

# Synthesis of High Molecular Weight Poly(L-lactic acid) via Melt/Solid Polycondensation: Intensification of Dehydration and Oligomerization During Melt Polycondensation

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**ABSTRACT:** Melt/solid state polycondensation (MP/SSP) is a cost-effective route for synthesis of high molecular weight poly(L-lactic acid) (PLLA). However, the reaction rates in its four stages need to be enhanced greatly and the reaction times to be shortened largely before the MP/SSP technology can be industrialized. In this study, a new catalyst addition policy, i.e., adding TSA at the dehydration stage and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at the MP stage, and more appropriate temperature and pressure programs were presented and applied in the MP process of LLA. The presence of TSA from dehydration appeared very effective for speeding up the dehydration and oligomerization stages as well as depressing racemization in the whole MP process. The polymerization degree ( $X_n$ ) of oligomer was

clearly increased, and the reaction time was shortened to a great extent. Direct using reduced pressure was also very helpful for intensifying the dehydration stage, only leading to LLA loss as little as 2%. A PLLA with  $M_w$  of 44,000 and optical purity of 96.8% suitable for subsequent SSP was produced after dehydration for 2 h, oligomerization for 2 h and MP for 4 h under appropriate conditions. And an interesting strong dependence of the  $M_w$  of final PLLA product on the  $X_n$  of the oligomer was observed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2780–2785, 2011

**Key words:** biodegradable polymers; poly(L-lactic acid); catalyst; melt polycondensation; solid-state polycondensation

## INTRODUCTION

Poly(L-lactic acid) (PLLA) is an important biobased and biodegradable polymer. PLLA has been commercially produced by Natureworks etc via ring-opening polymerization of L-lactide in large scale and by Mitsui Toatsu via solution polymerization (SP) in pilot scale<sup>1–5</sup> and has found many end-uses in biomaterials, fibers, disposable commodities, and package materials because of its good mechanical properties and excellent biodegradability and biocompatibility.<sup>6,7</sup> However, new cost-effective manufacturing technologies are still very desired to reduce the production cost and to enhance the marketability of PLLA.

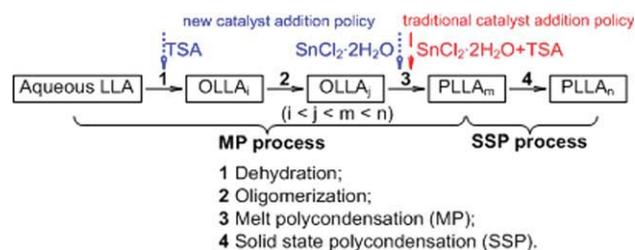
Melt/solid-state polycondensation (MP/SSP) for PLLA synthesis was first reported by Kimura and coworkers.<sup>8,9</sup> In the melt polycondensation process, aqueous LLA solution is dehydrated and oligomer-

ized to get oligomer of LLA (OLLA), and then the OLLA is melt polycondensed to produce PLLA prepolymer. In the SSP process, the PLLA prepolymer is crystallized and finally polycondensed at solid state to get high molecular weight PLLA. The four-stage MP/SSP process is illustrated in Scheme 1. It appears to be an attractive and promising route for PLLA synthesis due to its cost effectiveness which results from direct use of aqueous LLA other than L-lactide. However, it has not yet been industrialized up to now even though many efforts have been taken in the last decade,<sup>8–20</sup> mainly because its reaction rate is relatively low and thus very long reaction time is needed to reach high molecular weight.

Some typical results reported for MP/SSP of PLLA are summarized in Table I. It can be seen that all the four stages, especially dehydration, oligomerization, and SSP, need to be intensified to shorten the whole reaction time from the viewpoint of engineering. With these in mind, we intensively investigated all the four stages and obtained satisfactory results.<sup>18–20</sup> In this article, we report the intensification of dehydration and oligomerization stages via a new catalyst addition policy (see Scheme 1) and condition optimization.

