

# Ring-Opening Graft Polymerization of L-Lactide onto Starch Granules in an Ionic Liquid

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**ABSTRACT:** A room temperature ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) was a promising direct solvent for starch and nonderivitizing solvent for starch-effective dissolution, in which the ring-opening graft polymerization (ROGP) of L-lactide (L-LA) onto starch chains was carried out homogeneously. The obtained starch grafted poly(L-lactide) (starch-g-PLLA) was characterized by FTIR,  $^{13}\text{C}$  NMR, DSC, and WAXD, and the good adhesion between the two components was evidenced by SEM observations although the chains of grafted PLLA were not long. The grafting efficiency of PLLA reached

30% when the ROGP proceeded at 100°C for 10 h with L-LA/starch 0.5 : 1 (wt/wt) and stannous octoate ( $\text{Sn}(\text{Oct})_2$ ) as a catalyst, which was calculated according to a standard curve newly created by FTIR method. The homopolymerization of L-LA and the disconnection of grafted PLLA from starch-g-PLLA were the main competition reactions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2704–2713, 2008

**Key words:** grafting polymerization; homogeneous; ionic liquid; poly(L-lactide); starch

## INTRODUCTION

Starch is a potentially useful, economic, and the most abundant biodegradable material, and various physical and chemical modifications of starch granules including blending<sup>1–7</sup> and grafting<sup>8–13</sup> have been considered to improve its mechanical properties and process capability.

Recently, the biodegradable polymer-grafted starch attracts much attention and mostly, poly(L-lactide) (PLLA) and poly( $\epsilon$ -caprolactone) (PCL) are chosen as artificial segments for starch-g-PLLA, and starch-g-PCL can completely biodegrade under natural conditions in addition to their improved performance.<sup>8–15</sup> A noticeable way to introduce PLLA and PCL segments onto starch is the ring-opening graft polymerization (ROGP) of L-lactide (L-LA) and  $\epsilon$ -caprolactone (CL).<sup>16</sup>

The efficient dissolution of starch is a long-standing goal in starch research and development and still of great importance. Usually, suspension and bulk polymerization are applied for the starch graft and the reactions are carried out heterogeneously.<sup>8–11,16</sup>

The solvent for the suspension grafting can be toluene,<sup>8,9</sup> *N,N*-dimethylacetamide<sup>10</sup> and, sometimes, a caustic media.<sup>11</sup> The heterogeneous reaction and nongreen solvent have caused many problems such as volatility, toxicity, costly, difficulty for solvent recovery, or instability in processing.

The room temperature ionic liquids (ILs) are considered as green reaction media for processes including catalysis.<sup>17,18</sup> Cellulose can dissolve in some ILs<sup>19</sup> and high-grafted cellulose derivatives such as carboxymethyl cellulose and cellulose acetate and are synthesized using 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) as a solvent.<sup>20</sup> The degree of the polymerization ranges from 290 to 1200 without any catalyst, and no degradation of the polymer is observed. Very recently, Biswas et al.<sup>21</sup> reveals that starch and zein can also dissolve in [BMIM]Cl up to 15% (wt/wt) concentration at 80°C. What is more, just like [BMIM]Cl, 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) is found to have excellent capability for dissolving cellulose, and the solubility of cellulose in [AMIM]Cl is better than in [BMIM]Cl on the same dissolving conditions (90–100°C, 3–5% wt).<sup>22,23</sup> The ILs containing chloride anion, that can form strong hydrogen-bond contacts,<sup>24</sup> seems to be most appropriate for biopolymers such as starch, cellulose, and zein. And among them, the ILs containing one unsaturated substituent on the nitrogen of *N*-methyl-imidazole may be more effective.

The polymer synthesis using ILs as solvents are systematically studied in last few years.<sup>25–27</sup> Strehmel

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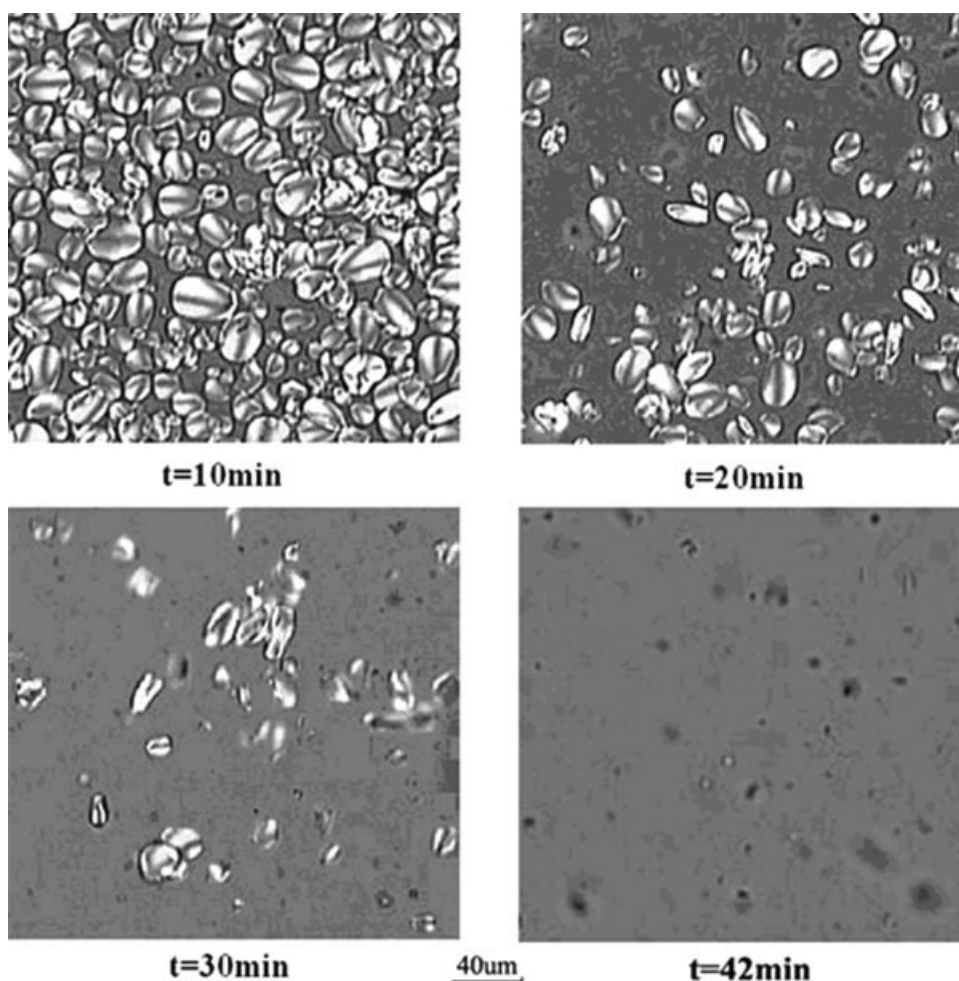


