SYNTHESIS AND CHARACTERIZATION OF CELLULOSE-GRAFT-POLY (*L*-LACTIDE) VIA RING-OPENING POLYMERIZATION

Shu Xiao,[a] Tongqi Yuan,[b] Huibo Cao,[a] Dai Lin,[a] Yue Shen,[a] Jing He,[a,*] and Bo Wang [b]

Cellulose-graft-poly (*L*-lactide) (cellulose-g-PLLA) was prepared under homogeneous mild conditions. Ring-opening polymerization (ROP) was carried out successfully using 4-dimethylaminopyridine (DMAP) as an organic catalyst in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). The structure of the polymer was characterized by GPC, ^{1}H NMR, ^{13}C NMR, FT-IR, TGA, WAXD, and AFM. The results indicated that the grafting rate of the polymer reached 4.44, which was higher than that reported in AmimCl with Sn(oct)$_2$ as a catalyst. In addition, AFM showed that the polymer in solution could aggregate and self-assemble into an approximately spherical structure, which was different from the rod-like structure of cellulose and round-like polylactic acid particles.

Keywords: Cellulose; Ring-opening polymerization (ROP); Graft polymerization; Ionic liquid

*Contact information: a: Institute of Materials Science and Technology, Beijing Forestry University, 10083, Beijing, China; b: Institute of Biomass Chemistry and Technology, Beijing Forestry University, 100083, Beijing, China; * Corresponding author: hejing2008@sina.com*

INTRODUCTION

Cellulose is the most abundant organic compound in nature as well as an inexpensive, biodegradable, and renewable resource. Cellulose consists of linear polymers of β-(1→4)-D-glucose units and constitutes the main load-bearing component of natural fibers. The use of natural fibers such as flax, jute, and wood fiber (Riedel et al. 1999; Bledzki et al. 1999) instead of traditional reinforcement materials such as glass fibers, carbon, and talc provides several advantages including low density, low cost, good specific mechanical properties, reduced tool wear, and biodegradability (Trejo-*O'* Reilly et al. 2000). Despite several advantages of using cellulose fibers as reinforcement in biocomposites, there are some limitations. The most important restraint is the poor compatibility between the hydrophilic fiber and the hydrophobic polymer (Gradwell et al. 2004; Baiardo et al. 2002). To improve the compatibility between the fiber and the polymer matrix, the reinforcing fiber can be physically or chemically modified (Li et al. 2011). One effective method for chemical modification of cellulose substrates is to grow polymers directly off the surface using the "grafting-from" approach (Bledzki et al. 1999; Xin et al. 2011).

Poly (*L*-lactic acid) (PLLA) is a biodegradable polymer that is a potential candidate for use as matrixes in biocomposites (Riedel et al. 1999; Mohanty et al. 2000; Garlotta et al. 2002; Van de Velde et al. 2002). However, PLLA is a hard, highly crystalline, and transparent polymer with a melting temperature (TM) of 170 to 180 °C, and glass transition temperature (TG) of 53 °C (Riedel et al. 1999; Garlotta et al. 2002).

Ring-opening polymerization (ROP) is a versatile technique for the synthesis of polymers from cyclic monomers (such as lactides) resulting in polymers with controlled molecular weight and molecular weight distribution (Kricheldorf et al. 2001; Endo et al. 2002). The ROP technique has been used frequently to graft biopolymers from substrates other than cellulose such as starch, silica nanoparticles, gold surfaces, and hydroxyapatite surfaces. It is believed that polymers obtained from L-lactide and cellulose will combine the advantages of both and can completely biodegrade under natural conditions in addition to their improved performance. The importance of biocompatible and biodegradable copolymers is continuously increasing in pharmaceutical applications, namely to prepare new controlled drug delivery systems (Allen et al. 1999; Jones et al. 1999; Kataoka et al. 2001; Kwon et al. 2003; Kwon et al. 1995; Kabanov et al. 2002; Hornig et al. 2001). Cellulose-graft-PLLA (cellulose-g-PLLA) copolymers have been synthesized 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 system and an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) (Mayumi et al. 2006; Dong et al. 2008). However, the amount of grafted PLLA in synthesized copolymers was relatively low, and the solubility of the graft copolymers in dimethyl sulfoxide (DMSO) and water was limited.

The aim of this study was to attempt grafting of biopolymers directly from the surface of solid cellulose. The better compatibility achieved in this way (between hydrophobic PLLA and hydrophilic cellulose) should improve the mechanical properties of biocomposites. The graft polymer was successfully synthesized by ROP of *L*-lactide (*L*-LA) onto cellulose in an ionic liquid AmimCl. The crystalline structure analysis and the morphology of the polymer were also studied.