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**Scheme 1** Schematic diagram of four-stage MP/SSP process. In traditional catalyst addition policy, both  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and TSA are added at the MP stage; in our new policy, TSA is added at dehydration stage and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at MP stage separately. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## EXPERIMENTAL

### Materials

Aqueous L-lactic acid (LLA, 90 wt %, 98% optical purity according to manufacturer) was purchased from Jiangxi Musashimo Bio-Chem, China. Tin (II) chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), toluene-4-sulfonic acid (TSA) and chloroform were all reagent-grade chemicals and used as received.

### Reaction procedure

The melt polymerization of L-lactic acid was carried out in three successive stages: dehydration, oligomerization, and melt polycondensation, using  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ /TSA (TSA/Sn 1/1 mol/mol,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  0.4 wt % based on lactate units) as a binary catalyst system. The detailed policies for catalyst addition are listed in Table II.

### Dehydration

Aqueous L-lactic acid (~190 g) with or without catalyst were added into a 250-mL preheated four-necked flask equipped with a mechanical stirrer, a thermocouple, a nitrogen inlet, and a condenser connected to a pressure sensor and a vacuum system. The dehydration was performed under a pressure of 2000–4000 Pa at predetermined temperature for 130

min. Water as well as a small amount of L-lactic acid was removed and collected in a cold trap.

### Oligomerization

The product after dehydration was further oligomerized, using a reflux condenser to reflux L-lactide and primary condensates of LLA back to the reactor. No catalyst was added at this stage. The reaction was conducted at a constant stirring speed of 500 rpm, under 250–400 Pa and at predetermined temperature for 2 h.

### Melt polycondensation

The oligomer was further melt polycondensed in the same reactor at 175°C/200–300 Pa and with sufficient stirring for 4 h, with or without catalyst addition. The reaction system became viscous gradually, indicating chain growth. After the PLLA melt was cooled down, the yield (defined as the ratio of actual mass of PLLA produced to theoretical value) was gravimetrically determined and other properties were characterized as follows.

### Characterizations

The amount of LLA in the distillate collected in dehydration stage is determined through a simple acid-base titration using standard NaOH solution.

The number average polymerization degree ( $X_n$ ) during dehydration was roughly estimated from the mass of water collected ( $m_w$ ) using eq. (1) where  $m_a$  was the mass of aqueous LLA and  $\phi_{\text{LLA}}$  (= 90%) was the weight fraction of LLA in it. It was supposed that the free water in aqueous LLA was rapidly removed at the beginning of dehydration. The  $X_n$  at the end of dehydration and during oligomerization was determined from the  $^1\text{H-NMR}$  spectrum, see eq. (2),  $S_{5.2}$  and  $S_{4.4}$  represent the area of peaks at 5.2 ppm ( $-\text{OCH}(\text{CH}_3)\text{CO}-$ ) and at 4.4 ( $\text{HOCH}(\text{CH}_3)-$ ), respectively. The values of  $X_n$  (at the end of dehydration) obtained in the two ways agreed well with each other. The weight average molecular weight ( $M_w$ ) of the product after melt polymerization stage was calculated with eq. (3) from its intrinsic viscosity which was determined using

**TABLE I**  
Some Typical Conditions and Results Reported for MP/SSP of PLLA

No	Dehydration stage $T/^\circ\text{C}$ , $P/\text{torr}$ , $t/\text{h}$	Oligomerization		Melt polycondensation		Solid-state polycondensation		Ref
		$T/^\circ\text{C}$ , $P/\text{torr}$ , $t/\text{h}$	$x_n$	$T/^\circ\text{C}$ , $P/\text{torr}$ , $t/\text{h}$	$10^{-3} M_w$	$T/^\circ\text{C}$ , $P/\text{torr}$ , $t/\text{h}$	$10^{-3} M_w$	
1	150, 760–100, 4	150, 30, 4	8	180, 10, 5	13	150, 0.5, 5	260–320	9,12,13
2	150, 760–30, 2	150, 30, 4	8	180, 10, 5	10–23	140–160, 0.5, 10	50–230	21
3	/	150, 30, 7	8	180, 10, 5	13	130–155, 2, 10–30	70–290	10
4	100, 760, 2	150, 760–1, 10	/	180, 1, 10	130	/	/	22
5	/	/	/	180, 16–5, 18	91	160, 3–1, 24	134	8

