Research Article

Synthesis of Poly(L-lactide) via Solvothermal Method

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Received 9 June 2009; Accepted 25 August 2009

Recommended by Yulin Deng

Poly(L-lactide) was obtained from the ring-opening polymerization of L-lactide through a solvothermal process. Tin (II) chloride (SnCl_2) was used as the catalyst for the polymerization reaction. The focus of this paper was on the effect of solvents, catalyst usage, temperature, time, and antioxidants on the ring-opening reaction in the solvothermal synthesis. Ubbelohde viscometer, FTIR, GPC, and DSC were used to characterize the products. It is found that the optimal reaction condition for the highest molecular weight of PLA is at 160°C for 10 hour with 0.4% SnCl_2 in 10 mL toluene as solvent, and the high crystallinity can be obtained. The addition of antioxidant prior to the polymerization is conducive to obtaining high molecular weight and augment T_m , T_c and X_c values of PLA.

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1. Introduction

Biodegradable polymers have recently been gained much more attention as the potential replacement for conventional synthetic (petroleum-based) materials [1, 2]. Among the new biodegradable polymers that have been developed during the last decade [3–5], polylactides (PLAs) are of particular interest [6]. Moreover, because of their excellent mechanical properties [7, 8], they are widely used in surgery (sutures, orthopaedic applications, tissue engineering). For the same reason, they are also applicable in packaging field as an environmental friendly substitute [9]. Furthermore, PLAs are easily synthesized from lactide, which is produced from renewable resources (corn, sugar beet). The degradation of PLAs depends on both external conditions (temperature, pH, ionic strength) and intrinsic structural parameters (molecular weight, polydispersity index, tacticity, chain ends) [10].

The synthesis of PLAs is carried out through a direct condensation polymerization or a ring-opening polymerization of lactide. The benefit from the direct polymerization is the ease of process but it is difficult to get the PLAs with a high molecular weight. There were three important factors to get the high molecular weight, including the dynamic control, the removal of water, and the control of degradation [11]. To avoid the disadvantage of the direct condensation,

poly(lactide) is usually synthesized by the ring-opening polymerization in bulk or solution [12]. Cationic, anionic, and insertion-coordination mechanisms [13–20] are involved in the ring-opening polymerization of PLAs. The shortcomings of the ring-opening polymerization include high reaction temperature and long vacuum duration which may risk precisely controlling the polymerization process.

Our previous research mainly involved the synthesis of new materials using the solvothermal method and characterization of the structure and properties of the as-made products. The solvothermal synthesis is normally carried out in a pressure vessel where the common-used solvents like toluene and alcohol will be stable beyond their boiling points under a high pressure. This technique was widely used in the synthesis of inorganic compounds such as NiO , ZnO , and Co_3O_4 [21]. Due to the increased solubility and reactivity of compounds and complexes under elevated temperatures and high pressures, solvothermal approaches are preferred to synthesize chemical compounds or copolymers that are extremely difficult to produce by traditional methods. Our previous works [22, 23] revealed that the solvothermal method was rather promising to prepare the grafting copolymer of high grafting degree because the reaction precursors in solvents were sealed in the vessel [24, 25]. Evaporation of the solvents and the monomers was prevented, which was favorable for the reactive environment.

This paper focuses on the synthesis of PLAs using the solvothermal synthesis. The effect of catalyst usage, reaction temperature, time, solvent, and antioxidant on the polymerization of L-lactid was systematically investigated.

2. Experimental

2.1. Materials. L-lactide (95%) and SnCl_2 were purchased from Nanjing Lihan Chemical Co., Ltd. (China). L-lactide (LA) was recrystallized three times from distilled ethyl acetate and dried under vacuum at 45°C for 4 hours to remove the water before use. Antioxidant agents IRGANOX 1010 and IRGAFOS 168 were purchased from Ciba Specialty Chemicals (Switzerland). Trichloromethane, toluene, acetone, and alcohol (Yonghua Fine Chemical Factory, China) of analytical grade were used as received.

2.2. Synthesis. The reactions were performed in a sealed vessel (50 mL) under various conditions. In a typical process, 15 g L-lactide, appropriate amount of SnCl_2 , and other reactants were mixed and purged with nitrogen for more than 3 minutes to remove the oxygen, and then poured into a sealed autoclave. Then the sealed vessel was put into an isothermal oven. After a certain time, the product was taken out of the vessel and dissolved in chloroform and precipitated in ethanol, and subsequently the solid residue was washed several times with ethanol to remove the unreacted reactants. The purified polymer was collected and dried in a vacuum oven at 50°C for 6 hours to a constant weight.