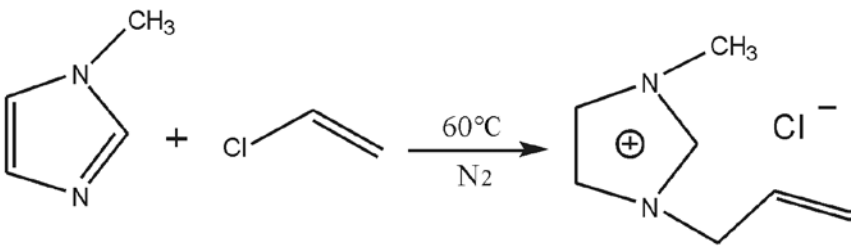
EXPERIMENTAL

Materials

Microcrystalline cellulose with a degree of polymerization (DP) of 225 was supplied by the J&K Chemical Reagent Co., Ltd, China. Allyl chloride of 98% concentration was purchased from Acros Organics, USA. N-methylimidazole of 99% concentration was from the J&K Chemical Reagent Co., Ltd, China. 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. PLLA with a weight-average molecular weight of 50 kD was purchased from Jinan Daigang Co., Ltd. Toluene and DMSO were used as analytical reagents without further purification.

Preparation of 1-allyl-3-methylimidazolium Chloride AmimCl

The room temperature ionic liquid AmimCl was firstly prepared as described by Ren et al. (2003). N-methylimidazole (50 mL) and allyl chloride (60 mL) at a molar ratio of 1:1.25 were added into a round-bottomed flask fitted with a reflux condenser for 8 h at 60°C while stirring. The non-reactive chemical reagents and other impurities were removed by vacuum distillation. The product obtained, i.e., AmimCl, was slightly amber. The obtained light yellow viscous ionic liquid was dried in vacuum for 48 h and the yield was 98%. The reaction equation of AmimCl is shown in Scheme 1.



Scheme 1. Synthesis of AmimCl

Dissolution and Regeneration of Cellulose

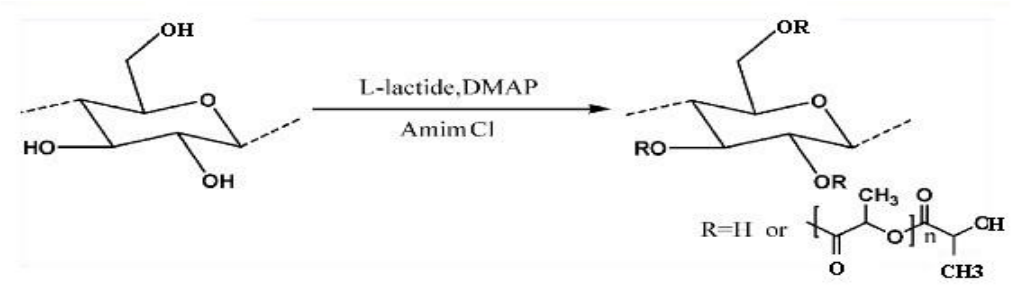
Under the protection of the argon atmosphere, a mixture of cellulose and AmimCl was stirred at 80°C until a transparent solution was formed. The dissolved cellulose was regenerated by precipitating with ethanol and dried in a vacuum overnight.

Preparation of Cellulose-Graft-Poly (*L*-lactide) (Cellulose-G-PLLA) Copolymers

Nucleophilic organic compounds such as DMAP and 4-pyrrolidinopyridine (PPY) are potential candidates for use as highly efficient catalysts for the controlled synthesis of PLLA reported by Hedrick et al. (Nederberg et al. 2001). The outline of the synthesis of cellulose-g-PLLA polymer is given in Scheme 2. A typical procedure for the grafting of PLLA from microcrystalline cellulose (DP 225) was as follows: A 4% (w/w) cellulose/ AmimCl solution was first prepared by mechanical stirring under 80°C for 1 h. The feed ratio of *L*-LA to cellulose in weight was 9:1 with the addition of 3.4 wt% DMAP as a catalyst, respectively. A dry magneton was added into a dry polymerization tube, the tube was then connected to a Schlenk line and put into an oil bath. The ROP of *L*-LA onto cellulose in AmimCl was carried out with nitrogen atmosphere protection at 80°C for 12 h. After cooling to room temperature, the resultant polymer was precipitated with plenty of deionized water and washed with DMSO to obtain the raw product. One gram of cellulose-*g*-PLLA/PLLA was stirred with 30 mL dichloromethane at room temperature for 72 h to dissolve homo-PLLA. After filtration, the precipitate was washed several times with dichloromethane. To confirm the absence of any free polymer, a few drops of filtrate were contacted with ethanol. The absence of any precipitate confirmed that no free polymer remained after the thoroughly efficient washing process. The purified copolymer was dried in a vacuum oven at 60°C until it reached a constant weight. The reaction of the DMAP-catalyzed polymerization of cellulose with poly (*L*-lactide) is shown in Scheme 2. The percentage of grafting (GP) was estimated by the following grafting formula:

$$GP = (M_2 - M_1)/M_1 \times 100\% \quad (1)$$

where M_1 is the amount of cellulose (g) and M_2 is the amount of graft copolymer after removing the homopolymer (g).



Scheme 2. Synthesis of cellulose graft polymer

Measurements

^{1}H-NMR and ^{13}C-NMR spectra of the cellulose-g-poly (L-lactide) polymer were obtained with a Bruker AV300 NMR apparatus by using DMSO-d_6 as solvent.

Wide-angle X-ray powder diffraction (WAXD) was performed with an XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Ni-filtered Cu Kα radiation (40 kV, 30 mA) with 4 °/min scanning rate at room temperature. Diffraction intensity was measured in a range of 2θ = 5 to 40^{o}.