Figure 1 Dissolving process of starch in [AMIM]Cl at 80°C traced by a polar microscope.

investigates the polymerization of *n*-butyl methacrylate in ILs. ILs have no detectable influence on polymer tacticity but in which the degrees of polymeriza-

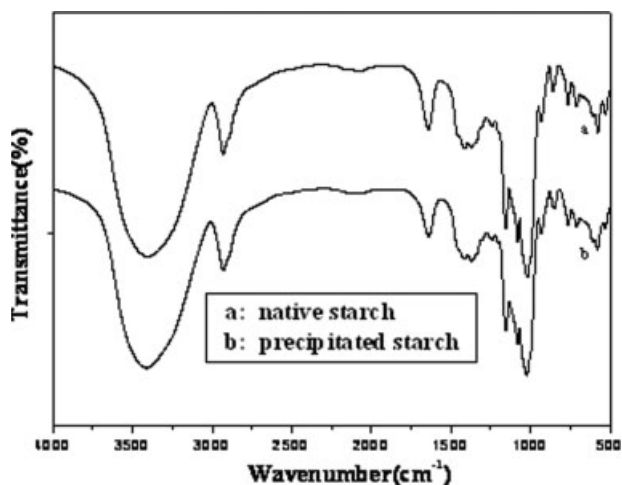


Figure 2 Typical FTIR spectra of native (a) and precipitated starch (b).

tion are significantly higher compared with polymerization in toluene, and can even exceed the values obtained by bulk polymerization.<sup>28</sup> Meanwhile, the ring-opening polymerization (ROP) of D,L-LA and L-LA in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, using Sn(Oct)<sub>2</sub> as a catalyst and benzyl alcohol as an initiator, proceeds smoothly and high molecular weight PDLLA ( $M_w$  187,700 g/mol, conversion 85.4%) and PLLA ( $M_w$  217,600 g/mol, conversion 97.6%) are obtained after a 16-h reaction.<sup>29</sup>

A homogeneous modification of starch by the ROGP of L-LA was thus investigated with [AMIM]Cl as a reaction media in our research. The behavior of starch granules dissolving in the IL and the results of the ROGP are presented in this article.

## EXPERIMENT SECTION

### Materials

Corn starch consists of 75% amylopectin and 25% amylose, that was dehydrated with toluene as azeotropic dehydration agent and dried in vacuum

