulose-g-PLLA fibers and disks produced by thermal processing: (a) cellulose-g-PLLA fibers; (b) cellulose-g-PLLA disks.

means of an optical microscope equipped with a hot-stage device. Figure 6 shows the optical micrographs of cellulose-g-PLLA copolymer ($MS_{PLLA} = 12.28$ and $DS_{PLLA} = 2.74$) obtained at different temperatures. It can be seen that, above 100 °C, the copolymer started to soften up. As the temperature further increased, the sample continued to soften gradually until 145 °C, when it began to flow, indicating a complete softening and flowing of the polymer synthesized in the present study. The dependence of flowing ability on the copolymer composition is shown in Table 2. The graft copolymers softened and flowed when $MS_{PLLA} \geq 4.40$ ($DS_{PLLA} \geq 1.74$), and the initial flowing temperature decreased with an increase in MS_{PLLA} .

Fibers and disks of these graft copolymers were prepared by conventional thermal processing methods such as melt spinning and hot compression molding. Figure 7 shows the photographs of cellulose-g-PLLA copolymer ($MS_{PLLA} = 12.28$ and DS_{PLLA}

= 2.74) fibers (a) spun at 140 °C and disks (b) obtained at different temperatures (140, 170, and 190 °C). It is seen clearly that the cellulose-g-PLLA copolymer disks exhibited a good homogeneity and optical transparency. With the increase of the molding temperature, the colorless sample became yellowish, which was caused by slightly thermal degradation of copolymer processed at relatively higher temperature.

4. Conclusions

In the present work, a convenient and efficient synthesis of cellulose-g-PLLA copolymers with a wide range of MS_{PLLA} was conducted successfully by homogeneous graft reaction of cellulose with LA using DMAP as an organic catalyst in an ionic liquid AmimCl. The resultant cellulose-g-PLLA copolymers exhibited single composition-dependent T_g in their corresponding DSC thermograms. The T_g decreased sharply with the increase of PLLA content up to $MS_{PLLA} = 8.28$ ($DS_{PLLA} = 2.19$) and increased a little with a further increase of the lactyl content. The graft copolymers were amorphous, which was confirmed by DSC and WAXD measurements. The graft copolymers softened and flowed at MS_{PLLA} above 4.40 ($DS \geq 1.74$), which was shown by optical microscopy. Their ability for thermal flow processing was also confirmed by melt spinning and hot compression molding, which favored the production of fibers, films, and so on. The studies on properties of the cellulose-g-PLLA copolymers, including mechanical properties, rheological properties, and biodegradation are now in progress. The factors influencing the grafting reaction will be further investigated, and the thermal processability of copolymers affected by the structure of copolymers such as the amount of grafted PLLA, length of PLLA side chains, and the molecular weight of cellulose substrates as well.

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