

# Synthesis of High-Molecular-Weight Poly(lactic acid) from Aqueous Lactic Acid Cocatalyzed by $\epsilon$ -Caprolactam and Tin(II) Chloride Dihydrate

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**ABSTRACT:** Poly(lactic acid) was synthesized from cheap, commercially available aqueous lactic acid (85–90% w/w) with  $\epsilon$ -caprolactam and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as catalysts in the absence of organic solvents. As a result, poly(lactic acid) with a molecular weight of 50,000 and a yield of 87–94% was prepared in 16 h. The new procedure is quite simple and cheap. The starting material is renewable aqueous lactic acid. The effects of the amount of the catalyst, the reaction temperature,

and the reaction time on the polymerization were investigated in detail. The polymers obtained by  $\epsilon$ -caprolactam and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were characterized with gel permeation chromatography, infrared, and nuclear magnetic resonance. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3597–3601, 2007

**Key words:** biodegradable; polyesters; step-growth polymerization

## INTRODUCTION

Poly(lactic acid) (PLA) is a biocompatible and biodegradable material with many environmental, biomedical, and pharmaceutical applications. Much attention has been devoted to poly(lactic acid) with the decline of petroleum reserves recently. The price of poly(lactic acid) has gradually become competitive with that of the average alkene polymers since the method for the preparation of lactic acid from starch fermentation has been developed. Poly(lactic acid) has usually been prepared by the ring-opening polymerization of L-lactide.<sup>1–5</sup> Unfortunately, PLA obtained by this method is usually highly priced, and this prohibits more general applications of poly(lactic acid). In comparison with the well-established method for the catalytic ring-opening polymerization of L-lactide, the direct dehydropolycondensation of L-lactic acid is rather difficult because of various factors, such as kinetic control and inappropriate catalyst activity. A breakthrough technology has recently been established. Moon and coworkers<sup>6–8</sup> succeeded in preparing a

high polymer of poly(L-lactic acid) (PLLA) by the direct melt polycondensation of lactic acid, using Sn(II) compounds activated by proton acids as the cocatalysts. In this polycondensation, the activity of Sn(II) adopted as the catalyst is well controlled by proton acids, although its action and the reaction mechanism have not yet been fully clarified. However, it still contains some disadvantages. For example, the utilization of a strong proton acid such as benzenesulfonic acid pollutes the environment and erodes the instrument. Furthermore, benzenesulfonic acid is difficult to eliminate, and the yield of this polymerization is only up to 60%. In our previous work,<sup>9</sup> we successfully synthesized poly(D,L-lactic acid) cocatalyzed by succinic anhydride and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . In this study, poly(L-lactic acid) was synthesized from cheap, commercially available aqueous lactic acid (85–90% w/w) with  $\epsilon$ -caprolactam and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as catalysts in the absence of organic solvents. As a result, poly(lactic acid) with a high molecular weight was obtained in a high yield and purity in a relatively short reaction time in the absence of organic solvents. The new procedure is quite simple, cheap, and outstanding in that the starting material is renewable aqueous lactic acid.

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## EXPERIMENTAL

### Materials

D,L-Lactic acid, purchased from Tianjin Chemical Reagent Factory (Tianjin, China), was an 85–90% aqueous

**TABLE I**  
Effect of the Amount of the Catalyst on the Molecular Weight and Yield of PLA

| Entry | SnCl <sub>2</sub> ·2H <sub>2</sub> O (wt %) | ε-caprolactam (wt %) | Yield (wt %) | $M_n$ (×10 <sup>4</sup> g/mol) <sup>a</sup> | $M_w$ (×10 <sup>4</sup> g/mol) <sup>a</sup> | PDI <sup>b</sup> |
|-------|---|----------------------|--------------|---|---|------------------|
| 1     | 0.00  | 0.00                 | 57.7         | 0.26  | 0.30  | 1.18             |
| 2     | 0.00  | 1.00                 | 29.2         | 0.64  | 0.85  | 1.32             |
| 3     | 1.00  | 0.00                 | 53.3         | 0.53  | 0.80  | 1.51             |
| 4     | 1.00  | 0.30                 | 60.7         | 0.92  | 1.31  | 1.43             |
| 5     | 1.00  | 0.50                 | 60.0         | 0.78  | 1.10  | 1.40             |
| 6     | 1.00  | 0.75                 | 70.7         | 1.05  | 1.53  | 1.46             |
| 7     | 1.00  | 1.00                 | 70.6         | 1.66  | 2.54  | 1.53             |
| 8     | 1.00  | 1.25                 | 69.6         | 1.24  | 1.80  | 1.45             |
| 9     | 1.00  | 1.50                 | 50.4         | 0.69  | 0.97  | 1.41             |
| 10    | 1.00  | 2.00                 | 46.2         | 0.85  | 1.15  | 1.36             |

Reaction conditions: 180°C, 10 h, 0.015 MPa, and 0.1 wt % phosphorous acid.