TABLE II  
Conditions and Results in Dehydration, Oligomerization, and Melt Polycondensation Stages in the Presence of SnCl<sub>2</sub>·2H<sub>2</sub>O/TSA Catalyst System (0.4 wt % SnCl<sub>2</sub>·2H<sub>2</sub>O, TSA/Sn 1/1 mol/mol)

Run	Dehydration <sup>a</sup>				Oligomerization <sup>b</sup>		Melt polycondensation <sup>c</sup>				
	T (°C)	Cat. add. <sup>d</sup>	LLA <sub>L</sub> <sup>e</sup> (%)	X <sub>n</sub> <sup>f</sup>	T (°C)	X <sub>n</sub> <sup>g</sup>	Cat. Add. <sup>d</sup>	M <sub>w</sub> <sup>h</sup> (10 <sup>3</sup> )	OP <sup>i</sup> (%)	Yield (%)	Clr <sup>j</sup>
1	140	None	1.6	2.6	160	6.1	TSA+Sn	21.6	93.2	81.0	W
2	140	TSA/2	2.0	4.4	160	12.6	TSA/2+Sn	25.3	96.5	85.4	W
3	140	TSA	2.2	5.7	160	17.6	Sn	44.4	96.8	80.0	SY
4	140	TSA+Sn	4.5	6.1	160	18.6	None	26.7	97.2	81.5	W
5	140	TSA	2.9	6.1	160	17.0	TSA+Sn	23.5	96.3	77.5	Y
6	130	TSA	2.4	4.7	150	13.2	Sn	24.7	98.3	80.9	W
7	150	TSA	8.1	7.4	170	22.0	Sn	52.4	96.3	68.6	SY

<sup>a</sup> Dehydration under ~ 3000 Pa for 130 min.

<sup>b</sup> Oligomerization under 250–400 Pa for 2 h.

<sup>c</sup> Melt polycondensation under 200–300 Pa for 4 h.

<sup>d</sup> Catalyst added.

<sup>e</sup> Loss of LLA.

<sup>f</sup> Polymerization degree at the end of dehydration.

<sup>g</sup> Polymerization degree at the end of oligomerization.

<sup>h</sup> Weight average molecular weight at the end of melt polycondensation.

<sup>i</sup> Optical purity.

<sup>j</sup> W, SY, and Y denote the color white, slightly yellow, and yellow, respectively.

an Ubbelohde viscometer in chloroform solution at 30°C. Thus obtained  $M_{wv}$  is equivalent to the  $M_w$  relative to polystyrene standard in GPC measurement.

$$X_n = \frac{1}{1 - \frac{m_w - (1 - \phi_{LLA})m_a}{18\phi_{LLA}m_a/90}} \quad (1)$$

$$X_n = S_{5.2}/S_{4.4} + 1 \quad (2)$$

$$[\eta] = 1.13 \times 10^{-4} M_w^{0.778} \quad (3)$$

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded using a Bruker Advance2B 400 MHz spectrometer using CDCl<sub>3</sub> containing 0.03% TMS as an internal reference. <sup>1</sup>H-NMR (ppm): 1.5 (HOCH(CH<sub>3</sub>)—), 1.6 (—OCH(CH<sub>3</sub>)CO—), 4.4 (HOCH(CH<sub>3</sub>)—), and 5.2 (—OCH(CH<sub>3</sub>)CO—); <sup>13</sup>C-NMR (ppm): 16.7 (—OCH(CH<sub>3</sub>)CO—), 69.1 (—OCH(CH<sub>3</sub>)CO—), 169.6 (—OCH(CH<sub>3</sub>)CO—).<sup>23,24</sup>