FTIR spectroscopy (Magna-IR 750, Nicolet, USA) was used to characterize the structure of cellulose-g-poly (L-lactide) using a KBr tablet method.

The molecular weight distributions of PLLA obtained by cellulose-g-poly (L-lactide) were measured by a gel permeation chromatography (GPC) (equipped with a PL-gel 10 mm Mixed-B 7.5 mm ID column) with DMSO as the eluent. The flow rate was 1 mL/min.

Thermogravimetric analysis (TGA-60, Shimadzu, Japan) was carried out to determinate the thermal stability with a heating rate of 10°C/min from 50 to 600°C while the apparatus was continually flushed with a nitrogen flow of 20 mL/min. All samples were dried under vacuum at 40°C for 24 h prior to TGA measurements.

The aggregated and self-assembled morphology of cellulose-g-PLLA was examined by Atom Force Microscopy (AFM) (Veeco diMultiMode V).

RESULTS AND DISCUSSION

Table 1 summarizes the experimental results obtained by changing the synthesis conditions. At low temperatures the product cellulose-g-PLLA had a low graft ratio, while at high temperatures the radical coupling would be increased. Therefore, the polymerization temperature was set at 80^{o}C. It can be seen that the grafting content of PLLA in polymers increased with the increase of weight ratio (LA to cellulose) in the feed. When the feed ratio of *L*-LA to cellulose in weight was 9:1 with the addition of 3.4 wt% catalyst, the molar substitution of PLLA (MS_{PLLA}) in the graft product was highest. At the same time, the MS_{PLLA} of the polymer with DMAP as a catalyst was higher than the polymer with $Sn(oct)_2$ as a catalyst under the same reaction condition. That is because *L*-LA reacts with DMAP to form an intermediate. This intermediate can attack alcohol hydroxyl groups of cellulose more easily than *L*-LA. Because of the tendency of hydroxyl

oxygen of cellulose to link with carboxyl group, DMAP is eliminated from the next cycle of catalyzation. As can be seen from Table 1, the highest MS, DS, and DP values of cellulose-g-PLLA copolymer were 4.44, 1.14, and 3.80, respectively. These values were much higher than those reported in the DMAc/LiCl system (Mayumi et al. 2005) and those in AmimCl with $Sn(oct)_2$ as a catalyst (Dong et al. 2008). Therefore, the cellulose-g-PLLA copolymer with MS 4.44 was selected for structure characterization.

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

No.	LA/cellulose (g/g)	Temp(^{o}C)	$Sn(Oct)_2$/DMAP(wt %)	Time (min)	DP_{PLLA}	DS_{PLLA}	MS_{PLLA}
1	1	80	$Sn(Oct)_2$ 3.4	12	1.45	0.69	0.99
2	2	80	$Sn(Oct)_2$ 3.4	12	1.49	0.97	1.45
3	4	80	$Sn(Oct)_2$ 3.4	12	1.58	1.07	1.81
4	6	80	$Sn(Oct)_2$ 3.4	12	1.70	0.75	1.27
5	9	80	$Sn(Oct)_2$ 3.4	12	1.94	1.29	1.87
6	4	80	DMAP 3.4	12	2.55	0.74	3.95
7	6	80	DMAP 3.4	12	3.75	1.09	4.40
8	9	80	DMAP 3.4	12	3.90	1.14	4.44

^{1}H NMR spectra of cellulose-g-PLLA polymers were measured with a Bruker AV 300 NMR apparatus using DMSO-d_6 as the solvent with a drop of trifluoroacetic acid-d to shift active hydrogen to a lower field area, and tetramethysilane (TMS) as an internal standard. Figure 1 exemplifies an ^{1}H NMR spectrum obtained for the cellulose-g-PLLA polymer. Besides, the carbon and hydrogen positions of the cellulose-g-PLLA polymers are also labeled in Fig. 2. The molar substitution (MS, an average number of introduced lactyl units per anhydroglucose of cellulose), the degree of lactyl substitution (DS_{LA}, an average number of introduced terminal lactyl units per anhydroglucose of cellulose), and the average degree of polymerization of the PLLA-side chain (DP_{LA}, the molar amounts of combined LA per glucopyranoside unit of cellulose-g-PLLA) were estimated directly by ^{1}H NMR analysis according to the following equations:

$$MS_{PLLA} = \text{lactyl units/anhydroglucose units} = [IA(b + b') / 3] / \{[IAc - IA(b + b') / 3] / 7\}$$

$$DS_{PLLA} = \text{terminal lactyl units/anhydroglucose units} = (IAb' / 3)/\{[IAc - IA(b + b') / 3]/ 7\}$$

$$DP_{PLLA} = MS/DS = [IA(b + b') / 3] / (IAb' / 3) = 1 + IAb / IAb' \quad (2, 3, 4)$$

In these equations the IAa and IAa' are an area from terminal methyl protons of lactyls in PLLS side-chains and an area from the terminal methyl protons of lactyls, respectively; the IAb and IAb' are a resonance peak area derived from internal methine protons of lactyls in PLLA side-chains and an area from terminal methine protons of lactyls in PLLA side-chains, respectively; the IAc is the area of all protons of anhydroglucose unit.