<sup>a</sup> Measured by GPC.

<sup>b</sup> Polydispersity index ( $M_n/M_w$ ).

solution of the monomer. ε-Caprolactam (analytical reagent) and tetrahydrofuran (THF; analytical reagent) were also obtained from Tianjin Chemical Reagent Factory. Methanol (analytical reagent), SnCl<sub>2</sub> · 2H<sub>2</sub>O (analytical reagent), phosphorous acid (analytical reagent), and acetone (analytical reagent) were obtained from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China). All these reagents and solvents were used as received without further purification.

### Polymerization

The typical polymerization experiments were conducted in a 100-mL, three-necked flask equipped with a magnetic stirrer and a water separator. Aqueous lactic acid (25 mL) and given amounts of SnCl<sub>2</sub>·2H<sub>2</sub>O, ε-caprolactam, and 0.1 wt % phosphorous acid were added to the reactor (Table I). The temperature gradually increased to 120°C in 3 h, and the reaction mixture was stirred; at the same time, the pressure of the reaction system was reduced stepwise to 0.015 MPa in 3 h, then the temperature was set at 180°C, and the reaction continued. After the reaction, the flask was opened at room temperature, and the contents were

dissolved in acetone. The polymer was precipitated from methanol and then reprecipitated from cold water. Filtration, followed by drying at 40°C in a vacuum, yielded a white solid.

### Measurements

Nuclear magnetic resonance (NMR) spectra were recorded with a JNM-ECP400 NMR spectrometer at room temperature with CDCl<sub>3</sub> as a solvent and tetramethyl silicone (TMS) as an internal reference. Fourier transform infrared spectra were taken on a FTS3000 instrument. Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed on a TG/DTA-6200 thermal analyzer (SII Nanotechnology Inc., Japan) in a nitrogen atmosphere. The measurements were run from 25 to 400°C at a heating rate of 10°C/min. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) were determined with respect to polystyrene standards by gel permeation chromatography (GPC) on a GPCV2000 machine at 40°C, THF was used as the mobile phase (flow rate = 1.0 mL/min). The intrinsic viscosity of PLA was measured in THF at

**TABLE II**  
Effect of the Reaction Time on the Polymerization

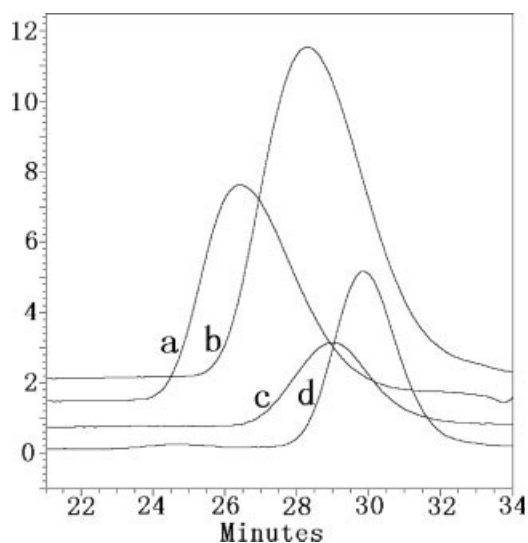
| Entry | Time (h) | Yield (wt %) | $M_v$ (×10 <sup>4</sup> g/mol) <sup>a</sup> | $M_n$ (×10 <sup>4</sup> g/mol) <sup>b</sup> | $M_w$ (×10 <sup>4</sup> g/mol) <sup>b</sup> | PDI <sup>c</sup> |
|-------|----------|--------------|---|---|---|------------------|
| 1     | 8        | 48.3         | 0.8   | 0.44  | 0.68  | 1.54             |
| 2     | 10       | 70.6         | 3.5   | 1.67  | 2.54  | 1.53             |
| 3     | 12       | 88.9         | 2.2   | 1.25  | 1.80  | 1.44             |
| 4     | 14       | 91.8         | 3.0   | 1.94  | 3.06  | 1.57             |
| 5     | 16       | 89.0         | 5.0   | 2.95  | 5.00  | 1.69             |
| 6     | 18       | 94.1         | 3.5   | 2.46  | 3.65  | 1.48             |
| 7     | 20       | 92.4         | 2.8   | 1.82  | 2.77  | 1.51             |

Reaction conditions: 180°C, 0.015 MPa, and 0.1 wt % phosphorous acid.

