



Synthesis of poly(L-lactic acid) with improved thermal stability by sulfonic acid-catalyzed melt/solid polycondensation



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ABSTRACT

Melt/solid polycondensation (MP/SSP) is deemed as an alternative synthetic route besides ring-opening polymerization (ROP) in synthesizing poly(L-lactic acid) (PLLA). However, it is found that PLLA synthesized by MP/SSP has much poorer thermal stability than that by ROP due to more residual Sn(II) metallic catalyst in the former, but sulfonic acids does not show any detrimental effect on the thermal stability of PLLA. To synthesizing PLLA with good thermal stability by MP/SSP, a variety of commercially available sulfonic acids were screened as catalysts in MP/SSP of PLLA. Among these nonmetallic catalysts, it was found that 1,3-propanedisulfonic acid (PSA) and 1,5-naphthalene disulfonic acid (NSA) exhibited satisfactory catalytic reactivity and PLLAs with excellent thermal stability, high molecular weight, little coloration and good optical purity were successfully synthesized by MP/SSP. The decomposition temperature was increased by 80–100 °C in comparison to SnCl₂-catalyzed PLLA, and the thermal stability is comparable to commercial PLLA produced by ROP.

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1. Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable thermoplastic polymer originating from annually renewable starch resources. It has been commercially produced in large scale via ring-opening polymerization (ROP) of L,L-lactide [1]. Owing to its reasonably good thermo-mechanical properties, excellent biodegradability and biocompatibility, PLLA-based materials have been widely applied to packing materials, agricultural films, fiber, commodity plastics and biomaterials [2].

Many metallic compounds including tin-, aluminum-, zinc- and rare earth-based ones are reported to be catalysts in synthesis of PLLA via ROP of lactide [3]. Among them, stannous octoate (Sn(Oct)₂) is the most used and has been applied to industrial production of PLLA [1]. However, it was reported that residual metallic catalysts in PLLA deteriorate its thermal stability though pure PLLA has excellent thermal stability [4–6]. PLLA usually undergoes thermal decomposition reactions including hydrolysis, lactide formation, transesterification and oxidative chain scission at temperature above 200 °C, resulting in a decrease in molecular weight and mechanical properties, coloration and change in rheological behaviors. Because PLLA has high melting temperature

(175–180 °C) and poor thermal stability, its temperature window for melt processing is narrow [7].

High molecular weight PLLA can also be synthesized via melt/solid state polycondensation (MP/SSP) of L-lactic acid [8–15]. MP/SSP is deemed as an alternative synthetic route having good cost-effectiveness. The most used catalyst for MP/SSP of PLLA is a binary catalyst system composed of tin(II) chloride and toluene-4-sulfonic acid (SnCl₂/TSA) [8–10]. However, as the amount of SnCl₂ used in polycondensation is usually one order of magnitude higher than Sn(Oct)₂ used in ROP (Sn > 2000 ppm [8–10] vs. Sn ~ 10² ppm [1,16]), the thermal stability of PLLA synthesized via MP/SSP may be much worse. Furthermore, residual Sn(II) in PLLA has shown certain cell toxicity for biomaterial application and environmental impact after biodegradation [17]. Besides, tin-based metallic catalysts often lead to side reactions like coloration and racemization during polycondensation reaction [8,18]. Therefore, although great progress has been made in last decade in increasing the molecular weight growth rate in MP/SSP of PLLA [8–11,14,15], improving the thermal stability and other properties of PLLA is still a great challenge for industrial development of the MP/SSP route.

Utilizing nonmetallic catalyst instead of metallic one is a promising solution for synthesis of PLLA by polycondensation [8,19–21] as well as by ROP [22–24]. It has been reported that TSA [8], methanesulfonic acid [19], some onium salts [20] and ionic liquids [21] can be used as nonmetallic catalysts for

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polycondensation of PLLA. But the impact of these catalysts on the thermal stability of PLLA was not reported. In our previous studies, we reported polycondensation of PLLA catalyzed by both metallic [15,25,26] and nonmetallic (1,3-dialkylimidazolium ionic liquids) [21] catalysts. However, for the nonmetallic catalysts, only low to moderate molecular weight PLLA were obtained though they are helpful to depress coloration and racemization [21].

In this study, the thermal stability of commercial PLLA and PLLAs prepared by SnCl₂- and SnCl₂/TSA-catalyzed MP was compared firstly. It was found that residual SnCl₂ resulted in serious deterioration of thermal stability of PLLA. But sulfonic acids have no detrimental effect on its stability. Encouraged by these findings, some commercially available disulfonic acids and aminosulfonic acids were screened to search efficient nonmetallic catalyst for MP/SSP of PLLA. It was found that 1,3-propanedisulfonic acid (PSA) and 1,5-naphthalene disulfonic acid (NSA) are satisfactory catalysts to synthesize high quality PLLA with excellent thermal stability, high molecular weight, little coloration and good optical purity. The factors that affect the catalytic reactivity are also discussed.

2. Experimental

2.1. Materials

L-lactic acid aqueous solution (90 wt%, optical purity 98%ee) was purchased from Jiangxi Musashimo Bio-Chem Co. Ltd., China. Tin(II) chloride dihydrate (SnCl₂) and toluene-4-sulfonic acid (TSA) were purchased from SCRC. 1,4-Butanedisulfonic acid (BSA) and 1,3-propanedisulfonic acid (PSA) were purchased from Chemsynlab and TCI respectively. Aminosulfonic acid (ASA), 2-aminoethane sulfonic acid (Tau), methanesulfonic acid (MSA), 4-aminobenzene sulfonic acid (APhSA), benzenesulfonic acid (PhSA) and 1,5-naphthalene disulfonic acid (NSA) were all purchased from Aladdin. Commercial poly(L-lactic acid) (4032D) was obtained from NatureWorks Co. Ltd. All of them were used as received.