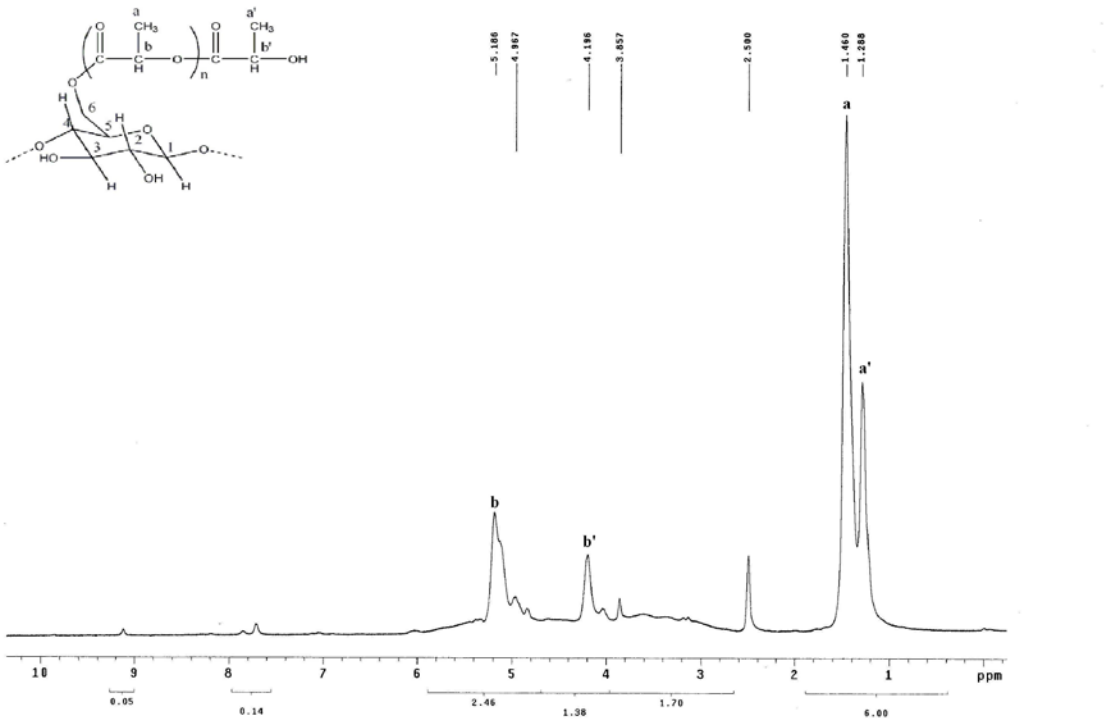


Fig. 1. ^{1}H NMR spectrum of cellulose-g-PLLA (MS = 4.44) in DMSO-d_6

Structure Characterizations of Cellulose-g-PLLA

According to the GPC curve, the Mn of polymers is 15320 g/mol (polystyrene as a standard contrast), and there is only one peak in the range of eluent time, which confirms the complete removal of homo-PLLA (Fig. 2).

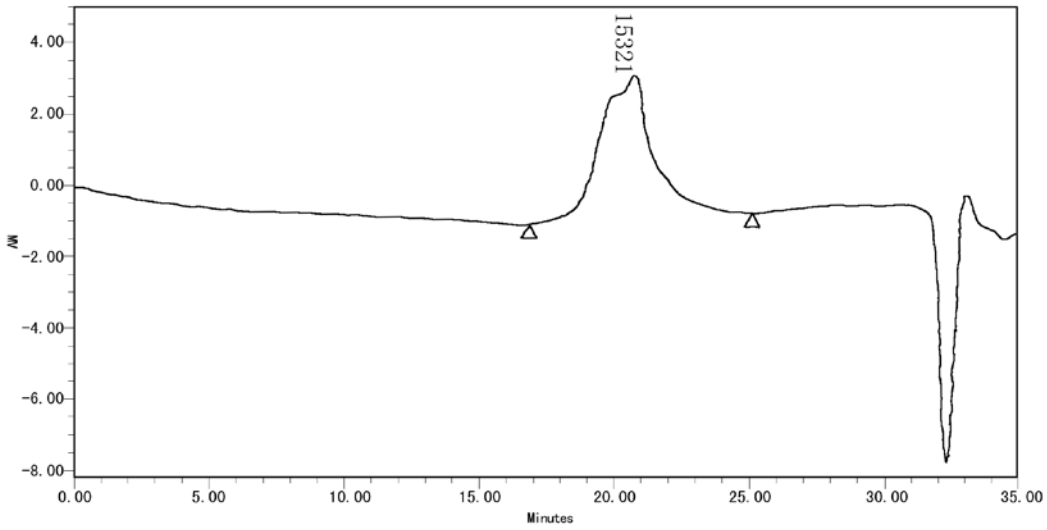


Fig. 2. GPC curve of cellulose-g-PLLA (MS = 4.44)