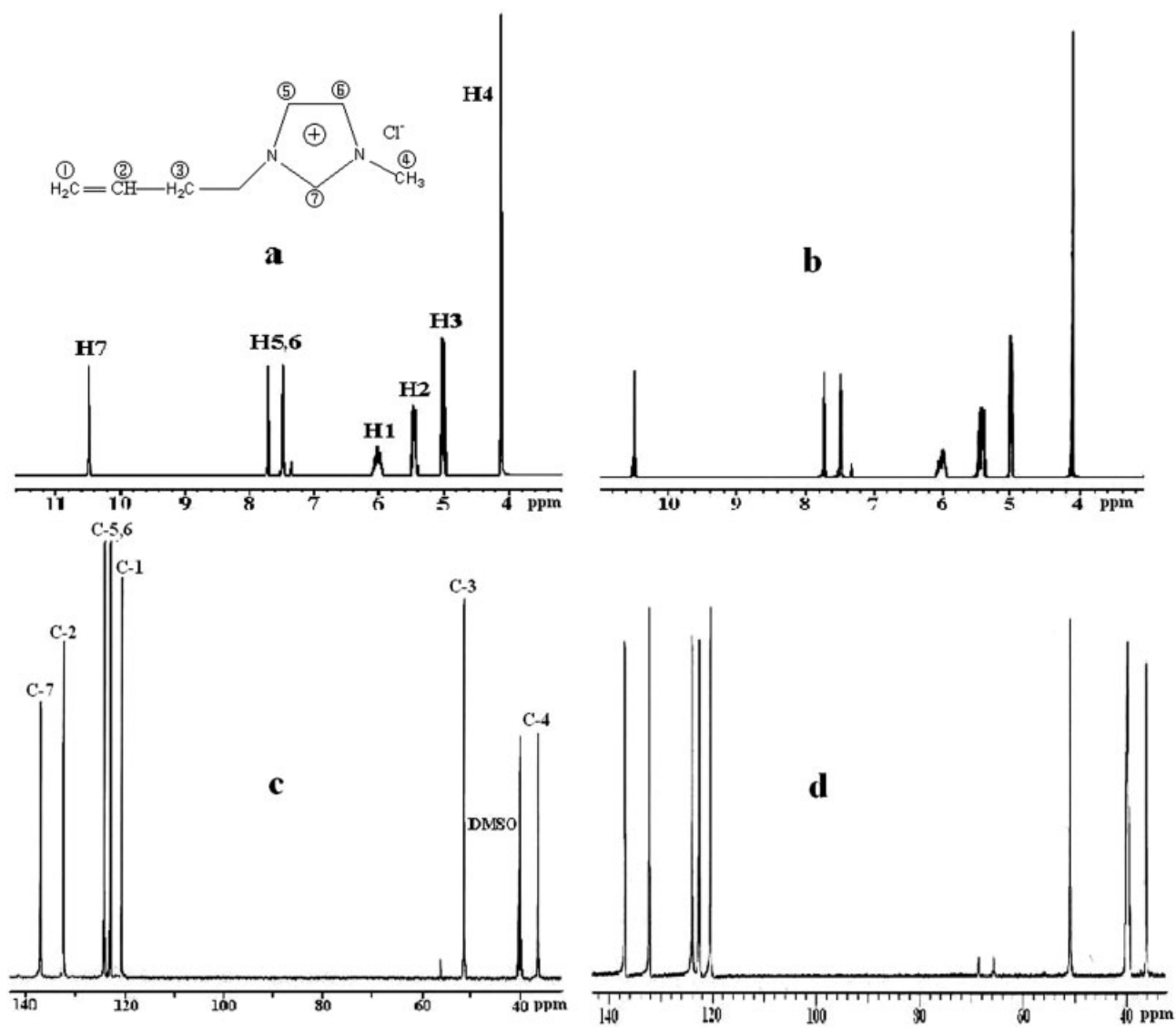


Figure 3 Typical  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of unused (a, c) and recovered [AMIM]Cl (b, d).

(80°C, 100 pa) for 48 h. L-LA was synthesized according to literature and recrystallized five times from anhydrous ethyl acetate. *N*-methyl-imidazole was dried over  $\text{CaH}_2$  for 2 days and distilled.  $\text{Sn}(\text{Oct})_2$  was distilled in vacuum and dissolved in freshly dried toluene. PLLA was purchased from NatureWorks LLC. All the other reagents were analytical grade and used as received.

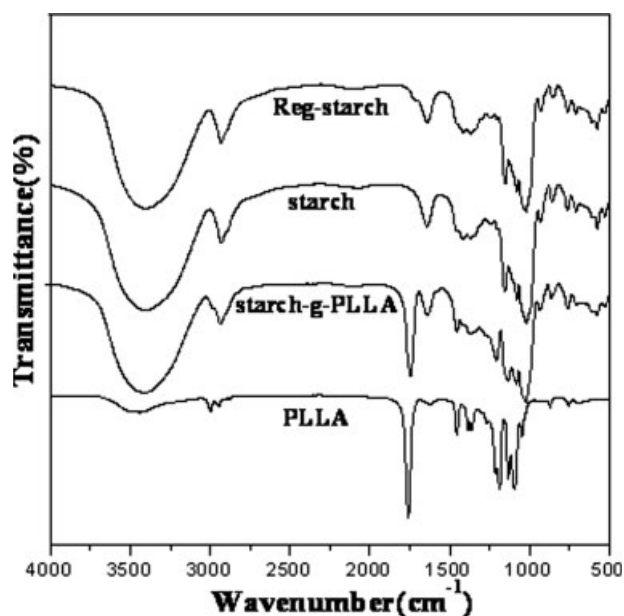
### Measurements

FTIR spectra were recorded on Perkin-Elmer-2 spectrometer. The samples were pressed as pellets with potassium bromide (KBr).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a MercuryVX-300 spectrometer using tetramethylsilane as an internal standard and  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  as solvents.

Differential scanning calorimetry (DSC) measurement was carried out on a DSC apparatus (DSC822<sup>e</sup>, mettler Toledo) under a nitrogen atmosphere at a heating rate of 10°C/min from 30 to 200°C. Wide-angle X-ray powder diffraction was performed by Shimadzu XRD-6000 X-ray diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 30 mA) with 4°/min scanning rate at room temperature.

Scanning electron microscopy (SEM) images were obtained with a Model XL 30 ESEM FEG from Micro FEI Philips after the sputter coating of gold on the specimen surface. The photographs of the starch granules in solid and [AMIM]Cl was measured by a polarizing light microscope (Olympus BX51).

$M_w$  and the polydispersity index ( $M_w/M_n$ ) of PLLA were determined by gel permeation chromatography (GPC) on a Waters high-pressure liquid chromatographic system equipped with a model 2690D separa-



**Figure 4** FTIR spectra of PLLA, starch-g-PLLA, native starch and Reg-starch.

tion module, a model 2410 refractive-index detector, and a Shodex K803 column. Chloroform was used as an eluent at a flow rate of 1.0 mL/min. GPC data were calibrated by standard polystyrene.

### Preparation of [AMIM]Cl

*N*-methyl-imidazole (41.06 g, 0.50 mol) and 3-chloropropylene (45.92 g, 0.60 mol) were added into a three-necked flask equipped with a mechanical stirrer and a water condenser. The reaction was conducted at 60°C for 6 h under the protection of argon atmosphere. The excess 3-chloropropylene was removed by distillation and the unreacted *N*-methyl-imidazole was extracted out with ether. The obtained light yellow viscous ionic liquid was dried in vacuum for 48 h and the yield was 98%.

### Dissolving and regeneration of starch

Under the protection of argon atmosphere, a mixture of starch (1 g) and [AMIM]Cl (5 g) was stirred at 80 or 100°C until a transparent solution was formed, and the dissolving process was traced by a polarizing light microscope. The dissolved starch was regenerated by precipitating it with ethanol.

### Grafting reaction of starch in [AMIM]Cl

Typical procedure: The ROGP of L-LA onto starch granules in [AMIM]Cl was carried out at 100°C for 10 h under argon atmosphere and anhydrous condition with 0.1 wt % Sn(Oct)<sub>2</sub> as a catalyst. The fed ratio of L-LA to starch in weight was 0.5 : 1, 1 : 1, 1.5 : 1,

respectively. The obtained reaction mixture was precipitated in ethanol to remove unreacted L-LA, residual catalyst, and [AMIM]Cl, and the precipitate was a mixture of the grafted copolymer and homo-PLLA (starch-g-PLLA/PLLA).

