

# Study on Synthesis and Mechanism of Melt Polymerization of L-lactic Acid

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**Abstract:** A two steps direct polymerization process was developed. The first step is to produce oligomer and then the oligomer of lactic acid is polymerized with binary catalyst tin chloride dihydrate/p-toluenesulfonic acid. In this way, the direct synthesis of poly (lactic acid)(PLLA) without any organic solvents was investigated. The properties and structures of products were characterized by nuclear magnetic resonance (NMR), FT-IR spectra, and so on. The results show that comparatively high molecular weight polymer of lactic acid can be prepared by direct processing under appropriate technological conditions and that the melt polymerization of PLLA behaviors are as the second-order reaction mechanism.

**Keywords:** melt polymerization, L-lactic acid, nuclear magnetic resonance (NMR), mechanism

## 1. Introduction

Poly(lactic acid) (PLA) is expected to have wide applications not only as a biodegradable plastic but also as a biomedical material [1-4] due to its excellent properties, such as mechanical strength, transparency, safety and adjustable hydrolyzability. Main advantages of polylactic acid are good compatibility and safety. As it is degradable in the human body, it is particularly suitable for the application of implants which are used only temporarily for the healing process.

In this paper, poly(L-lactic acid) (PLLA) is prepared by direct melt polymerization instead of ring-open process (ROP) which has been already used in a great deal of literatures [3,4]. Melt polymerization is utilized to prepare a series of high Mw PLLA samples. High-resolution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are performed to characterize the as-polymerized copolymer and reaction mechanism is also studied.

## 2. Experimental

### 2.1 Materials and Reagents

L-lactic acid as a 90 wt% aqueous solution (PH90, pharmaceutical grade) was purchased from Purac Corp. (Netherland). Tin (II) chloride dihydrate, p-toluenesulfonic acid monohydrate (TSA), chloroform, and molecular sieve (3Å) were purchased from Shanghai Chemical Corp. Molecular sieve was activated at 300°C for 24 hours. All other reagents were analytical grade and used as received.

### 2.2 Melt Polycondensation

The first step was to make the oligomer: A given amount of L-LA aqueous solution 90 wt% was charged into a 100 mL three-necked flask. The flask was equipped with a mechanical stirrer and a reflux condenser packed with molecular sieve (3Å). The reaction system was connected with a vacuum system through a cold trap. The mixture of aqueous L-LA

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was then dehydrated at a constant temperature of 150°C by stepwise vacuumizing the reaction system. First, the reaction system was kept at atmospheric pressure for 2 hours, then at a reduced pressure of 13,300 Pa for 2 hours and finally under a pressure of 1300 Pa for more than 4 hours. Thus viscous oligomers of L-LA were formed and the amount of water removed from the system was measured. The water byproduct and solvent was removed to obtain the oligomer. After purification, the samples were subjected to <sup>1</sup>H NMR testing, from which the degree of polymerization of the oligomer was calculated to be about 6.

The second step was to make polymer: tin(II) chloride dihydrate corresponding to 0.4wt% of the oligomer and TSA with molar ratio of tin(II)/TSA of 1/1, were mixed with oligomers in the flask. Along with the pressure being reduced stepwise to reach 100 Pa, the mixture was gradually heated to appropriate reaction temperatures (typical reaction temperature was 180°C) under mechanical stirring. Then the reaction system was maintained under these conditions for predetermined hours. With the proceeding of the reaction, gradually the reaction system became viscous, and the resultant L-lactide was refluxed through the reflux condenser. At the end of the reaction, the flask was cooled down under vacuum. The obtained product was then dissolved in chloroform and subsequently precipitated into diethyl ether. Finally, the resulting solids were filtered and dried under vacuum at 65°C.

### 2.3 Polymer Characterization

Both <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra were carried out at a temperature of 300 K on a Bruker DMX-500 NMR spectrometer. All polymer samples were dissolved in deuterated chloroform with tetramethylsilane as an internal standard. Chemical shifts in ppm were referenced relatively to chloroform at 77.00 ppm and 7.26 ppm in <sup>13</sup>C-NMR and <sup>1</sup>H-

NMR spectra respectively. <sup>1</sup>H-NMR spectra were acquired as 1 % solution at 500 MHz. The <sup>13</sup>C-NMR measurements were acquired as 10% solution at 125 MHz, with a pulse angle of 25°, an acquisition time of 1.6s, and a delay time of 10s. The distribution of monomer sequence was investigated through <sup>13</sup>C-NMR spectra, and monomer sequence length was derived from these data. The number-average molecular weights ( $\overline{Mn}$ ) of L-LA oligomers and polymers were determined by <sup>1</sup>H-NMR spectra. In <sup>1</sup>H-NMR spectra of PLLA the peaks at 5.1-5.3 ppm are due to methine protons in LA repeat units, while the peaks at 4.4 ppm are due to methine protons in the end groups of polymers. PLLA  $\overline{Mn}$  can be measured by comparing the integrated area of peaks at 5.1-5.3 ppm with that at 4.4 ppm.

FT-IR spectra were recorded on a MANMNA IR-550 spectrometer (Nicolet Corp.). The samples were examined on NaCl discs. For each spectrum, 32 scans were taken at a resolution of 4cm<sup>-1</sup>. All spectra presented here were expanded to full scale.

The molecular weights of PLLA were also measured by Waters 1525 HPLC. Spectroscopic-grade tetrahydrofuran (THF) was used as the mobile phase at 1ml/min. Molecular weights were calculated by the universal calibration method using polystyrene reference materials (Shodex Mw 10000, 30000, and 60000). The detection of the polymer fractions was performed with a Waters 2410 RI detector.

## 3. Results and Discussion

### 3.1 The Characterization of PLLA

In direct synthesis of L-LA polymers at high temperature and under vacuum, high Mn polymers could be obtained through promoting the dehydrative equilibrium to esterification direction and reducing the depolymerization of polymers to lactides. The