

Kinetics of Ring-Opening Polymerization of L-lactide by Using a Tubular Static Mixing Reactor

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Abstract. The kinetics of ring-opening polymerization of L-lactide in a tubular static mixing reactor was investigated for the first time. The polymerization of L-lactide was initiated by stannous octoate/triphenylphosphine catalyst system at a temperature of 170 °C - 190 °C and molar ratio of monomer to initiator of 1000:1 - 2500:1. The experimental results showed that the polymerization of L-lactide is first-order in monomer and catalyst concentration. Furthermore, the apparent activation energy of 58.0 kJ mol⁻¹ obtained in this study was compared with other reports. The result indicated that less energy consumption was needed by using a tubular static mixing reactor as the polymerization reactor. The tubular static mixing reactor could be a promising apparatus for ring-opening polymerization of L-lactide with low energy consumption.

Introduction

Poly(lactide) (PLA) is one of the most promising biodegradable thermoplastic polymers due to its good mechanical properties and raw material resources from the viewpoint of environmental protection and natural energy resource preservation. It has many significant applications in the fields such as packaging materials[1], tissue engineering[2] and automotive interior trim[3]. Therefore, efficient synthetic methods for PLA industrialization with low energy consumption are highly needed.

There are two primary synthetic routes for PLA polymers. The polycondensation of lactic acid and the ring-opening polymerization (ROP) of lactide[4]. Compared with the polycondensation of lactic acid, the ROP of lactide is generally used in PLA industry by kettle or tower reactors. However, the reaction time for ROP of lactide by these methods is usually more than 20 hours, which will result in unstable properties of products and high energy consumption. By contrast, some researchers used twin-screw extruder as the reactor to accelerate the ROP of lactide[5, 6]. However, the dynamic mixing screws can't avoid the water and oxygen during the operation processing. Trace amounts of water and oxygen may deteriorate the properties of the products. Thus, the sealability remains a problem of PLA industrialization for screw extruders.

In our laboratory experiments, a tubular static mixing reactor was established and used as the reactor for the synthesis of poly(L-lactide)(PLLA) through ROP of L-lactide. The polymerization of L-lactide was initiated by stannous octoate/triphenylphosphine catalyst system at a temperature of 170°C - 190 °C and a monomer to initiator molar ratio([M]/[Sn]) of 1000:1 - 2500:1. Moreover, the kinetics of ROP of L-lactide in the tubular static mixing reactor was investigated for the first time. The apparent activation energy(ΔE_a) and the frequency factor(A) for the ROP of L-lactide were determined.

Experimental Methods

Monomer and Catalysts. L-lactide (>95 wt-%, Changchun Sinobiom Co., Ltd., China), stannous octoate(Sn(Oct)₂, 95 wt-%, Sigma-Aldrich Co., Ltd., USA), triphenylphosphine (PPh₃, 99 wt-%,

Acros Organics Co., Ltd., Belgium) and antioxidant 24 (THP-24, 98 wt-%; Adamas-Beta Reagent Co., Ltd., China) were used as received and without further purification.

Polymerization. Ring-opening polymerizations of L-lactide were carried out in a tubular static mixing reactor. This polymerization apparatus was a loop reactor consisting of a gear pump and four similar corrugated plates-type static mixers. The typical procedure was as follows. Prior to polymerization, equimolar Sn(Oct)₂ and PPh₃ were added into the molten L-lactide, which was previously mixed with 0.5 wt-% THP-24. One melted stream containing the above reactive reagents (monomers, antioxygen, and catalytic system) was fed into the tubular static mixing reactor using a plunger pump. The gear pump in the reactor supplied the reactants with an initial flow rate of 3.71 mm/s. The ROPs of L-Lactide were conducted under temperatures of 170°C - 190 °C and a monomer to initiator molar ratio of 1000:1 - 2500:1 for predetermined periods. The resulting polymers were collected at the discharge gate and rapidly cooled down to room temperature.

