



# Influence of decomposition temperature of aromatic sulfonic acid catalysts on the molecular weight and thermal stability of poly(L-lactic acid) prepared by melt/solid state polycondensation

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## HIGHLIGHTS

- Aromatic sulfonic acids were used as the catalysts in the polycondensation of PLLA.
- The catalysts were found to be removed by thermal annealing of the PLLA products.
- p-Xylenesulfonic acid was the most effective catalyst for the process control.

## ARTICLE INFO

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## ABSTRACT

Melt/solid polycondensation (MP/SSP) of poly(L-lactic acid) (PLLA) was conducted by using several aromatic sulfonic acids as the catalysts. It was clarified that the increase in molecular weight and the thermal stability of the obtained polymer are correlated with the 5% weight loss temperatures ( $T_{d,5\%}$ ) of the sulfonic acids determined by thermal gravimetric analysis. When 2,5-dimethyl-, 2,4-dimethyl- and 4-methyl-benzenesulfonic acids showing  $T_{d,5\%}$  around 150 °C were used as the catalysts, PLLA polymers with high molecular weight and excellent thermal stability could be obtained. On the other hand, 2,4,6-trimethylbenzenesulfonic acid showing  $T_{d,5\%}$  around 100 °C and 4-dodecylbenzenesulfonic acid with  $T_{d,5\%}$  above 200 °C gave PLLA polymers with remarkably low thermal stability. The residual catalyst involved in the product polymer or  $\text{SO}_3$  generated during the polymerization decreased the thermal stability of the polymer. The oligomeric fractions of the PLLA products were extracted with acetone and analyzed by  $^1\text{H}$  NMR and mass spectra. It was verified that the catalyst had efficiently been removed by thermal annealing while it remained active during the SSP to produce a thermally stable PLLA with high molecular weight.

## 1. Introduction

Poly(L-lactic acid) (PLLA) is a synthetic biodegradable polymer that can be prepared from renewable resource. It has been applied to wide variety of purposes because of its excellent physico-chemical properties and reasonable cost-property balance. PLLA is manufactured by multi-step processes, i.e., L-lactide monomer is prepared from L-lactic acid (LLA) via depolymerization step of PLLA oligomers, and it is purified and polymerized by ring-opening polymerization (ROP) [1–3]. This method is highly effective to obtain PLLA with high molecular-weight, although the synthetic process of L-lactide requires high energy consumption, making the PLLA product costly. Therefore, various attempts have been made in the past two decades to develop an alternative route [4–10], which is based on direct polycondensation of L-lactic acid. This

route is considered to be more cost-effective than the conventional ROP route, although it is difficult to obtain high molecular weight of PLLA because of the unfavorable formation of cyclic oligomers and uneasy control of the dehydration/hydration equilibrium between ester and acid/hydroxyl groups. Until now, many researchers have claimed optimum polymerization conditions and catalysts for the direct polycondensation of lactic acid. Among them, Moon et al. disclosed a binary catalyst system composed of tin(II) dichloride dihydrate/p-toluene sulfonic acid ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}/\text{TSA}$ ), with which a high-molecular-weight PLLA was readily prepared by melt-solid polycondensation (MP/SSP). In this catalyst system, the activity of Sn(II) is well controlled by protonic acid. It has accordingly been utilized as the most popular catalyst in the MP/SSP of PLLA [6,7]. However, the Sn(II) compound, showing toxicity, is hardly removed from the polymeric product, and the

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resultant PLLA containing the remaining Sn(II) should have limited use as medical, pharmaceutical, and agricultural materials. Furthermore, it has been reported that the remaining catalyst is likely to deteriorate the thermal stability of the polymeric products [11,12]. To solve this problem, various non-metallic catalysts that can easily be removed from polymeric products have been utilized in the SSP as the more desirable catalysts. Such non-metallic catalysts examined involved sulfonic acids, onium salts, organic acid anhydrides, ionic liquids, creatinine, and so on [13–17]. Bo Peng et al., for example, recently analyzed the relationship among the acidity of sulfonic acids, their miscibility with PLLA oligomer, and the thermal stability of the PLLA products in the MP/SSP [12]. They reported that PLLA with excellent thermal stability, high molecular weight, and least coloration can be obtained with 1,3-propanedisulfonic (PSA) acid and 1,5-naphthalene disulfonic (NSA) acid as the catalysts. However, further study was needed to clarify the influence of the properties of sulfonic acid catalysts on the molecular weight increase and thermal stability of the resultant PLLA, because we recently found out that their behavior is greatly affected by the desulfonation reaction of the sulfonic acid catalyst in the MP/SSP [18]. In addition, the fate of the sulfonic acid catalysts ought to give a profound effect not only on the molecular weight change during the polymerization but also on the thermal annealing and melt-processing that are conducted at high temperature.

In this study, several aromatic sulfonic acids having different number of alkyl substituents were examined as the organic catalysts of MP/SSP. Since they showed different thermal degradation behaviors at the temperatures of MP/SSP, their degradation was found to give strong influence on the degree of polymerization and thermal stability of the PLLA finally obtained. Here, we report on how the sulfonic acids can work as catalysts in the SSP and how they can be removed from the SSP products by their thermal annealing.