The specific optical rotation ( $[\alpha]_D^{25}$ ) of PLLA was measured in a chloroform solution of 1.0 g/dL at 25°C using an automatic polarimeter (WOPO IV, Rudolph) at a wavelength of 589 nm. The optical purity (OP, %ee) was calculated from eq. (4) based on the fact that the specific optical rotation of pure PLLA without D-lactic acid unit is  $-156^\circ$ .<sup>13</sup>

$$OP(\%ee) = \frac{[\alpha]_D^{25}}{-156} \times 100 \quad (4)$$

## RESULTS AND DISCUSSION

In typical MP of PLLA, aqueous LLA is first dehydrated at atmospheric pressure (or low vacuum) and low temperature to avoid loss of LLA monomer and

its primary condensates, and then oligomerized and melt polycondensed at stepwisely reduced pressures and increased temperatures to match with the continuous decrease of volatility and increase of viscosity of the reaction system. The binary catalyst system, SnCl<sub>2</sub>·2H<sub>2</sub>O and TSA (1/1 mol/mol),<sup>12</sup> is the most effective catalyst reported for PLLA polycondensation up to now. It is often added at MP stage but not the first two stages because the high polarity of water, LLA and its primary condensates at the early two stages deteriorates the catalyst activity.<sup>12</sup> The absence of catalyst and inappropriate temperature and pressure programs slowed down the rate of the first two stages. We noticed that in the binary catalyst system, only SnCl<sub>2</sub>·2H<sub>2</sub>O is sensitive but TSA is tolerant to the high polarity. If the first two stages are carried out in the presence of TSA and using more appropriate temperature and pressure programs, they may be greatly accelerated. So we presented here a new catalyst addition policy, i.e., adding TSA at the dehydration stage and then SnCl<sub>2</sub>·2H<sub>2</sub>O at the MP stage, and optimized temperature and pressure programs to speed up dehydration and oligomerization.

To improve the pressure and temperature programs, the volatilities of water, LLA, L-lactide, and OLLA<sub>i</sub> (i is X<sub>n</sub>) were first estimated. The saturated vapor pressure ( $P^*$ ) at various temperature was calculated from the integral form of Clausius–Clapeyron Equation [eq. (5)], where  $\Delta H$ ,  $R$ ,  $T$ , and  $C$  are the evaporation enthalpy, universal gas constant, temperature, and integral constant, respectively. The  $\Delta H$  was calculated using Advanced Chemistry Development software V9.04 for solaris (1994–2010 ACD/Lab), and  $C$  was calculated using eq. (5), see

**TABLE III**  
The Boiling Temperatures ( $T_b$ ), Evaporation Enthalpies ( $\Delta H$ ), and Integral Constants ( $C$ ) of the Volatiles

Volatile	Water	LLA	L-lactide	OLLA <sub>2</sub>	OLLA <sub>3</sub>
$T_b$ (°C)	100.0	227.6	285.5	315.2	399.1
$\Delta H$ (kJ/mol)	42.31	61.62	52.45	64.51	75.11
$C$	10.90	11.43	9.91	10.73	10.84

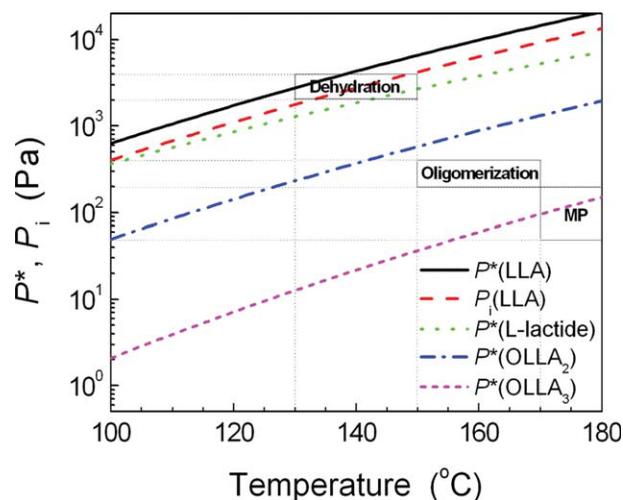
$T_b$  and  $\Delta H$  were calculated using Advanced Chemistry Development software V9.04 for solaris (1994-2010 ACD/Lab);  $C$  was calculated using Clausius–Clapeyron Equation.