One gram of starch-g-PLLA/PLLA was stirred with 30 mL of dichloromethane at room temperature for 72 h to dissolve homo-PLLA. After filtration the residue was washed several times with dichloromethane and dried in vacuum for 48 h before it was characterized by FTIR, <sup>13</sup>C NMR, WAXD, DSC as well as SEM.

### Recovery of [AMIM]Cl

To separate [AMIM]Cl from the waste liquid produced at the step of precipitation in the grafting of starch, ethanol was first eliminated by evaporation and the other impurities such as unreacted L-LA and residual catalyst were extracted by acetone. The such recovered [AMIM]Cl, which was characterized by <sup>1</sup>H and <sup>13</sup>C NMR, was qualified for the recycle in the ROGP.

### Calculation of the grafting efficiency of PLLA

The grafting efficiency (*G*%) is calculated as follows:

$$G\% = \frac{m_{ST}}{m_{LA}} \times \frac{\text{PLLA wt \%}}{1 - \text{PLLA wt \%}}$$

where *m*<sub>ST</sub> is the weight of dried native starch and *m*<sub>LA</sub> is the weight of fed L-LA monomer. PLLA wt % is the weight percentage of PLLA in starch-g-PLLA, which is estimated by the following equation:

$$\text{PLLA wt \%} = 4.55 + 0.62\Delta I$$

where,  $\Delta I$  is defined as the difference between the intensities of two FTIR signals at 1745 and 1645 cm<sup>-1</sup>, which are characteristic peaks of PLLA and starch segment in starch-g-PLLA, respectively.

## RESULTS AND DISCUSSION

### Evaluation on the starch/[AMIM]Cl system

[AMIM]Cl as a media for the ROGP of L-LA onto starch was evaluated by the solubility and stability of starch in [AMIM]Cl and the structure of [AMIM]Cl recovered from waste liquid phase of the ROGP mixture.

A dissolving process of starch in [AMIM]Cl at 80°C is presented in Figure 1 and the concentration of starch is 15% (wt). The amount of starch granules decreased with time, which disappeared almost completely after 40 min. The trace results depict that a solution of starch in [AMIM]Cl was formed as expected. At 100°C, a complete dissolving of 20%



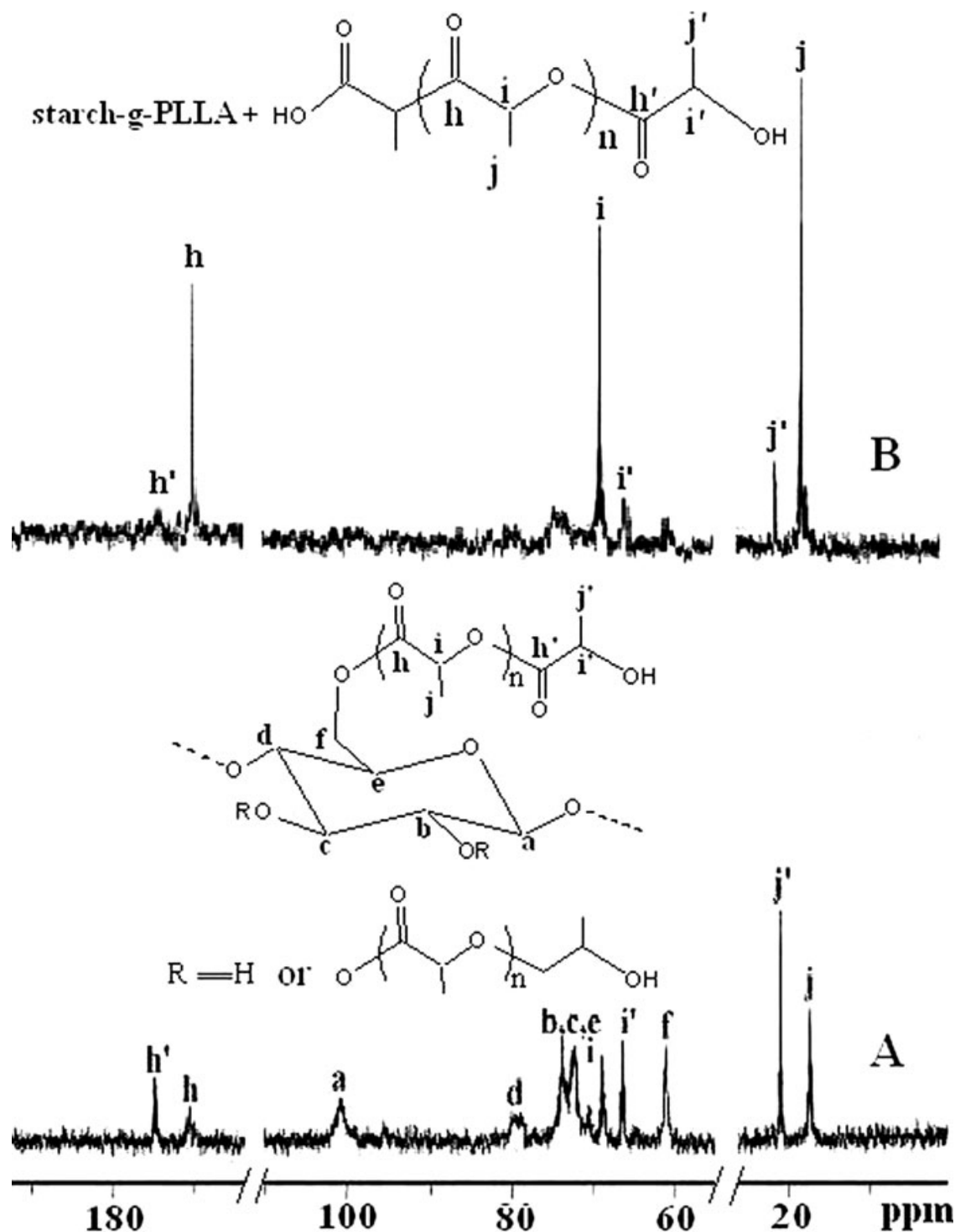
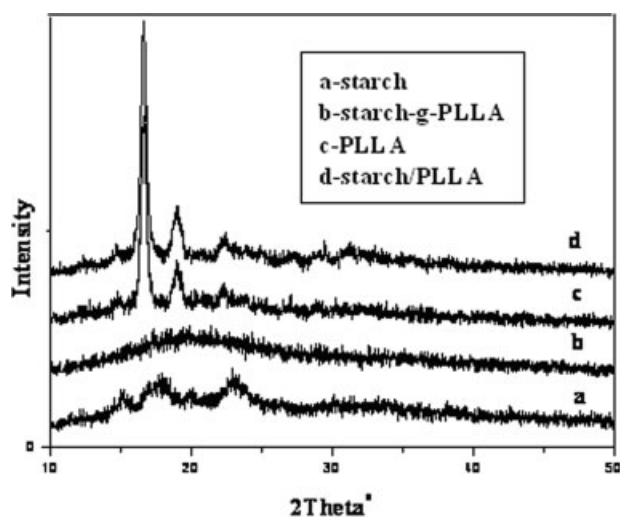