2.3. Viscometric Average Molecular Weight (M_η). The viscometric average molecular weight (M_η) of PLAs was determined according to solution intrinsic viscosity $[\eta]$ using Ubbelohde viscometer (Shanghai Liangjin Glass Instrument Company, Shanghai, China). M_η is calculated as follows:

$$[\eta] = KM_\eta^\alpha. \quad (1)$$

The solvent was chloroform and the test temperature was 25°C ($K = 1.33 \times 10^{-3}$, $\alpha = 0.79$, Polymer Handbook) [26].

2.4. NMR. ^1H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer at 400 MHz; CDCl_3 was used as solvent and tetramethylsilane (TMS) as internal standard.

2.5. FTIR. The PLA samples were dissolved in chloroform and cast the film on KBr for Fourier transform infrared (FTIR) characterization. Infrared spectroscopy of PLA sample was obtained on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer (Waltham, USA) ranging from 450 cm^{-1} to 4000 cm^{-1} at a resolution of 2 cm^{-1} and 1 scan.

2.6. DSC. The thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and enthalpies of fusion (ΔH_m) were measured using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) (Waltham, USA). Transition temperatures were calibrated using indium and

FIGURE 1: The characterization of the sample.

zinc standards. Samples (about 5 mg) were heated from the room temperature to 180°C at a rate of $40^\circ\text{C}/\text{min}$ and held for 3 minutes to eliminate the thermal history of samples before being cooled to room temperature at $10^\circ\text{C}/\text{min}$, and then reheated to 180°C at a rate of $10^\circ\text{C}/\text{min}$.

3. Results and Discussion

The solvothermal reaction was carried out at 170°C for 12 hours in an autoclave which contained 15 g PLA, 10 mL toluene, and 0.06 g SnCl_2 . The autogenous pressure in the autoclave far exceeded the ambient pressure at 170°C . Furthermore, the high temperature and the autogenous pressure out of heating greatly increased reactivity of LA, which is favorable to the polymerization within shorter time than that needed in the traditional process. The FTIR and ^1H NMR spectra of the sample were shown in Figure 1.

As seen in FTIR spectra (Figure 1(a)), the strong absorb peaks at $1758\sim 1763\text{ cm}^{-1}$ and $2994\sim 2997\text{ cm}^{-1}$ are corresponding to the characteristic peaks of $\text{C}=\text{O}$ and $-\text{CH}_2$, the absorption peak at $1184\sim 1190\text{ cm}^{-1}$ for $\text{C}-\text{O}-\text{C}$ ester group proves the formation of $-\text{COO}-$, the peak at $1452\sim 1457$ and $1382\sim 1389$ reveals the presence of $-\text{CH}(\text{CH}_3)$, and all of

The reaction condition			
L-lactide (g)	SnCl ₂ (g)	Temperature (°C)	Time (h)
15	0.045	170	12

FIGURE 2: The effect of solvent type on M_η of PLAs.

The reaction condition			
L-lactide (g)	Toluene (mL)	Temperature (°C)	Time (h)
15	10	170	12

FIGURE 3: The relationship between the amount of catalyst and M_η of PLAs.

those FTIR characteristic peaks indicate that the PLA was successfully obtained [27]. The typical peak of the $-\text{CH}$ bond on the ring of lactide at $932\sim 934\text{ cm}^{-1}$ was not observed for all the samples, indicating that the lactide was fully ring-opened. The ^1H NMR result (Figure 1(b)) further proves

that PLA was successfully prepared [12, 28, 29] through the precisely-controlled solvothermal process.