Table III. The boiling temperature ( $T_b$ ) was also calculated using the software and listed in Table III. The partial pressure of LLA in a 90 wt% aqueous solution was estimated by Raoult's law, see eq. (6). The calculated  $P$ - $T$  relationships are shown in Figure 1. Although these results may be rough to certain extent, they do indicate that (1) the volatilities abide by such an order: water > LLA > L-lactide > OLLA<sub>2</sub> > OLLA<sub>3</sub> and (2) LLA is hardly to evaporate at atmospheric pressure and temperature higher than 100°C, so the dehydration stage can be conducted directly at reduced pressure. On the basis of these  $P \sim T$  relationships, we carried out dehydration at 130–150°C/∼ 3000 Pa, oligomerization at 150–170°C/∼ 300 Pa and melt polymerization at 170–180°C/∼ 200 Pa. The conditions and results are shown in Table II and Figures 2 and 3.

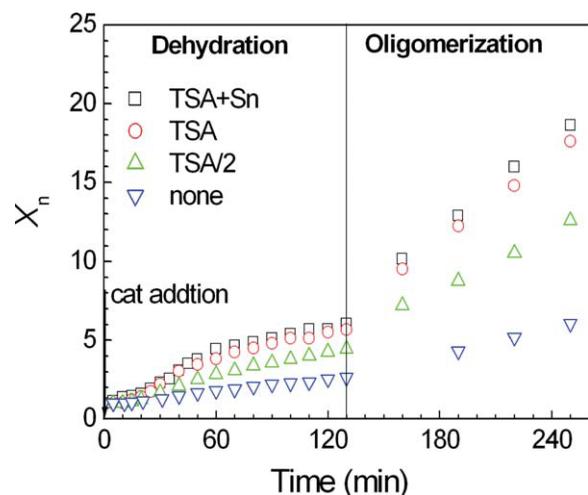
$$\lg P^* = -\frac{\Delta H}{2.303RT} + C \quad (5)$$

$$P_i = P_i^* x_i \quad (6)$$

Figure 2 shows the growth of number average polymerization degree ( $X_n$ ) during dehydration at

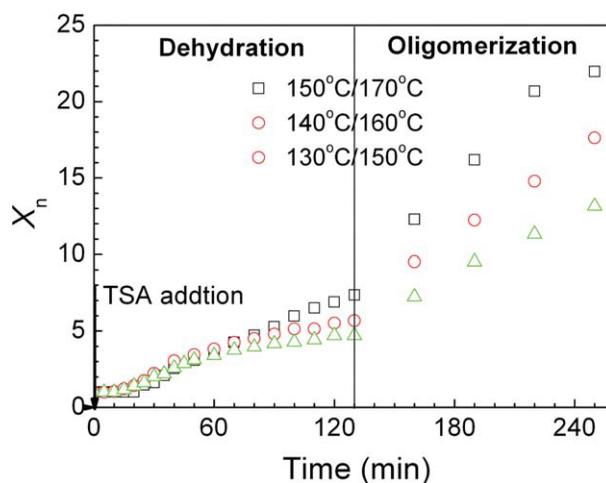


**Figure 1** The calculated saturated ( $P^*$ ) and partial ( $P$ ) vapor pressure of L-lactide and OLLAs with various polymerization degrees. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 2** Time evolution of polymerization degree ( $X_n$ ) during dehydration and oligomerization of LLA using different catalyst addition policies. (Dehydration: at 140°C and under the pressure of 3000 Pa for 130 min; Oligomerization: at 160°C and under the pressure of 250 (400 Pa for 120 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

140°C/∼ 3000 Pa and subsequent oligomerization at 160°C/∼ 300 Pa. The  $X_n$  grew slowly in both stages in the absence of catalyst, reaching 2.6 after dehydration for 2 h and 6 after oligomerization for another 2 h. However, its growth rate increased clearly when TSA was added at the very beginning of dehydration. The  $X_n$  reached 4.4 and 5.7 after dehydration and 13 and 18.6 after oligomerization, when half and total TSA were added, respectively. The addition of TSA at dehydration was also beneficial to improve the molecular weight (from 22,000 to 44,000) and