Figure 5 Typical  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ) spectra of starch-g-PLLA (A) and starch-g-PLLA + PLLA ( $M_n = 3500$  from GPC) (B).

(wt) starch in [AMIM]Cl was observed at 15 min under argon anhydrous atmosphere without any pretreatment or activation, by which the substantial degradation of starch upon dissolution was prevented. In addition, a viscous solution of 50% (wt) starch in [AMIM]Cl was also obtained, which still kept clear and transparent after cooling to room tem-

perature. It was thus concluded that [AMIM]Cl was an efficient solvent for starch.

The FTIR spectra of starch precipitated by ethanol from [AMIM]Cl solution [Fig. 2(b)] was nearly the same as that of native starch [Fig. 2(a)], which indicated that the starch structure was not altered by the interaction between starch and [AMIM]Cl in the



**Figure 6** WAXD spectra of starch, starch-g-PLLA, PLLA ( $M_n = 3500$ , from GPC) and starch/PLLA with the same PLLA wt % as in starch-g-PLLA.

solution, and [AMIM]Cl was a promising direct and nonderivatizing solvent for starch.

As shown in Figure 3, seven proton signals [4.1(H-4), 5.0(H-3), 5.5(H-1), 6.0(H-2), 7.5(H-6), 7.7(H-5), and 10.5 ppm (H-7)] and seven carbon signals [36.48(C-4), 51.18(C-3), 120.73(C-1), 122.90(C-6), 124.33(C-5), 132.59(C-2), and 137.34(C-7) ppm] were detected by  $^1\text{H}$  and  $^{13}\text{C}$  NMR method from the unused and recovered [AMIM]Cl, respectively, which were the characteristic signals to the structure of [AMIM]Cl. The consistency of the two kinds of [AMIM]Cl in their NMR properties depicts that no by-product left in the recovered [AMIM]Cl and the reusing of [AMIM]Cl was feasible.

### Characterization of starch-g-PLLA

Starch-g-PLLA was purified via dichloromethane extraction to remove homo-PLLA from the reaction mixture, which was inevitably formed during the graft polymerization. Thus, the obtained starch-g-PLLA was characterized by various methods such as FTIR,  $^{13}\text{C}$  NMR, WAXD, DSC as well as SEM. The specimens of pure PLLA and native starch were also measured as contrast.

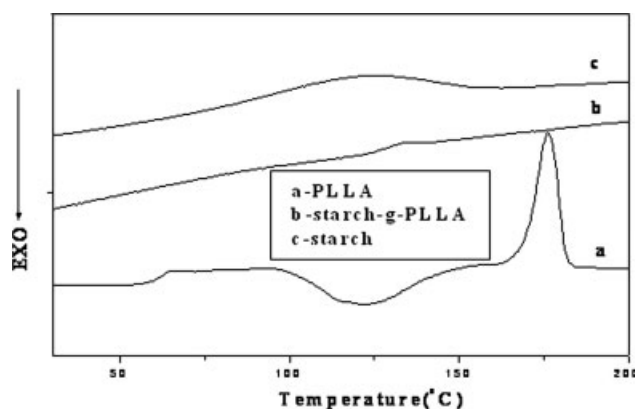
The notable difference between the FTIR spectra of starch and PLLA was that the strongest peak for starch appeared at  $3400\text{ cm}^{-1}$  but that for PLLA at  $1745\text{ cm}^{-1}$  (Fig. 4), which was assigned to the carbonyl group in PLLA. However, both the peaks were recorded in the spectrum of purified starch-g-PLLA. To confirm that the signal at  $1745\text{ cm}^{-1}$  was just from the PLLA grafted on starch but not homo-PLLA mixed with native starch, a sample of regenerated starch (Reg-starch) was prepared by stirring a mixture of starch and pure PLLA in [AMIM]Cl at

$100^\circ\text{C}$  for 10 h and then extracting PLLA with dichloromethane. The FTIR spectrum of Reg-ST (Fig. 4) shows that almost all mixed homo-PLLA was removed by dichloromethane extraction. Thus, it is reasonable to deduce that the ROGP of lactide onto starch granules took place.