2.2. Melt/solid state polycondensation

Oligomer synthesis. L-lactic acid aqueous solution (850 g) was added into a 1000 mL four-neck flask equipped with a mechanical stirrer, a nitrogen inlet, a thermocouple and a condenser connected with a pressure sensor and a vacuum pump. It was dehydrated at 140 °C and about 3000 Pa for 5 h and then oligomerized without catalyst at 160 °C and about 600 Pa for another 5 h. The average polymerization degree of the obtained oligomer (OLLA) was determined to be 9.3 by ¹H NMR [8].

Melt polycondensation (MP). First, a so-called “film melt polycondensation” was carried out to speed up the preliminary screening of catalyst. Five grams of OLLA was dissolved in 20 mL chloroform. The solution was divided into 10 aliquots and a catalyst (cat/LLA 0.12 mol%) was added into each one. After stirring at room temperature for 1 h and ultrasonic oscillating for 20 min, the solutions were transferred to ten petri dishes. The solvent was removed after volatilizing for 24 h and then vacuum-drying for 2 h at room temperature. Thin films with thickness less than 1 mm were formed. Finally, the petri dishes were put into a vacuum oven to perform melt polycondensation at 180 °C and about 80 KPa for 8 h.

After the preliminary screening, melt polycondensation was further conducted in a 100 mL glass reactor. OLLA (60 g) and catalyst were added into the reactor. Then, the melt polycondensation was performed at 180 °C and 180–430 Pa for 2 or 5 h. In synthesis of prepolymers used for solid state polycondensation, the melt polycondensation lasted for 2.5–3 h. The PLLA melts were quenched by liquid nitrogen to obtain amorphous prepolymers.

Thus obtained prepolymers were smashed and sieved to obtain particles with size of 0.4–0.5 mm.

Solid state polycondensation (SSP). The pre-crystallization and SSP were carried out in succession in two same SSP reactors preheated at 70 and 150 °C respectively in two oil baths. The reactors were specially designed and composed of an external tube and an internal tube. The internal tube was designed to be able to be easily inserted into and taken out from the external tube to facilitate the successive operation of pre-crystallization and SSP. The detailed structure of the reactors was reported previously [15]. Three grams of particles was charged into the internal tube and the tube was inserted into the first reactor (used as a crystallizer here) to pre-crystallize the particles at 70 °C in the presence of preheated N₂ flow for 60 min, and then the internal tube was taken out and inserted immediately into the second reactor to start SSP reaction at a preheated N₂ flow rate of 0.04 L/g/min. The SSP temperature program was set as: 150 °C/2 h + 152 °C/2 h + 154 °C/2 h + 156 °C/2 h + 158 °C/2 h.

2.3. Characterization

The intrinsic viscosity of PLLA was determined in chloroform at 30 °C using an Ubbelohde viscometer. The weight average molecular weight (*M_w*) was calculated from Equation (1) [26].

$$[\eta] = 1.13 * M_w^{0.778} \quad (1)$$

The molecular weight distribution of PLLAs with *M_w* lower than 10⁴ g/mol was also measured by gel permeation chromatography (GPC, PL GPC50 Plus) at 30 °C using three polystyrene columns (Waters Styragel) and a refractive index detector (Waters 2414). Tetrahydrofuran was used as an eluant at a flow rate of 1.0 mL/min. All samples were dissolved in THF at a concentration of 3.0% (w/v).

The specific rotation of PLLA was measured with an automatic polarimeter (WOPO IV, Rudolph Company) at 25 °C using a 1.0 g/L chloroform solution. The solution was filtrated by a 450 nm micropore membrane before measurement. The optical purity was calculated with Equation (2) where the specific rotation of 100% crystallized PLLA is –156° [27].

$$OP(\%ee) = \frac{[\alpha]_D^{25}}{-156} \times 100 \quad (2)$$

Thermal transition behaviors of PLLAs were recorded by differential scanning calorimetry (DSC, TA Q200, USA). Typically, a PLLA sample (5~8 mg) was first heated from room temperature to 190 °C at 10 °C/min, staying at 190 °C for 3 min, then cooled to 30 °C at 10 °C/min and held at 30 °C for another 3 min, and finally, the sample was heated to 190 °C at 10 °C/min again. The crystallinity of PLLA was calculated from the melt enthalpy by rating it to the value of 100% crystalline PLLA, 93.6 J g⁻¹ [28].

Thermal gravimetric analysis (TGA, PerkinElmer instruments, USA) was used to characterize the thermal stability of some catalysts and PLLA samples. The catalysts were measured isothermally at 180 °C for 1 h. The PLLAs were measured from 50 to 800 °C at 10 °C/min. All measurements were under nitrogen atmosphere.

The PLLA samples used for TGA included PLLAs prepared by MP or MP/SSP catalyzed by various catalysts (denoted as PLLA-cat), commercial PLLA (4032D), purified PLLA-SnCl₂ after removing residual SnCl₂ (*p*-PLLA-SnCl₂), purified 4032D after removing residual Sn(Oct)₂ (*p*-4032D), and PLLAs obtained after removing SnCl₂ or Sn(Oct)₂ and then adding extra catalyst (*p*-PLLA-SnCl₂ + cat or *p*-4032D + cat). The procedure to pretreat PLLA samples was as follows. Twenty grams of PLLA-SnCl₂ or 4032D was dissolved in 250 mL chloroform. The solution was extracted with 1 M HCl solution three times. Then, the separated PLLA solution was washed

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