## 2. Experimental

### 2.1. Materials

L-Lactic acid (LLA, HiPure 90) containing 10 wt% of water was commercially supplied by Corbion Purac (Gorinchem, Holland). 2,4,6-Trimethylbenzenesulfonic acid (MSA) was purchased from Sigma-Aldrich Co. LLC (St. Louis, USA). 2,4-Dimethylbenzenesulfonic acid (m-XSA), 2,5-dimethylbenzenesulfonic acid (p-XSA), p-toluenesulfonic acid monohydrate (TSA) and dodecylbenzenesulfonic acid (DBSA) were purchased from Tokyo Chemical Industries, Co. Ltd. (Tokyo, Japan). PLLA samples, U'z<sup>o</sup> S-06 ( $M_w$   $18.9 \times 10^4$ ,  $M_w/M_n = 2.2$ ) and LAYCIA<sup>o</sup> ( $M_w$   $13.8 \times 10^4$ ,  $M_w/M_n = 2.3$ ) were purchased from Toyota Motor Co., Ltd. (Aichi, Japan) and Mitsui Chemicals, Inc. (Tokyo, Japan), respectively. All these materials were used without purification.

### 2.2. Melt polycondensation

Melt polycondensation (MP) to obtain a PLLA prepolymer was conducted as follows. L-Lactic acid and a sulfonic acid (0.25 mol% amount relative to L-lactic acid) as a catalyst were charged into a flask and well mixed by mechanical stirring. The mixture was then heated at 150 °C under 30 mmHg for 3 h. The generated water was trapped in a cold vessel connected to a vacuum pump throughout the MP. A PLLA prepolymer having a molecular weight of several thousands and a melting temperature ( $T_m$ ) around 110–150 °C was finally obtained. It was quenched in a cold bath for making it keep amorphous state.

### 2.3. Solid state polycondensation

The PLLA prepolymer obtained above was pulverized with an electrical mill (WB-1, Osaka Chemical Co., Japan) to a size less than 150 μm in diameter, and the resulting powders were divided into several test tubes. Each tube was annealed by increasing the temperature

from 80 to 110 °C in a period of 2.5 h to make the powdery prepolymer crystallize and then heated at a predetermined temperature under 10 mmHg for a predetermined time to conduct SSP. The finally obtained product in powdery form was then analyzed.

### 2.4. Thermal stability of PLLA products

The PLLA products obtained above were subjected to thermal annealing at 220 °C for 30 min, and their molecular weight was measured by gel permeation chromatography (GPC). The molecular weight retention was calculated by the following formula.

Molecular weight retention =  $100 \times (M_w \text{ after annealing}/M_w \text{ after SSP})$ .

### 2.5. Extraction of oligomeric products from obtained PLLA products

A portion of a PLLA product obtained above (0.5 g) was dispersed in an acetone (50 mL) for 30 min. Then, the acetone solution was separated by filtration and evaporated to dryness. The remaining extract was analyzed by <sup>1</sup>H NMR and MS spectra.

### 2.6. Measurements

Number- ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights and dispersity ( $M_w/M_n$ ) of PLLA polymers were determined by GPC on an apparatus (GL-7400, GL Science Inc., Japan) with a refractive index detector (GL-7454, GL Science Inc., Japan). A combination of three columns (Shim-pack<sup>o</sup> GPC-802C, 804C and 806C, Shimadzu Co., Japan) were used at 40 °C with chloroform as the mobile phase. Polystyrene (PS) standards were used to calibrate the relative molecular weights. The optical purity (OP in %ee) of the PLLA products was determined by the following formula:

$$OP (\%ee) = 100 \times (L - D)/(L + D)$$

where  $L$  and  $D$  denote the contents of L- and D-lactate units, respectively. To determine  $L$  and  $D$ , a portion of a polymer sample was hydrolyzed in a 2 N NaOH for 12 h at room temperature, and the resultant solution was neutralized with 1 N H<sub>2</sub>SO<sub>4</sub>. Then, the contents of L- and D-lactic acids were determined by high-performance liquid chromatography (HPLC) on a system with a UV detector (LC-20A, Shimadzu) at 254 nm. A resolving column (MCI gel CRS10W, Mitsubishi Chemical Co., Japan) was used at 35 °C with 1 mM CuSO<sub>4</sub> as the mobile phase. The melting temperature ( $T_m$ ) of polymer samples was determined by DSC on a DSC-50 thermal analyzer (Shimadzu) at a heating rate of 10 °C/min.

Thermal gravimetric analysis (TGA) was conducted on an apparatus of TGA-2950 (TA Instruments, USA) in a temperature range from 23 to 500 °C at a heating rate of 10 °C/min to evaluate the thermal decomposition temperatures. All measurements were conducted under nitrogen atmosphere. <sup>1</sup>H NMR spectra were recorded on a spectrometer ARX-type (Bruker Co., USA) at 300 MHz. The content of an aromatic sulfonic acid in the resultant polymer was determined by the <sup>1</sup>H NMR signals in reference to those of an internal standard, 1,1,2,2-tetrachloroethane. Mass spectra (MS) of oligomeric extracts from the PLLA products were measured by LC-Mass spectra using an instrument of LCMS-Q8000 (Shimadzu). The MS measurement was carried out in the negative mode in the maximum mode of 1000 in mass number.

## 3. Results and discussion

### 3.1. Aromatic sulfonic acid catalysts

The direct polycondensation of PLLA catalyzed by various metal compounds have been extensively investigated in the past decades. Through these studies, stannous dichloride dihydrate combined with a sulfonic acid has been known as the most active catalyst in the

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