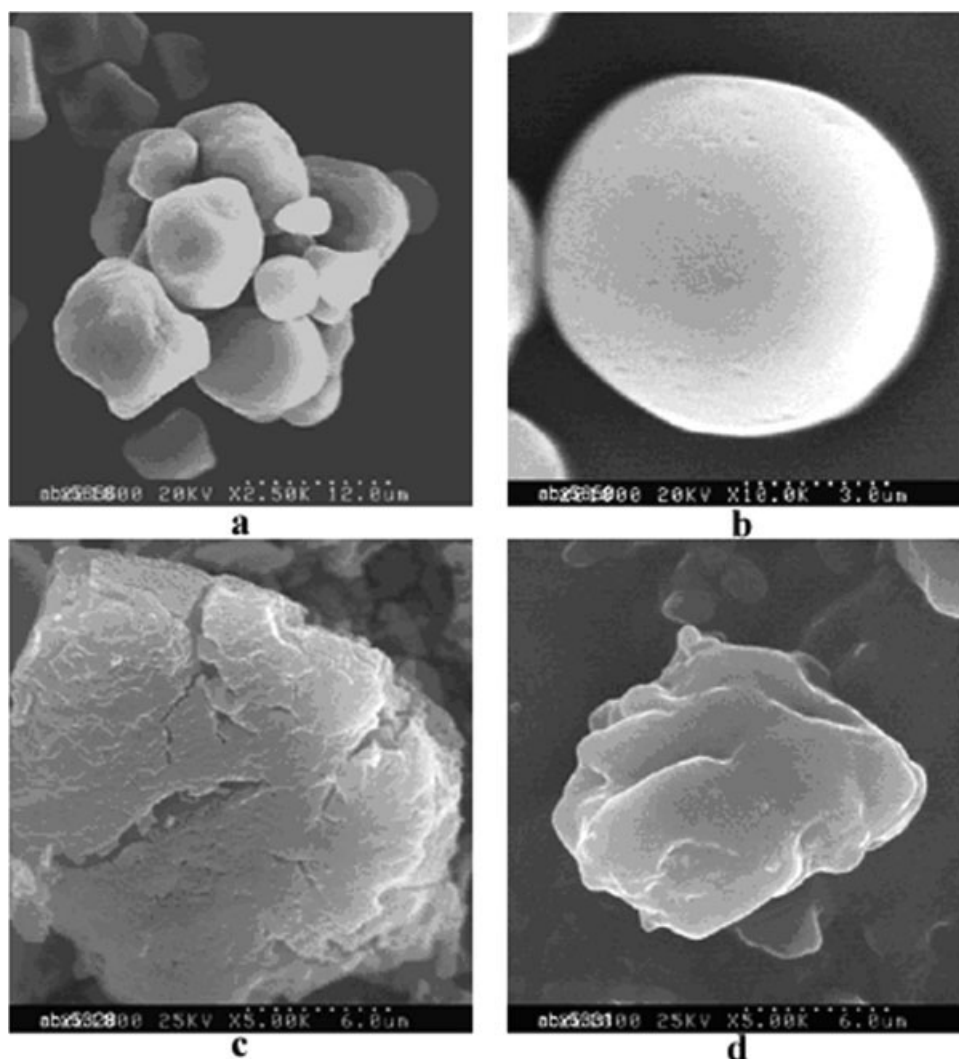
The grafting of PLLA onto starch was also confirmed by  $^{13}\text{C}$  NMR spectroscopy as starch-g-PLLA dissolved well in DMSO. In addition to the  $^{13}\text{C}$  signals of starch, two groups of PLLA peaks were recorded at 17.41 (j), 69.69 (i), and 170.37 (h), and 21.0 (j'), 66.66 (i'), and 174.67 (h') ppm [Fig. 5(A)], which were corresponding to the middle and terminal subunit in PLLA chain, respectively. Group h, i, j was recognized as the middle subunit for their intensity increased significantly with the addition of pure PLLA [Fig. 5(B)]. It seems that most PLLA chains grafted on starch were short as the area ratio of h/h', i/i', and j/j' were close [Fig. 5(A)].

The crystallinity of starch, starch-g-PLLA, PLLA, and starch/PLLA are discussed on the basis of WAXD patterns (Fig. 6). PLLA shows two main diffraction peaks at  $2\theta = 16.6^\circ$  and  $19.1^\circ$ , whereas starch shows three at  $2\theta = 15.2^\circ$ ,  $17.1^\circ$ , and  $23.3^\circ$ . However, in the case of starch-g-PLLA neither the crystallization peak of PLLA nor that of starch was observed but a dispersive peak around  $2\theta = 18.9^\circ$ . The pattern was totally different from that of starch/PLLA, in which both the diffraction peaks of crystal PLLA and starch were determined. Yet, the variety depicted that PLLA was grafted onto starch.

The DSC thermogram of starch-g-PLLA was recorded and compared with those of native starch and pure PLLA (Fig. 7). It is noticeable that no melting peak ( $115.9^\circ\text{C}$ ) of native starch and no glass transition line ( $62.5^\circ\text{C}$ ), crystallization and melting peaks ( $122.4$  and  $177.2^\circ\text{C}$ ) of pure PLLA were observed from the thermogram of starch-g-PLLA but a small baseline wander around  $133.1^\circ\text{C}$ . No melting peak appeared in the thermogram. The results indicated that starch-g-



**Figure 7** Second heat DSC curves of native starch, starch-g-PLLA and PLLA ( $M_n = 80,000$ , from GPC).



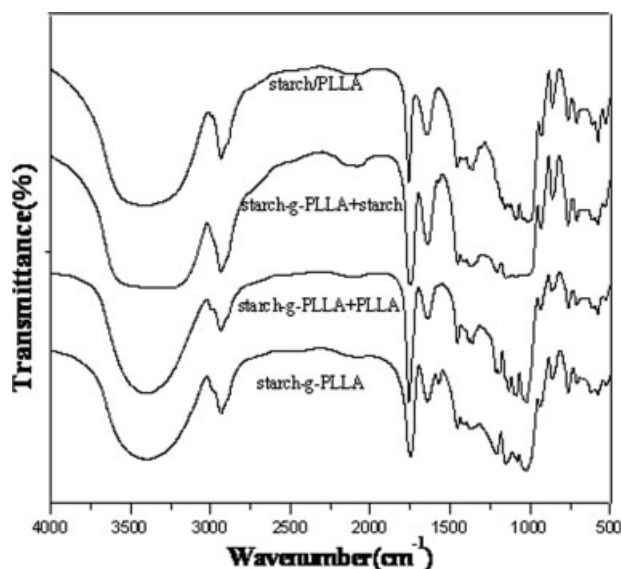
**Figure 8** SEM images of native starch (a, b), Reg-starch (c) and starch-g-PLLA (d).