<sup>a</sup> Measured in THF at 30°C with an Ubbelohde viscometer.

<sup>b</sup> Measured by GPC.

<sup>c</sup> Polydispersity index ( $M_n/M_w$ ).



**Figure 1** GPC chromatograms of PLA: (a) 16-h product,  $M_w = 5.00 \times 10^4$ ; (b) 12-h product,  $M_w = 1.80 \times 10^4$ ; (c) 10-h product,  $M_w = 2.54 \times 10^4$ ; and (d) 8-h product,  $M_w = 0.68 \times 10^4$ .

30°C with an Ubbelohde viscometer (Shanghai, China). The viscosity-average molecular weight ( $M_v$ ) of PLA was calculated according to the following equation:<sup>10</sup>

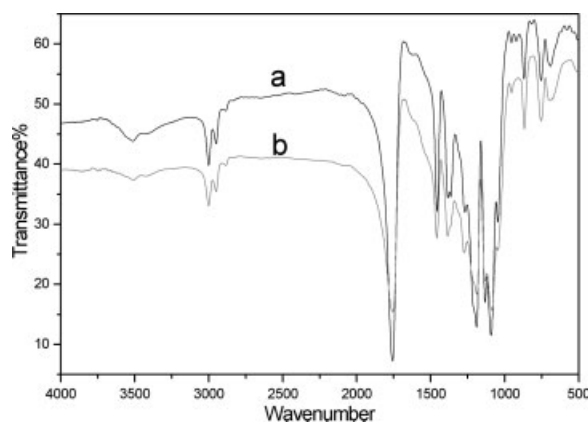
$$[\eta] = 1.25 \times 10^{-4} M_v^{0.717}$$

where  $[\eta]$  is the intrinsic viscosity.

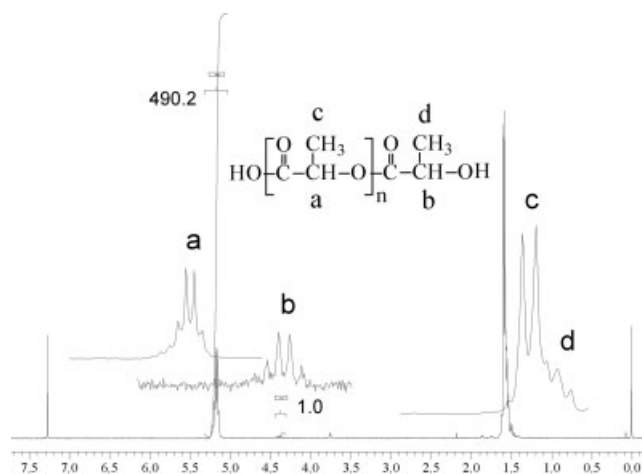
## RESULTS AND DISCUSSION

### Effect of the amounts of the catalysts on the polymerization

The amount of the catalyst is the main factor affecting the polymerization. Therefore, we first examined the effect of the amounts of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\epsilon$ -caprolactam