Fourier Transform Infrared Spectra and Monomer Conversion Analysis. Fourier transform infrared (FT-IR) spectra of the resultant polymer were obtained by a FT-IR spectrometer(Nicolet Nexus 670 - Raman Module Mode) in a range of wavenumber from 4000 cm⁻¹ to 500 cm⁻¹, using the KBr disk method. L-lactide conversion can be calculated from the FT-IR spectra of the obtained polymer according to the reported method[7].

Results and Discussion

The kinetics of ROP of lactide in the tubular static mixing reactor was investigated at 170 °C, 180 °C and 190 °C. The polymerization was initiated by Sn(Oct)₂/PPh₃ catalyst system and the [M]/[Sn] were 1000:1, 1500:1, 2000:1 and 2500:1. To determine the order of the reaction, the following relationship for monomer and catalyst concentration can be applied:

$$-d[M]/dt = k_p[M]^m[Sn]^n = k_{app}[M]^m \quad (1)$$

where [M] is the concentration of monomer, [Sn] is the concentration of catalyst, m and n are the order of reaction for [M] and [Sn], respectively. $k_{app} = k_p[Sn]^n$, k_p is the propagation rate coefficient.

To determine the order of [M], m, the equation (2) could be used:

$$\ln\left\{\frac{([M]_0 - [M]_{eq})}{([M] - [M]_{eq})}\right\} = \ln\left\{\frac{X_{eq}}{X_{eq} - X}\right\} \quad (2)$$

where X_{eq} is the equilibrium monomer conversion, X is the monomer conversion of different reaction time (t), [M]₀ and [M]_{eq} are the initial and equilibrium monomer concentrations, respectively. The experimental data of $\ln\left\{\frac{([M]_0 - [M]_{eq})}{([M] - [M]_{eq})}\right\}$ versus reaction time at different temperatures presented from Figure 1 to Figure 3 were linear, indicating all polymerization of L-lactide followed first-order dependence on the concentration of monomer at all range of temperatures in this study.

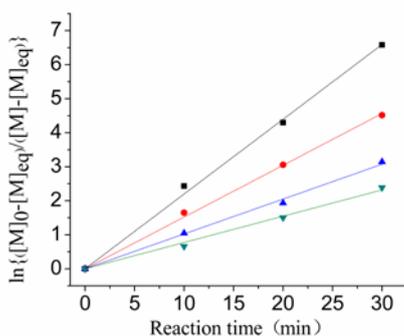


Fig. 1. Kinetic plots for ROP of L-lactide at 170 °C and different ratios of [M]/[Sn].

([M]/[Sn]: ■ 1000:1; ● 1500:1; ▲ 2000:1; ▼ 2500:1)

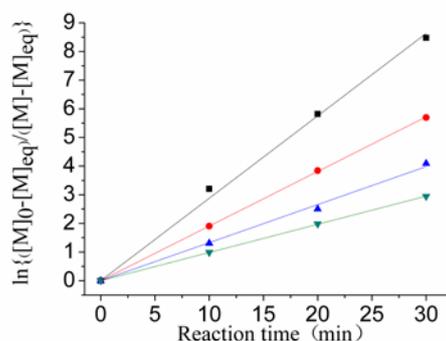


Fig. 2. Kinetic plots for ROP of L-lactide at 180 °C and different ratios of [M]/[Sn].

([M]/[Sn]: ■ 1000:1; ● 1500:1; ▲ 2000:1; ▼ 2500:1)

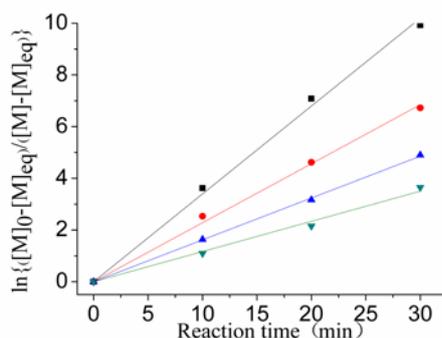


Fig. 3. Kinetic plots for ROP of L-lactide at 190 °C and different ratios of [M]/[Sn]. ([M]/[Sn]: ■ 1000:1; ● 1500:1; ▲ 2000:1; ▼ 2500:1)