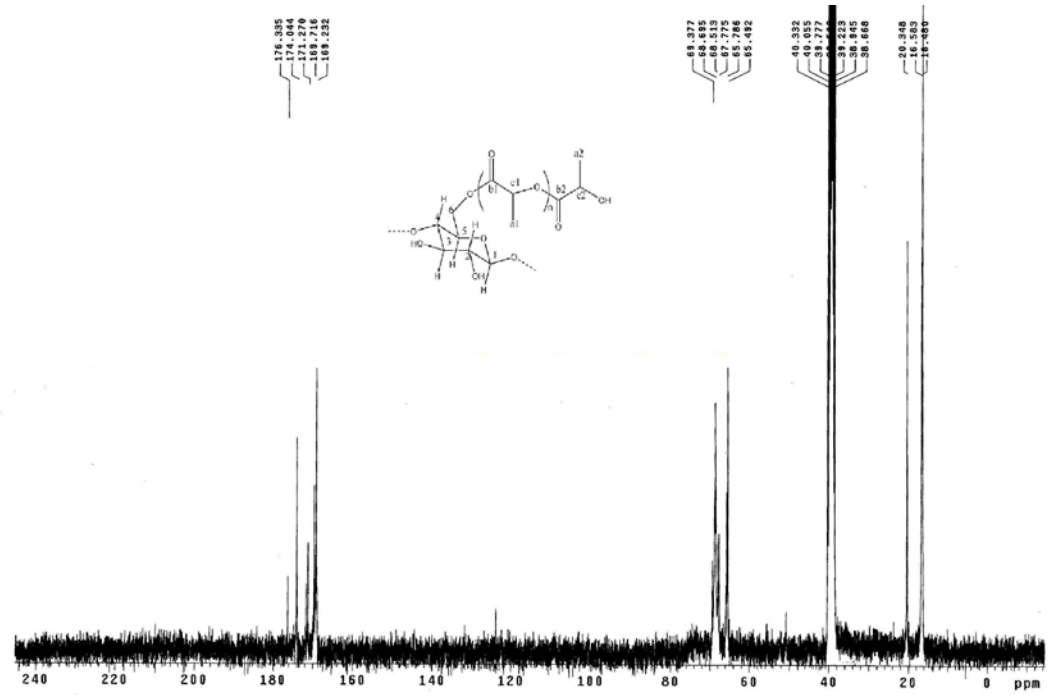


Fig. 3. ^{13}C NMR spectrum of cellulose-g-PLLA (MS = 4.44) in DMSO-d_6

The ^{13}C NMR method was employed to characterize the structure of cellulose-g-PLLA. The ^{13}C NMR spectrum of cellulose-g-PLLA in DMSO-d_6 (Fig. 3) exhibits signals at chemical shifts (δ) of 16.53, 20.35, 65.78, and 68.33 ppm, which are ascribed to the a1, a2, c2, and c1 carbons of ring-opened L-LA portions, respectively. Carbonyl carbons from b1 and b2 appeared at 171.27 and 176.34 ppm, respectively. The peaks at 65.49, 69.39, 68.69, 68.51, 68.38, and 123.8 ppm are assigned to the C-6, C-4, C-5, C-3, C-2, and C-1 carbons of origin cellulose, respectively. The peak for C-6' is due to the C-6 carbons of LA-substituted hydroxyl groups of cellulose and appears at around 65.78 ppm, ca. at a δ of 0.29 ppm lower than for the original C-6. Another peak, C-4', is assigned to C-4 carbons adjacent to C-3 carbons bearing a substituted hydroxyl group (Miyamoto et al. 1984). In the magnified scale of 170 to 180 ppm, there are two peaks (a2-C-6 176.3, a2-C-3 174.1 ppm) for carbonyl carbons of a2, which are assigned to the *O*-lactyl carbonyl carbons in C-6 and C-3 positions with the reference to the assignment of a chemical shift of carbonyl carbons (Hornig et al. 2008; Kamide et al. 1981). These results indicate that the L-LA molecule not only combines at the C-6 position, but also combines at the C-3 position. Obviously, a preferential reaction with L-LA is at the cellulose C-6 and the order of reactivity is C6-OH > C3-OH > C2-OH, which is well consistent with the reported work for cellulose in AmimCl ionic liquid (Wu et al. 2004). As shown in the FT-IR spectra in Figs. 4 and 5, the peak at 3453 cm^{-1} is assigned to the OH stretching vibration; the new strong band appears at 1754 cm^{-1} is assigned to the carbonyl group. The above two mentioned peaks exist in cellulose-g-PLLA, which supports the synthesis of the graft copolymer. According to the FT-IR and ^{13}C NMR, it is reasonable to deduce that the ROP of L-LA onto cellulose took place.