**Figure 2** IR spectra of poly(D,L-lactic acid): (a)  $M_w = 0.68 \times 10^4$  and (b)  $M_w = 5.0 \times 10^4$ .

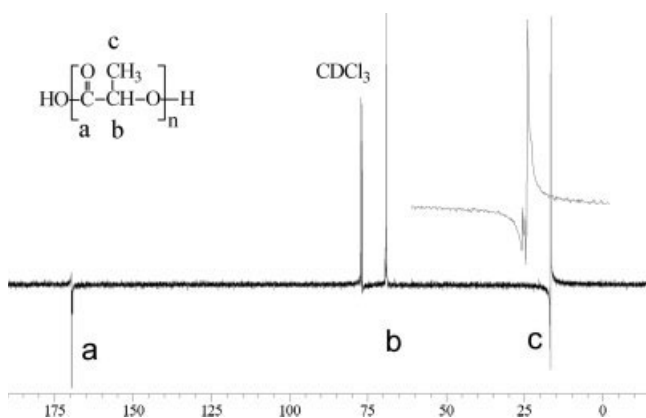


**Figure 3**  $^1\text{H-NMR}$  spectrum of poly(D,L-lactic acid) ( $M_w = 5.0 \times 10^4$ ).

tam on the polymerization under the conditions of 180°C, 10 h, and 0.015 MPa (Table I). When the polymerization was carried out without the use of any catalyst,  $M_w$  of the resulting poly(lactic acid) obtained under identical reaction conditions was only 3000. When the reaction was conducted with only  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (1.00 wt %) as the catalyst,  $M_w$  of the resulting polymers was 8000, and the yield was 53.3%. The addition of  $\epsilon$ -caprolactam (1.00 wt %) resulted in obvious increases in the molecular weight (from 8000 to 25,400) and yield (from 53.3% to 70.6%) under the same reaction conditions. To investigate the effect of  $\epsilon$ -caprolactam on the molecular weight and yield of poly(lactic acid), we carried out the experiments at 180°C, using 1.00 wt %  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . We found that the molecular weight of the resulting poly(lactic acid) was increased remarkably with the variation of the amount of  $\epsilon$ -caprolactam (from 0.00 to 1.00 wt %). In 10 h, the molecular weight reached 25,400 when the polymerization was carried out with 1.00 wt %  $\epsilon$ -caprolactam and 1.00 wt %  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .

The polymers obtained in this system are generally light yellow. Our experiments showed that it is necessary to use an antioxidant in the reaction. To prevent the polymers from being oxidized at the high temperature and get a colorless poly(lactic acid), we used 0.1 wt % phosphorous acid in each of the reactions, and by doing this, we got a white polymer. We found that phosphorous acid did not affect the yield or molecular weight. Phosphorous acid is easy to wash out when the polymer is precipitated from methanol and then reprecipitated from cold water.

With an increase in the amount of the catalysts, the yield and molecular weight of PLA increased, but they did not parallel the amount of  $\epsilon$ -caprolactam. When the amount of the catalysts exceeded 1.00 wt %, the yield and molecular weight showed a slight reduction. The optimum concentration of  $\epsilon$ -caprolactam and



**Figure 4**  $^{13}\text{C}$ -NMR spectrum of poly(D,L-lactic acid) ( $M_w = 5.0 \times 10^4$ ).

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was about 1.00 wt % for a high molecular weight and a high yield.

#### Effect of the polymerization time

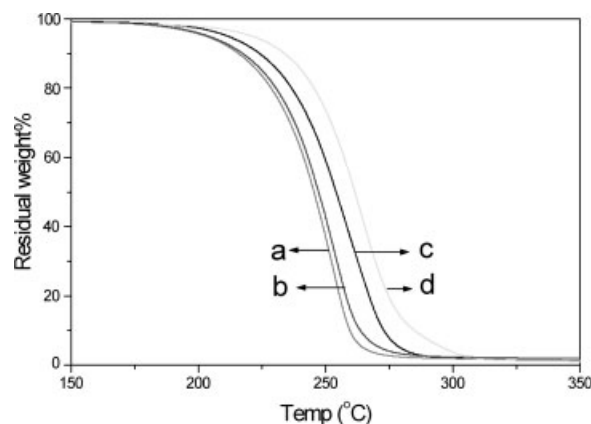
Table II and Figure 1 show the influence of the polymerization time on the yield and molecular weight of PLA. We can see from Table II that the yield was 89% and the molecular weight of PLA reached 50,000 after the reaction was carried out for 16 h. However, after 16 h, the yield and molecular weight began to drop with the reaction time. This may be attributed to the thermal degradation.

From the experiments, we can conclude that the optimal reaction conditions are a reaction temperature of  $180^\circ\text{C}$ , a time of 16 h, and a pressure of 0.015 MPa with cocatalyst concentrations of 1.00 wt %  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and 1.00 wt %  $\epsilon$ -caprolactam. We obtained poly(lactic acid) with a molecular weight of 50,000 and a yield of 89% under these reaction conditions.

#### Characterization of PLA

Infrared (IR) spectra of the poly(lactic acid) obtained by  $\epsilon$ -caprolactam and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  are shown in Figure 2. Similar trends were found in cases a and b (case a,  $M_w = 0.68 \times 10^4$ ; case b,  $M_w = 5.00 \times 10^4$ ). IR analysis was used only as a qualitative tool to check if the differences in the end groups could be seen in the spectra of the prepared polymers. All IR spectra exhibited characteristic absorption peaks of ester (at  $1760$  and  $1090\text{ cm}^{-1}$  for  $-\text{COO}-$  and  $-\text{O}-$ ) and  $-\text{CH}_2-$  and  $\text{CH}_3$  groups (at  $2850$ – $3050\text{ cm}^{-1}$ ). The hydroxyl absorption peak around  $3500\text{ cm}^{-1}$  almost disappeared, indicating that the number of hydroxyl groups was reduced when the polymer was synthesized.