**Figure 3** The time evolution of polymerization degree ( $X_n$ ) during dehydration and oligomerization of LLA at different reaction temperature programs. (TSA was added at the very beginning of dehydration. Dehydration: 3000 Pa/130 min; Oligomerization: 250–400 Pa/120 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

optical purity (from 93.2 to 96.8%) of the final product after melt polycondensation, but no clear effect on the final yield was observed. When  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added together with TSA at the beginning of dehydration (Run 4), the  $X_n$  growths during dehydration and oligomerization and the final optical purity after MP were similar to the case only TSA was added (Run 3), but the final molecular weight was smaller, suggesting deactivation of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at the early stages. Extra addition of TSA at MP stage (Run 5) resulted in clear discoloration and decrease of the molecular weight though the optical purity kept unchanged, supporting the conclusion that a 1/1 M ratio of TSA to  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is optimal.<sup>12</sup> All these results indicated TSA was very robust in polar media, and its presence was very beneficial for shortening the times of dehydration and oligomerization. Therefore, the new catalyst addition policy, i.e., adding TSA at dehydration and then  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at MP, appears very helpful for polycondensation of LLA.

Figure 3 shows the growth of  $X_n$  during dehydration and oligomerization using the new catalyst addition policy at various temperature programs, 130°C/150°C (Run 6), 140°C/160°C (Run 3), and 150°C/170°C (Run 7). Clearly, the  $X_n$  grew more rapidly at higher temperature. It reached 7.4 after dehydration at 150°C for 2 h and 22 after oligomerization at 170°C for another 2 h. The molecular weight of the final product after melt polycondensation increased from 24,700 to 52,400 but the optical purity decreased from 98.3% to 96.3% with increasing the temperatures of the first two stages (from 130°C/150 to 150°C/170°C), see Table II.

The  $P \sim T$  data in Figure 1 suggest that LLA could but OLLA was hard to be evaporated with distillation of water if dehydration was conducted at 140°C/ $\sim 3000$  Pa. L-lactide had appropriate volatility ( $\sim 2000$  Pa) but it was seldom formed at this temperature range. The loss of LLA was small under such conditions. Only about 2% LLA was lost after dehydration for 130 min. No clear dependence of LLA loss on the amount of TSA added was observed though the addition of TSA at dehydration enhanced growth of  $X_n$  and therefore ought to be helpful to certain extent to decrease LLA loss. This may be attributed to the relatively large pressure fluctuation and experimental error in determination of LLA loss. When the dehydration temperature was raised to 150°C, the partial pressure of LLA reached 4000 Pa, so the LLA loss clearly increased, reaching 8%. In addition, the product after dehydration at 140°C/ $\sim 3000$  Pa for 2 h had an  $X_n$  of about 6 and therefore had a weight fraction of LLA monomer less than 3% according to Flory's classical molecular weight distribution. Such product containing only a little LLA was very suitable for next oligomerization at higher