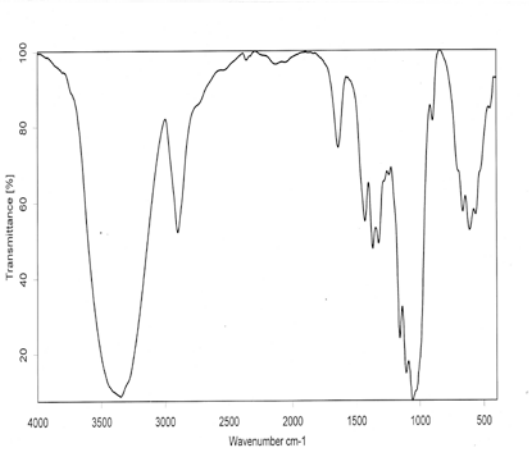


Fig. 4. FT-IR spectrum of cellulose

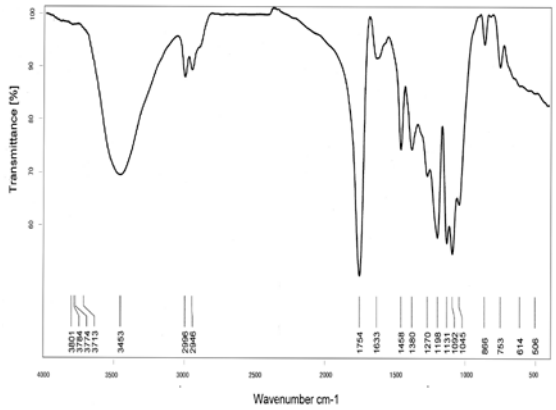


Fig. 5. FT-IR spectrum of cellulose-g-PLLA (MS = 4.44)

Crystalline Structure Analysis and Thermal Stability of Cellulose-g-PLLA

As shown in Fig. 6, the crystalline structure of cellulose, cellulose-g-PLLA, and PLLA are semicrystalline with the strongest diffraction peak at $2\theta = 17.0^{o}$ and three diffraction peaks at $2\theta = 15.2$, 19.2, and 22.6^{o} for PLLA and three peaks at $2\theta = 15.0$, 16.4, and 22.6^{o} for cellulose. However, the introduction of PLLA to the cellulose backbone greatly changed its melting and crystallizing behaviors. In the WAXD curve, a dispersive broad peak around $2\theta = 19.4^{o}$ appears, which indicates that cellulose becomes amorphous when being grafted by PLLA. It was shown that CDA-g-PLLA copolymers had a crystalline diffraction pattern when $MS_{PLLA} > 14.0$, which should be caused by the relatively long PLLA side-chains (Teramoto et al. 2003). The results are in accordance well with the TGA results. As shown in Fig. 7, the onset decomposition temperature (T_{onset}) and the maximum decomposition temperature (T_{max}) of cellulose-g-PLLA polymers were lower than those of both cellulose and PLLA homopolymer. The decreased thermal stability of polymers 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 results.

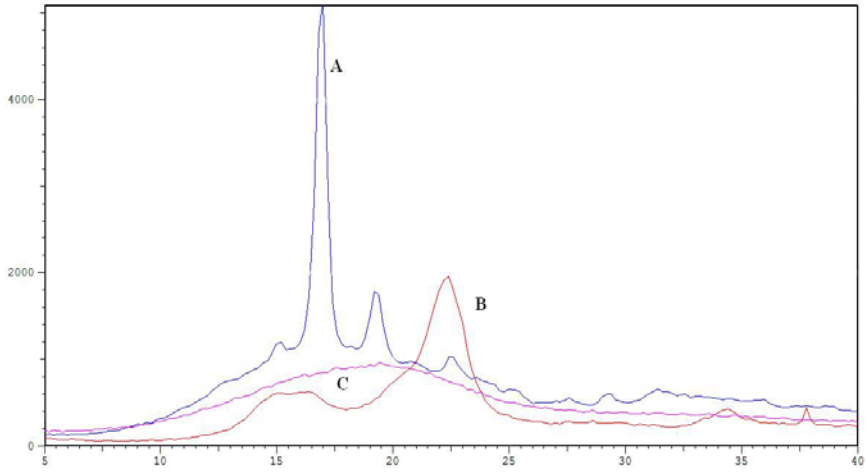


Fig. 6. WAXD spectra of cellulose (B), PLLA (A), and cellulose-g-PLLA (MS = 4.44) (C)

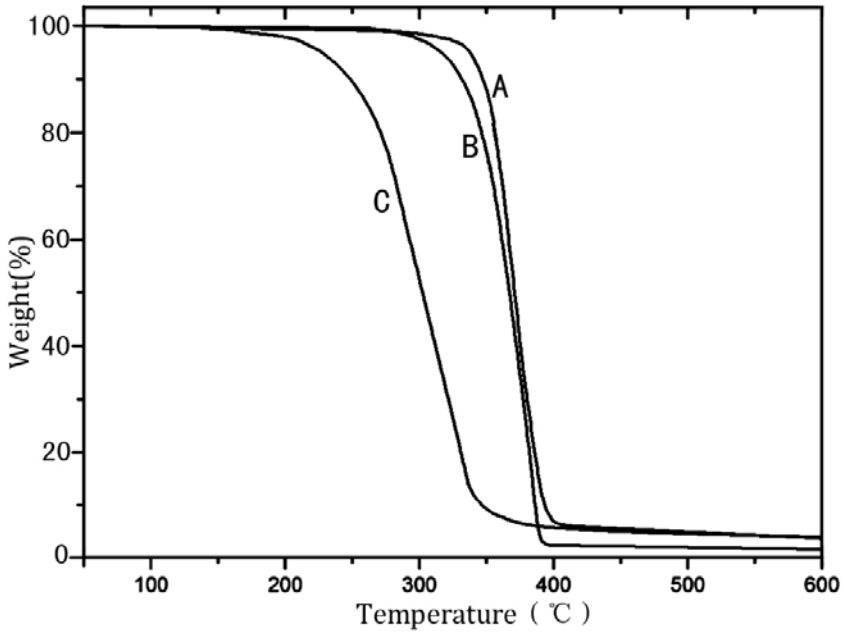


Fig. 7. TGA curves of cellulose (A), PLLA (B), and cellulose-g-PLLA (MS = 4.44) (C)