PLLA was amorphous and the conclusion was accordant with that by WAXD measurement.

The SEM images of native starch (a, b), Reg-starch (c), and starch-g-PLLA (d) are shown in Figure 8. The good interfacial adhesion was obtained after starch was grafted by PLLA, but the rough surface was formed when starch was only physically dealt with PLLA in [AMIM]Cl.

#### Estimation of PLLA wt % in starch-g-PLLA

From the FTIR spectrum of starch-g-PLLA (Fig. 4), it was observed that the peak at  $1645\text{ cm}^{-1}$  was a characteristic signal of starch segment and that at  $1745\text{ cm}^{-1}$  was from PLLA segment. The intensity of the signal of starch segment increased with the addition of native starch and that of PLLA segment was enhanced by pure PLLA. The addition of native starch or pure PLLA to starch-g-PLLA showed no influence on the independence of the two peaks,



**Figure 9** FTIR spectra of starch-g-PLLA, starch-g-PLLA + PLLA, starch-g-PLLA + starch and starch/PLLA with the same PLLA wt % as in starch-g-PLLA.

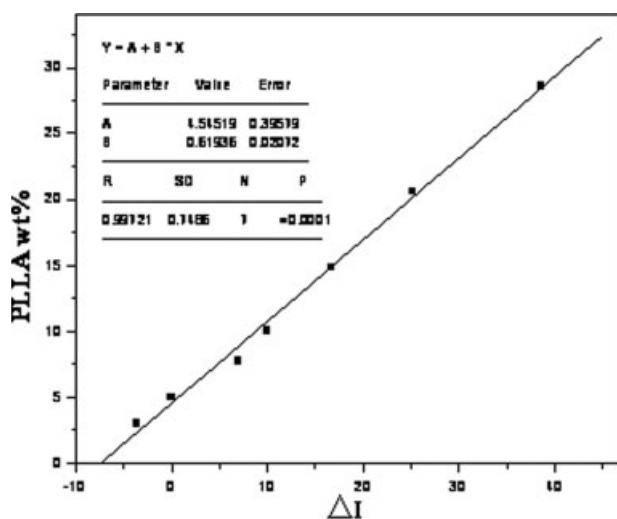


Figure 10 Standard curve of PLLA wt % to  $\Delta I$ .

which kept independent also for the mixture of starch and PLLA (Fig. 9). So, PLLA wt % in starch-g-PLLA was able to be estimated by the difference of intensity ( $\Delta I$ ) between the signals of PLLA and starch segment using a linear regression equation (Fig. 10), which was created from starch/PLLA system (Fig. 11).

#### Ring-opening graft polymerization of L-lactide onto starch

The ROGP of L-LA onto starch was conducted with a solution of 20 wt % starch in [AMIM]Cl.

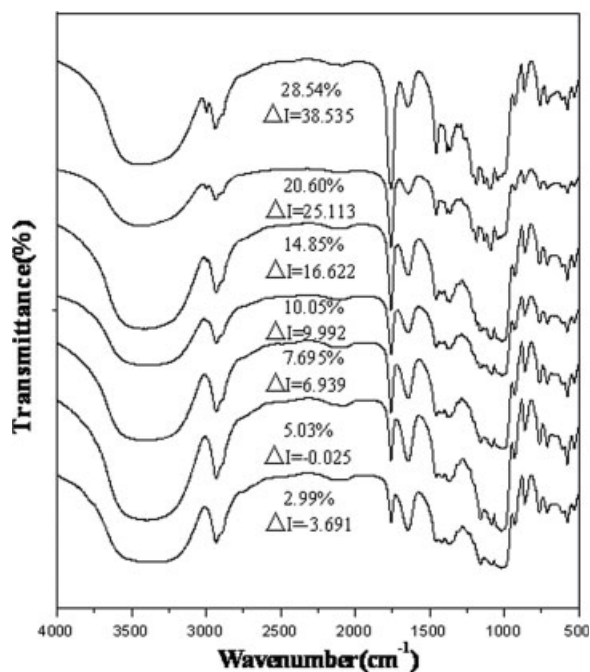


Figure 11 FTIR spectra of starch/PLLA with varied PLLA wt %.

TABLE I  
The Effect of Reaction Conditions on the Grafting Polymerization of Starch with L-LA<sup>a</sup>

Entry	L-LA/ Starch (wt)	Catalyst concentration (%)	PLLA wt %	Grafting efficiency (%)
1	0.5 : 1	0.1	13.2	30.3
2	1 : 1	0.1	22.2	28.5
3	1.5 : 1	0.1	21.1	17.8
4	1 : 1	0	0.3	0.3
5	1 : 1	0.2	18.4	22.6
6	1 : 1	0.3	16.7	20.0
7	1 : 1	0.5	14.8	17.4

<sup>a</sup> The grafting polymerization time and temperature were 10 h and at 100°C, respectively.

The PLLA wt % and G% with varied L-LA/starch ratio (Entry 1–3, Table I) are shown in Figure 12 (0.1% Sn(Oct)<sub>2</sub>, 100°C, 10 h). The highest grafting efficiency (30.3%) was detected at 0.5 : 1 but the increasing in PLLA wt % was broken at 1 : 1, which indicated that the graft polymerization was more influenced by starch.