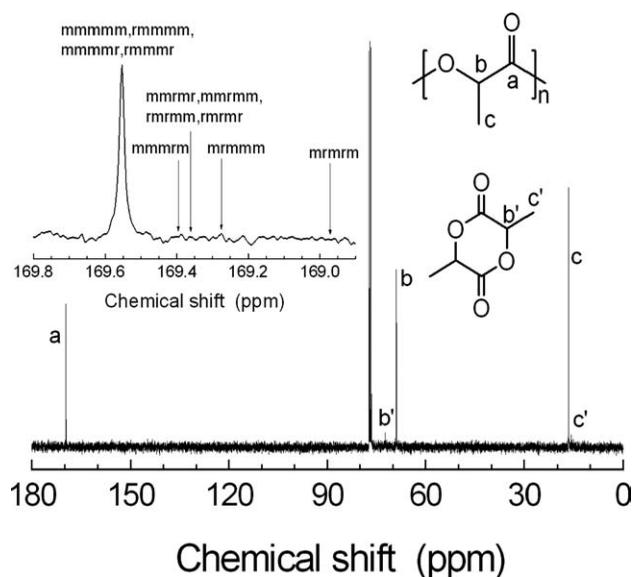


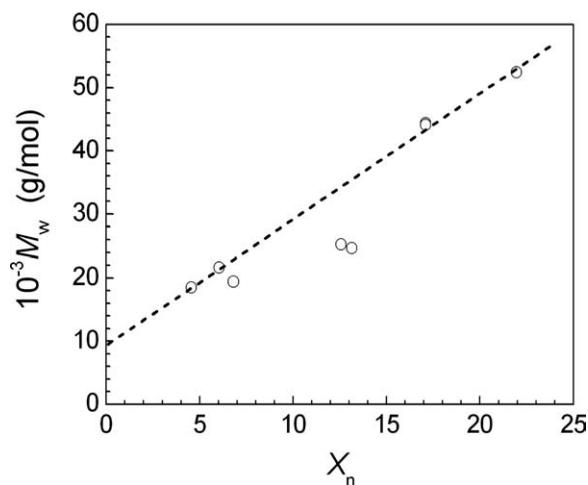
Figure 4  $^{13}\text{C}$ -NMR spectrum of PLLA (Run 3).

temperature and under lower pressure. Therefore, both the calculated  $P \sim T$  data and the experimental results indicate that it is appropriate to conduct dehydration at 140°C and  $\sim 3000$  Pa.

For oligomerization at 150–170°C/ $\sim 300$  Pa and melt polycondensation at 170  $\sim$  180°C/ $\sim 200$  Pa, the formation of L-lactide started. Under these conditions, LLA, L-lactide, and OLLA<sub>2</sub> were all volatilizable. So, condensation and reflux of these volatiles were necessary for oligomerization as well as melt polycondensation. However, their losses were not determined because of the difficulty in collecting them under high vacuum.

The high optical purity obtained using the new catalyst addition policy is attributed to the ability of TSA to depress racemization from the very beginning of the reaction. This was confirmed by  $^{13}\text{C}$ -NMR spectrum of PLLA. As shown in Figure 4, in addition to a single carbonyl signal at 169.55 ppm, other signal assignments because of the racemic (r) and meso (m) sequences of the lactate units<sup>25–29</sup> were not clearly detected, indicating little racemization. The improvement of optical purity is a desired result because high optical purity will lead to high crystallinity of the final product.<sup>30</sup> As racemization is resulted from ester exchange reaction via cleavage of alkyl-oxygen bond, the less racemization in the presence of TSA suggests that it is able to depress this kind of ester interchange.

When the oligomers with various polymerization degrees ( $X_n$ ) were further melt polycondensed in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ /TSA at 175°C/200–300 Pa for 4 h, it was found that a small increase of  $X_n$  ( $\sim 17$ ) led to a very large increase ( $\sim 34,000$ ) of the weight average molecular weight ( $M_w$ ) of the final PLLA products, as shown in Figure 5. This



**Figure 5** The dependence of the weight average molecular weight ( $M_w$ ) of the final PLLA products after melt polymerization on the polymerization degree ( $X_n$ ) of OLLA prepared after dehydration and oligomerization. All the melt polycondensations were carried out at 175°C/200–300 Pa for 4 h in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ /TSA (0.4 wt %, 1/1).

interesting increase of  $M_w$  is not in agreement with classical polycondensation kinetics. If the  $M_w$  growth abided by a normal kinetics, i.e., it grew linearly with reaction time, the increase of  $M_w$  should be as large as the increase of the initial  $X_n$ . In further study, we found that the melt polycondensation of PLLA did exhibit a nonlinear  $M_w$  growth with reaction time, which seems to be responsible for the strong  $X_n$ -dependence of  $M_w$ . The kinetics and modeling of melt polycondensation and intensification of SSP will be reported later.

## CONCLUSIONS

A new catalyst addition policy, i.e., adding TSA at the dehydration stage and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at the MP stage, and more appropriate temperature and pressure programs were presented and applied in melt polycondensation of LLA to speed up the dehydration and oligomerization stages. The presence of TSA from dehydration appeared very effective for increasing polymerization degree of the oligomer and shortening the reaction times as well as depressing racemization. Dehydrating directly under reduced pressure was also very helpful for removing water and promoting the condensation reaction, only leading to LLA loss as little as 2%. A PLLA product with weight average molecular weight of 44,000 and optical purity of 96.8% was synthesized after dehydration at 140°C/ $\sim$  3000 Pa for 2 h, oligomerization at 160°C/ $\sim$  300 Pa for 2 h and melt polymerization at 170–180°C and under  $\sim$  200 Pa for 4 h.