Morphological Characterization of Cellulose-g-PLLA

The cellulose-g-PLLA was dissolved in dimethylformamide (DMF), then the morphology of the aggregates was examined by AFM. As shown in Fig. 8, the average diameter and height of a single polymer itself are about 300 nm and 353 nm, respectively, which suggested that the surface morphology of the graft copolymer was approximately spherical, differing from the rod-like structure of cellulose and round-like polylactic acid particles.

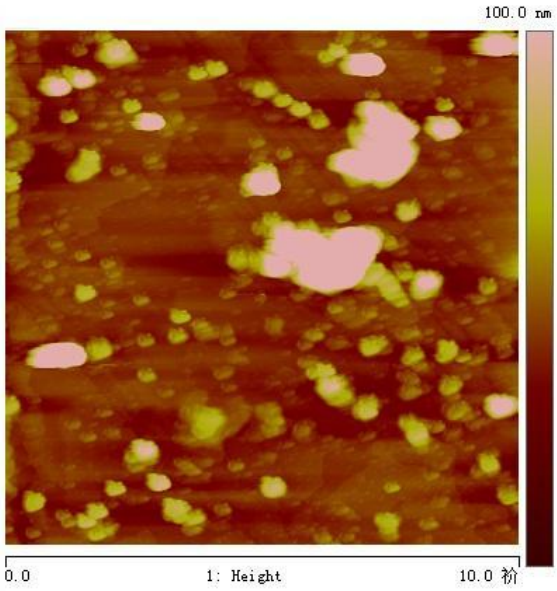


Fig. 8. AFM image for the aggregates formed from cellulose-g-PLLA (MS = 4.44)

Figure 9 shows the 3D image of cellulose-g-PLLA. It is clear that the height of the aggregation area is higher than the single area formed by cellulose-g-PLLA. It is likely that the manner of aggregation for small particles was not only parallel but overlapping. The small particles aggregated into large independent particles, which indicated the aggregation tendency of cellulose-g-PLLA polymers in solution. The aggregation and self-assembly of the polymers to the micelles in DMF provide the basis for the changes in morphology before the use of drug.

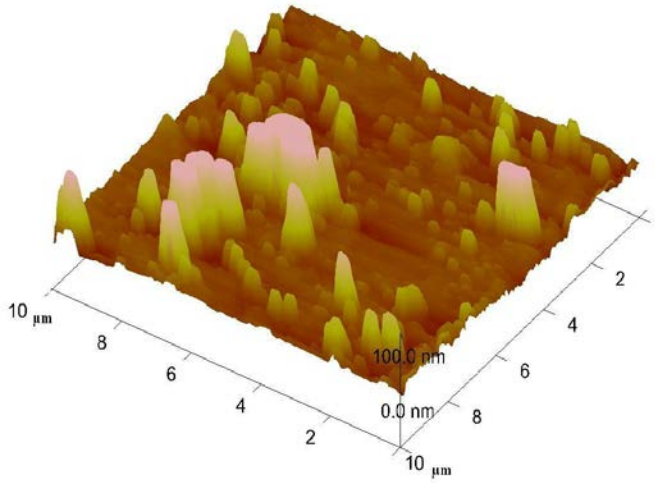


Fig. 9. 3D image of Fig. 8 (scan size: 10 × 10 µm)

CONCLUSIONS

An effective method for grafting L-lactide (LA) from unmodified cellulose by ring-opening polymerization (ROP) under homogeneous conditions was carried out. A biocompatible and biodegradable polymer comprised of hydrophobic PLLA and hydrophilic cellulose was successfully synthesized in AmimCl with DMAP as a catalyst. The graft polymers were amorphous, which was confirmed by WAXD and TGA measurements. The amount of grafted PLLA in synthesized polymers was higher than that reported in the DMAc/LiCl system and that in AmimCl with $Sn(oct)_2$ as a catalyst. Moreover, the graft polymers were well dissolved in common organic solvents and water, which provides the basis for its application in drug release systems. The single graft polymer was approximately spherical and could aggregate into large particles, as shown by AFM. The DP of cellulose and the length of PLLA side chains will also be considered to analyze the reaction mechanism and the characteristic of polymers in a future study.

ACKNOWLEDGMENTS

The authors are grateful for the support of this research from Major State Basic Research Projects of China (973-2010CB732204) and the National Natural Science Foundation of China (31170556).

REFERENCES CITED

Allen, C., Maysinger, D., and Eisenberg, A. (1999). "Nano-engineering block copolymer aggregates for drug delivery," *Colloid. Surface. B.* 16(1-4), 3-27.