When the polymerization was carried out without Sn(Oct)<sub>2</sub> (L-LA/starch (wt) = 1 : 1, 100°C, 10 h), the values of G% and PLLA wt % were as low as 0.34 (Fig. 13), which was considered as the residue of PLLA physically adsorbed by starch. The results present that the catalyst was necessary. However, the decline of G% and PLLA wt % was observed with catalyst concentration increasing from 0.1 to 0.5% (Entry 4–7, Table I), and the value for G% ranged as 28.5, 22.6, 20, and 17.4 but that for PLLA wt % was 22.5, 18.4, 16.7, and 14.8. It seems that the competitive homopolymerization of L-LA was enhanced with the higher catalyst concentration.

Figure 14 shows the results of the ROGP conducted at 100°C with L-LA/starch (wt) = 1 : 1, 0.1% Sn(Oct)<sub>2</sub>. It was observed that G% and PLLA wt %

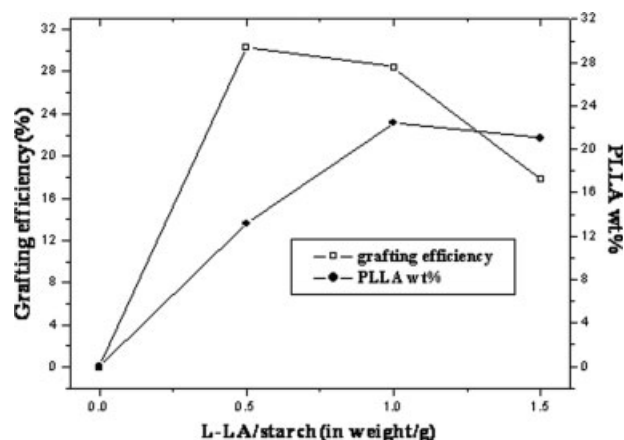
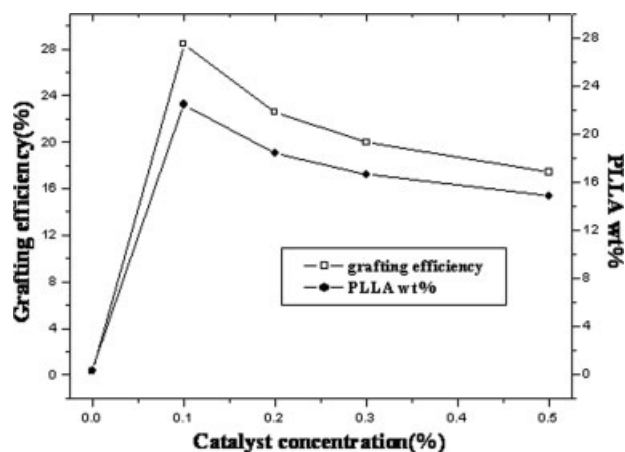


Figure 12 Effect of L-LA/starch (in weight) on the graft polymerization [0.1% Sn(Oct)<sub>2</sub>, 100°C, 10 h].

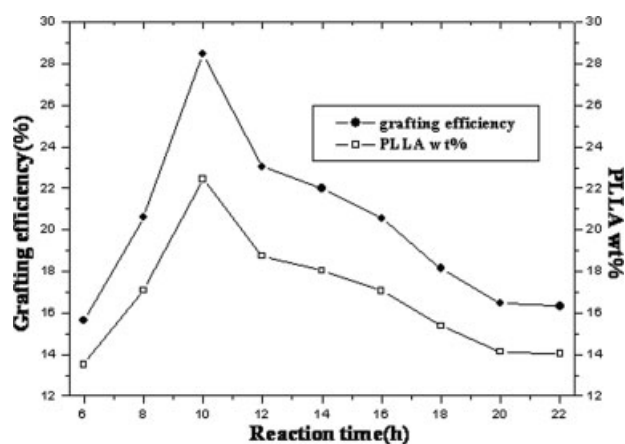




**Figure 13** Influence of catalyst concentration on the graft polymerization [100°C, 10 h, L-LA/starch (wt) = 1 : 1].

both increased within 10 h but decreased afterward, which depicted that the disconnection of the grafted PLLA chains from starch-g-PLLA must take place after 10 h as well as the degradation of grafted PLLA by the transesterification to form the homo-PLLA and other by-reactions. The breaking occurred mostly at the linkage between PLLA and starch segment as the PLLA chains combined with starch were not long (Fig. 5). The maximums of G% and PLLA wt % reached 28.5 and 22.5% at 10 h, respectively.

The temperature also took an important role in the ROGP. When the temperature was raised from 100 to 130°C, G% of the polymerization proceeded for 10 h decreased from 28.6 to 16.1%. However, G% maintained around 20% with the variation in temperature if the reaction time was shortened to 8 h (Table II). The results may attribute to an increase in the rates of transesterification and chain decoupling with the increase of temperature at a long reaction time.



**Figure 14** Effect of reaction time on the graft polymerization [L-LA/starch (wt) = 1 : 1, 0.1% Sn(Oct)<sub>2</sub>, 100°C].

**TABLE II**  
The Effect of Reaction Temperature on the Grafting Polymerization<sup>a</sup>

Entry	Reaction temperature (%)	Reaction time (h)	PLLA wt %	Grafting efficiency (%)
8	100	8	17.1	20.6
9	110	8	18.4	22.6
10	120	8	16.9	20.3
11	130	8	16.2	19.3
12	110	10	21.3	27.1
13	120	10	17.0	20.5
14	130	10	13.9	16.1

<sup>a</sup> L-LA/Starch (wt) was 1 : 1, the catalyst concentration was 0.1%.

## CONCLUSIONS

[AMIM]Cl is a promising direct solvent for starch and nonderivitizing solvent for starch-effective dissolution. The ROGP of L-LA onto starch was carried out smoothly with [AMIM]Cl as a reaction media and the grafting efficiency of PLLA reached 30%, which was calculated according to a standard curve created by FTIR method.

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