3.1. Effect of Solvents on the Molecular Weight of PLAs. The solvent is one of the important factors to the formation of PLAs because it can promote the higher solubility and reactivity of compounds and complexes at elevated temperatures under a high pressure. In other words, the above-mentioned solvothermal method could be an effective approach to the synthesis of chemical compounds or copolymers that are hard to obtain using traditional methods. It is worth mentioning that in a hermetic system at high temperature, the pressure went up quickly when a volatile organic solvent was heated, which was suspected to affect the final polymerization. Therefore, two typical solvents chloroform and toluene representing the good solvent and the poor solvent, respectively, were chosen for further clarification. The optimal reaction condition for normal lactide open-ring polymerization was at 170°C for 24 hours with 0.8 wt% SnCl_2 (as catalyst) [30]. Considering the faster reaction speed of solvothermal reaction, we shortened the initial reaction time to 12 hours. Figure 2 gives the effect of solvent types and their amount on the molecular weight. It can be seen from Figure 2 that M_η of PLA increases with the increasing amount of toluene, while M_η of PLA hardly changes with the increase of chloroform content.

It is very clear that more toluene in the system can be conducive to raising the system pressure and thus accelerating the polymerization while a good solvent like chloroform has a negative impact. The possible explanation for this phenomenon includes two points. The first is due to the depolymerization caused by the trace amount of water and the solvent. The second came from the fact that the lone-pair electrons of chlorine could coordinate with the empty orbit of Sn^{2+} and reduce the catalysis of catalyst.

3.2. The Effect of Catalyst Usage on the Molecular Weight of PLAs. The catalysts used in the ring-opening polymerization of lactide include Bronsted acids, halides, and anionic species. SnCl_2 was used as the catalyzer for PLA formation due to its high efficiency, good solubility in molten lactide, and thermal stability at elevated temperatures. The reaction mechanism was illustrated in Scheme 1. It can be seen from Figure 3 that the molecular weight of PLA initially increases with increasing the amount of catalyst and reaches a maximum when the amount of catalyst is 0.4 wt% and then decreases with higher catalyst content, indicating that the optimized amount of catalyst is close to 0.4 wt% of the total weight. In other words, the different molecular weight of PLAs can be obtained through the effective control of the amount of the SnCl_2 catalyst.

The acceptable explanation for the above phenomena include the following: (1) the SnCl_2 catalyst is more active to initiate the polymerization of L-lactide when its content is less than 0.4 wt%, (2) more insertion-coordinative centers form while the SnCl_2 loading is more than 0.4 wt%, which increases the reactive polymer quantity and in the meantime shortens the polymer chain length, and (3) tin

SCHEME 1: Catalytic mechanism of SnCl_2 for PLA polymerization.

The reaction condition			
L-lactide (g)	SnCl_2 (g)	Toluene (mL)	Time (h)
15	0.06	10	12

FIGURE 4: The relationship between the reaction temperature and M_n of PLAs.

The reaction condition			
L-lactide (g)	SnCl_2 (g)	Toluene (mL)	Temperature (°C)
15	0.06	10	165

FIGURE 5: The relationship between the reaction time and M_n of PLAs.

salt catalyst not only initiates the polymerization of L-lactide but also accelerates the depolymerization at high temperature.

3.3. The Effect of Reaction Temperature on the Molecular Weight of PLAs. In general, the temperature plays an important role in PLA polymerization because the polymerization and depolymerization of PLA take place simultaneously. The relationship between the polymerization temperature and the final PLA molecular weight was investigated in this work (Figure 4).

As shown in Figure 4, the molecular weight of PLAs increased with the temperature increasing from 120°C to 180°C. When the reaction temperature was beyond 165°C, the PLA's molecular weight reduced remarkably. The major reason for such phenomena came from the mutual competition between the catalytic polymerization and thermal degradation. When the temperature is low, the catalyzed polymerization is dominant. With the temperature increases to certain point, the molecules become active enough to assist the growth of insertion-coordinative center and lead to high molecular weight products. Once the temperature

exceeds the critical point, the polymerization speed cannot catch up with the thermal degradation speed, and triggers the thermal degradation, and thus reduces the polymer molecular weight.

3.4. The Effect of Reaction Time on PLAs Molecular Weight. Based on the same dosage of SnCl_2 catalyst and reaction temperature, the relationship between the different reaction times and PLA's molecular weights was also evaluated. Figure 5 showed that the highest molecular weight was obtained when the reaction lasted for 10 hours. The impact of the reaction time on polymerization is reflected into three stages. First, the longer the reaction time, the longer the polymer chain and the higher molecular weight can be obtained. Second, with the reaction carrying on, less monomer remains for further reaction which leads to slower polymerization while the competitive depolymerization is accelerated. Finally, the PLAs are also easily degraded at elevated temperatures. When the reaction time varied, the low molecular weight and wide molecular weight distribution of PLAs can be obtained. The results prove that the optimal reaction duration is 8–10 hours.