Baiardo, M., Frisoni, G., Scandola, M., and Licciardello, A. (2002). "Surface chemical modification of natural cellulose fibers," *J. Appl. Polym. Sci*. 83(1), 38-45.

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibres," *Prog. Polym. Sci.* 24(2), 221-274.

Dong, H. Q., Xu, Q., Li, Y. Y., Mo, S. B., Cai, S. J., and Liu, L. J. (2008). "The synthesis of biodegradable graft copolymer cellulose-graft-poly(L-lactide) and the study of its controlled drug release," *Colloid. Surface. B.* 66, 26-33.

Endo, T., Shibasaki, Y., and Sanda, F. (2002). "Controlled ring-opening polymerization of cyclic carbonates and lactones by an activated monomer mechanism," *J. Polym. Sci. Pol. Chem.* 40(13), 2190-2198.

Garlotta, D. (2002). "A literature review of poly(lactic acid)," *J. Polym. EnViron*. 9(2), 63-84.

Gradwell, S. E., Renneckar, S., Esker, A. R., Heinze, T., Gatenholm, P., Vaca-Garcia, C., and Glasser, W. (2004). "Surface modification of cellulose fibers: towards wood composites by biomimetics," *Comptes Rendus Biologies* 327(9-10), 945-953.

Hornig, S., and Heinze, T. (2008). "Efficient approach to design stable water-dispersible nanoparticles of hydrophobic cellulose esters," *Biomacromolecules* 9(5), 1487-1492.

Jones, M. C., and Leroux, J. C. (1999). "Polymeric micelles – a new generation of colloidal drug carrier," *Eur. J. Pharm. Biopharm.* 48, 101-111.

Kabanov, A. V., and Alakhov, V. Y. (2002). "Pluronic block copolymers in drug delivery: from micellar nanocontainers to biological response modifiers," *Crit. Rev. Ther. Drug* 19, 1-72.

Kamide, K., and Okajima, K. (1981). "Determination of distribution of O-acetyl group in trihydric alcohol units of cellulose acetate by carbon-13 nuclear magnetic resonance analysis," *Polym. J.* 13, 127-133.

Kataoka, K., Harada, A., and Nagasaki, Y. (2001). "Block copolymer micelles for drug delivery:design,characterization and biological significance," *Adv. Drug Deliver. Rev.* 47(1), 113-131.

Kricheldorf, H. R. (2001). "Syntheses and application of polylactides," *Chemosphere* 43 (1), 49-54.

Kwon, G. S., and Kaoka, K. (1995). "Block copolymer micelles as long-circulating drug vehicles," *Adv. Drug Deliver. Rev.* 16, 295-309.

Kwon, G. S. (2003). "Polymeric micelles for delivery of poorly watersoluble compounds," *Crit. Rev. Ther. Drug* 20, 357-403.

Li, H., Liu, H., Fu, S., and Zhan, H. (2011). "Surface hydrophobicity modification of cellulose fibers by layer-by-layer self-assembly of lignosulfonates," *BioResources* 6(2), 1681-1695.

Mayumi, A., Kitaoka, T., and Wariishi, H. (2006). "Partial substitution of cellulose by ring-opening esterification of cyclic esters in a homogeneous system," *J. Appl. Polym. Sci. 102*, 4358-4364.

Miyamoto, T., Sato, Y., Shibata, T., and Inagaki, H. (1984). "^{13}C nuclear magnetic resonance studies of cellulose acetate," *J. Polym. Sci. Pol. Chem.* 22, 2363-2370.

Mohanty, A. K., Misra, M., and Hinrichsen, G. (2000). "Biofibres, biodegradable polymers and biocomposites: an overview," *Macromol. Mater. Eng*. 276-277, 1-24.

Nederberg, F., Connor, E. F., Möller, M., Glauser, T., and Hedrick, J. L. (2001). "New paradigms for organic catalysts: the first organocatalytic living polymerization," *Angew. Chem. Int. Edit*. 40, 2712-2715.

Riedel, U., and Nickel, J. (1999). "Natural fibre-reinforced biopolymers as construction materials-new discoveries," *Angew. Makromol. Chem.* 272, 34-40.

Teramoto, Y., and 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.

Trejo-O'reilly, J. A., Cavaille, J. Y., Paillet, M., Gandini, A., Herrera-Franco, P., and Cauich, J. (2000). "Interfacial properties of regenerated cellulose fiber/polystyrene composite materials. Effect of the coupling agent's structure on the micromechanical behavior," *Polym. Composite*. 21, 65-71.

Van de Velde, K., and Kiekens, P. (2002). "Biopolymers: overview of several properties and consequences on their applications," *Polym. Test.* 21(4), 433-442.

Wu, J., Zhang, J., Zhang, H., He, J. S., Ren, Q., and Guo, M. L. (2004). "Homogeneous acetylation of cellulose in a new ionic liquid." *Biomacromolecules* 5, 266-268.

Xin, T. T., Yuan, T. Q., Xiao, S., and He, J. (2011). "Synthesis of cellulose-graft-poly(methyl methacrylate) via homogeneous ATRP," *BioResources* 6(3), 2941-2953

Article submitted: November 5, 2011; Peer review completed: January 29, 2012; Revised version received and accepted: February 17, 2012; Published: February 20, 2012.