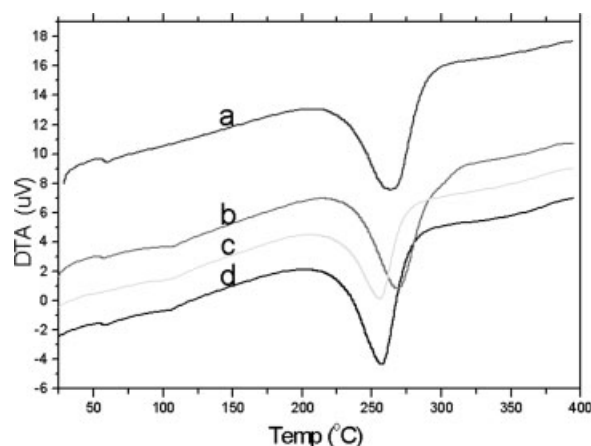
Figure 3 shows a typical  $^1\text{H}$ -NMR spectrum of a PLA sample obtained by  $\epsilon$ -caprolactam and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The major peaks at 1.55 and 5.18 ppm were assigned to the methyl and methine proton reso-



**Figure 5** TG thermogram of poly(D,L-lactic acid): (a)  $M_w = 0.68 \times 10^4$ , (b)  $M_w = 1.2 \times 10^4$ , (c)  $M_w = 1.8 \times 10^4$ , and (d)  $M_w = 5.0 \times 10^4$ .

nances in the main chain. A very weak peak (b,  $\delta = 4.35\text{ ppm}$ ) was assigned to the methine proton next to the terminal hydroxyl group. The  $M_n$  values of the PLA samples could be determined from the ratio of the peak intensity of the main chain methine proton (a) to that of the methine proton (b) next to the end hydroxyl group in the  $^1\text{H}$ -NMR spectrum.<sup>11</sup> The polymerization number ( $n$ ) in Figure 3 is 490, calculated from the ratio of the integrated area of proton a to proton b ( $490.2/1$ ).  $M_n$  of PLA, calculated from the ratio, is about  $3.54 \times 10^4$  (GPC,  $M_n = 2.95 \times 10^4$ ). The result confirms that high-molecular-weight poly(lactic acid) was formed. The  $^{13}\text{C}$ -NMR (Fig. 4) spectrum was used in a qualitative analysis of the structure of poly(lactic acid) polymers. The result is in accordance with the  $^1\text{H}$ -NMR analysis.

Figures 5 and 6 present TG/DTA thermograms of PLAs with different molecular weights. DTA thermograms of polyesters with molecular weights of  $1.8 \times 10^4$ ,  $5.0 \times 10^4$ ,  $1.2 \times 10^4$ , and  $0.68 \times 10^4$  exhibit



**Figure 6** DTA thermogram of poly(D,L-lactic acid): (a)  $M_w = 1.8 \times 10^4$ , (b)  $M_w = 5.0 \times 10^4$ , (c)  $M_w = 1.2 \times 10^4$ , and (d)  $M_w = 0.68 \times 10^4$ .

endothermal peaks at about 220–295°C, 225–315°C, 220–280°C, and 220–280°C, respectively. The change in the position of the endothermal peak in the DTA thermogram was about 17°C when the molecular weight of the polymer increased from  $0.68 \times 10^4$  to  $5.0 \times 10^4$ . The change in the position of the endothermal peak in the DTA thermogram was small when the molecular weight of the polymer changed in the range of  $0.68 \times 10^4$  to  $1.8 \times 10^4$ , although it shifted to a slightly higher temperature span with the increase in the molecular weight of the poly(lactic acid). As shown in Figure 6, the thermal degradation temperature also increased only a little with the molecular weights of the polymers in the range of  $0.68 \times 10^4$  to  $5.0 \times 10^4$ .

### CONCLUSIONS

The melt polymerization of D,L-lactic acid was first carried out with tin(II) chloride and  $\epsilon$ -caprolactam as cocatalysts. The characteristics of this method are that a high-quality polymer can be obtained in a high yield and purity in a relatively short reaction time. Furthermore, aqueous lactic acid is cheap and comes from a renewable resource. The procedure is environmen-

tally benign and uses no solvents. This direct process might be a new route to the synthesis of poly(D,L-lactic acid) with a high molecular weight and even an alternative to the currently adopted lactide polymerization method.

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