And an interesting strong dependence of the final molecular weight of PLLA after melt polycondensation on the polymerization degree of the oligomer after the first two stages was observed. This phenomenon will be further studied and reported later.

## References

- Maharana, T.; Mohanty, B.; Negi, Y. S. *Prog Polym Sci* 2009, 34, 99.
- Mehta, R.; Kumar, V.; Bhunia, H.; Upadhyay, S. N. *J Macromol Sci C: Polym Rev* 2005, 45, 325.
- Garlotta, D. *J Polym Env* 2001, 9, 63.
- Lunt, J. *Polym Degrad Stab* 1998, 59, 145.
- Ajioka, M.; Enomoto, K.; Suzuki, K.; Yamaguchi, A. *B. Chem Soc Jpn* 1995, 68, 2125.
- Gross, R. A.; Kalra, B. *Science* 2002, 297, 803.
- Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv Mater* 2000, 12, 1841.
- Fukushima, T.; Sumihiro, Y.; Koyanagi, K.; Hashimoto, N.; Kimura, Y.; Sakai, T. *Int Polym Proc* 2000, 15, 380.
- Moon, S. I.; Lee, C. W.; Taniguchi, I.; Miyamoto, M.; Kimura, Y. *Polymer* 2001, 42, 5059.
- Moon, S. I.; Taniguchi, I.; Miyamoto, M.; Kimura, Y.; Lee, C. W. *High Perform Polym* 2001, 13, S189.
- Fukushima, K.; Kimura, Y. *J Polym Sci Part A: Polym Chem* 2008, 46, 3714.
- Moon, S. I.; Lee, C. W.; Miyamoto, M.; Kimura, Y. *J Polym Sci part A: Polym Chem* 2000, 38, 1673.
- Moon, S. I.; Kimura, Y. *Polym Int* 2003, 52, 299.
- Essawy, H. A.; Helaly, F. M.; Shabana, M. A. *J Elastomers Plast* 2007, 39, 303.
- Helaly, F. M.; Shabana, M. A.; Essawy, H. A. *Egyptian J Textile Polym Sci Tech* 2007, 11, 71.
- Sedlarik, V.; Kucharczyk, P.; Kasparikova, V.; Drbohlav, J.; Salakova, A.; Saha, P. *J Appl Polym Sci* 2010, 116, 1597.
- Wu, L. B.; Cao, D.; Huang, Y.; Li, B. G. *Polymer* 2008, 49, 742.
- Wang, W. C.; Wu, L. B.; Huang, Y.; Li, B. G. *J Mater Sci Eng* 2005, 23(special issue), 11 (in Chinese).
- Hou, H. B.; Wu, L. B. to be submitted.
- Wu, L. B.; Hou, H. B. *J Appl Polym Sci* 2010, 115, 702.
- Fukushima, K.; Hirata, M.; Kimura, Y. *Macromolecules* 2007, 40, 3049.
- Chen, G. X.; Kim, H. S.; Kim, E. S.; Yoon, J. S. *Eur Polym Mater* 2006, 42, 468.
- Espartero, J. L.; Rashkov, I.; Li, S. M.; Manolova, N.; Vert, M. *Macromolecules* 1996, 29, 3535.
- Liu, X. B.; Zou, Y. B.; Li, W. T.; Cao, G. P.; Chen, W. *J Polym Degrad Stab* 2006, 91, 3259.
- Chabot, F.; Vert, M.; Chapelle, S.; Granger, P. *Polymer* 1983, 24, 53.
- Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym Bull* 1994, 32, 617.
- Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, J. I.; Munson, E. J. *Macromolecules* 1997, 30, 2422.
- Coudane, J.; UstarizPeyret, C.; Schwach, G.; Vert, M. *J Polym Sci Part A: Polym Chem* 1997, 35, 1651.
- Spassky, N.; Wisniewski, M.; Pluta, C.; LeBorgne, A. *Macromol Chem Phys* 1996, 197, 2627.
- Hiltunen, K.; Seppala, J. V.; Harkonen, M. *Macromolecules* 1997, 30, 373.