FIGURE 6: The effect of antioxidant on M_n . A: without antioxidant; B: adding antioxidant before polymerization; C: adding antioxidant 5 hours during polymerization processing.

FIGURE 7: The effect of antioxidant on the structure of PLA by FTIR. A: without antioxidant; B: adding antioxidant before polymerization; C: adding antioxidant 5 hours during polymerization processing.

3.5. The Effect of Antioxidants on PLAs Polymerization. The presence of moisture, lactic acid residues, and metal catalysts is known to accelerate the thermal degradation of PLA. Quinone or tropolone compounds were used to stabilize PLA [31]. Oxidative stabilizers were added in order to improve the stability of PLA during molding or extrusion. The incorporation of antioxidants affects the solvothermal polymerization on different stages. The effect of antioxidant on the polymerization and PLA properties was investigated on basis of the optimal reaction condition (165°C

TABLE 1: The DSC data of different PLA samples.

Samples	$T_m/^\circ\text{C}$	ΔH_m (J/g)	$T_c/^\circ\text{C}$	$X_c/\%$
A	162.58	47.75	97.57	51.29
B	165.70	48.55	105.37	52.15
C	166.24	44.93	102.14	48.26

for 10 hours with 0.4 wt% SnCl₂ and in 10 mL toluene solvent). The antioxidant mixtures of IRGANOX 1010 and IRGAFOS 168 as 50/50 blending ratio were used due to its excellent oxidation-resistant performance as revealed in general plastic industry. Total 0.5 wt% antioxidant was added during the polymerization. The FTIR was used to identify the polymerization reaction. It can be seen from Figure 7 that FTIR spectra of all samples are almost identical in terms of characteristic absorption of functional groups, which indicates that the molecular structure of PLA does not change with the antioxidant. The effect of antioxidant additives on PLA molecular weight was also studied. The results were given in Figure 6.

It is well known that the disconnection of ester linkage can lead to the degradation of PLA. Apart from the well-known biological degradation, temperature, pH value, water, oxygen, and polymer structure are also responsible for the PLA degradation. From Figure 6, it can be shown that the added antioxidant can help to improve the molecular weight of PLAs. As mentioned earlier, without antioxidant, the degradation of PLAs generates the lactide and blocks the chain growth of PLA. In the presence of antioxidants, the degradation of PLAs is hampered effectively and thus enables the better control of molecular weight and its distribution.

3.6. Melting and Crystallization Behavior. The thermal property of final PLA products by the solvothermal method was studied using DSC. The crystallinity was determined as the ratio of ΔH_m of actual samples to the standard ΔH_m^0 of ideal crystallized PLA. The standard ΔH_m^0 is 93.1 J/g [32]. The crystallinity (X_c) was calculated by (2):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%. \quad (2)$$

The results were summarized in Figure 8 and Table 1. The crystallinity of all the samples is higher than 48%, which indicates that the solvothermal polymerization is favorable to the formation of PLA crystal. Compared to the three samples, it can be found that both T_m and T_c increase with the addition of antioxidant, which means that the antioxidant can effectively inhibit the degradation of PLA in polymerization processing. This is in agreement with the above results. It is interesting to find that the sample with antioxidant before polymerization could get the highest T_m , T_c , and X_c . So adding antioxidant prior to the polymerization is the best option for improved values of T_m , T_c , and X_c .

FIGURE 8: The Effect of antioxidants on the thermal properties of PLA by DSC. Sample A: without antioxidant; sample B: adding antioxidant before polymerization; sample C: adding antioxidant 5 hours after polymerization start.

4. Conclusion

In this paper, the solvothermal method was introduced for macromolecular polymerization. PLA from the polymerization of L-lactid has been successfully obtained through solvothermal synthesis. The effect of the amount of catalyzer, reaction temperature, time, solvent, and antioxidant on the polymerization of L-lactid was systematically investigated. The optimal reaction condition for the highest molecular weight of PLA is at 160°C for 10 hours with 0.4%SnCl₂ in 10 mL toluene solvent, and the high crystallinity can be obtained. The addition of antioxidant prior to the polymerization helps to obtain high molecular weight and augment T_m , T_c , and X_c values of PLA.

Acknowledgment

This work was financially supported by Shanghai Leading Academic Discipline Project (no. B202).

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