Therefore, the polymerization of L-lactide in the tubular static mixing reactor most likely proceeds according to equation (3):

$$-d[M]/dt = k_p [M]^1 [Sn]^n = k_{app} [M]^1 \quad (3)$$

To determine the value of n, taking the natural logarithms of both sides of $k_{app} = k_p [Sn]^n$, we obtained:

$$\ln k_{app} = \ln k_p + n \ln [Sn] \quad (4)$$

By plotting $\ln k_{app}$ to $\ln [Sn]$ at 170 °C, 180 °C and 190 °C shown in Figure 4, the slopes (i.e. n) of the three lines are 1.15, 1.17 and 1.18, respectively. These values are approximately equal to 1, indicating that the polymerization was first-order in [Sn]. Therefore, the ROP of L-lactide initiated by Sn(Oct)₂/PPh₃ catalyst system in the tubular static mixing reactor obeys an overall kinetic law of the form:

$$-d[M]/dt = k_p [M]^1 [Sn]^1 \quad (5)$$

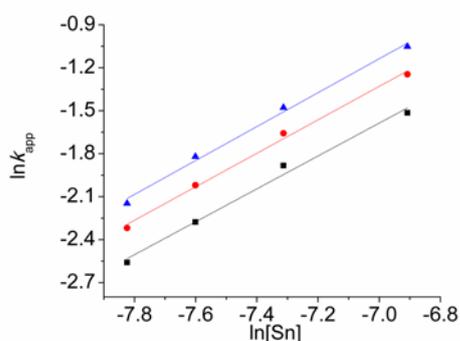


Fig. 4. Linear plots of $\ln k_{app}$ vs. $\ln [Sn]$ at different polymerization temperatures. (Polymerization temperature: ■ 170 °C, ● 180 °C, ▲ 190 °C)

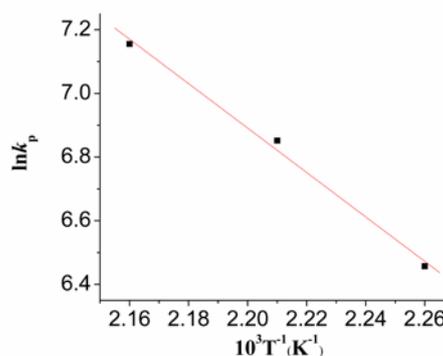


Fig. 5. Linear plots of $\ln k_p$ vs. $10^3 T^{-1}$. (The solid line represents the linear fit of experimental data: $Y = 22.2471 - 6.9800X$, coefficient of determination (r^2) is 0.9885)

According to the above experimental data, the apparent activation energy for the ROP of L-lactide in the tubular static mixing reactor could be obtained from Arrhenius equation. Linear plots of $\ln k_p$ versus $10^3/T$ (where T is the polymerization temperature in Kelvin scale) were shown in Figure 5. The apparent activation energy (ΔE_a) and the pre-exponential factor (A) for the ROP of L-lactide could be deduced to be 58.0 kJ mol⁻¹ and 4.58E+9, respectively. It is emphasized that the value of the apparent activation energy in this study was smaller than that reported in literature[8](91.1 kJ mol⁻¹) by using Haake Rheocord mixer as the reactor and the same catalyst system for ROP of L-lactide. This distinction of activation energy values may attribute to the differences of the polymerization reactor. The tubular static mixing reactor is advantageous because of its unique structure of the

corrugated plates-type static mixers. Thus could ensure high-level mixing of materials to satisfy the polymerization time for increasing monomer conversions. Therefore, less energy consumption was needed for ROP of lactide using a tubular static mixing reactor.

Summary

The kinetic parameters of ROP of lactide using a tubular static mixing reactor were estimated for the first time. The polymerization was initiated by $\text{Sn}(\text{Oct})_2/\text{PPh}_3$ catalyst system. The kinetic data showed a first-order dependency on both monomer and catalyst concentration. The apparent activation energy (ΔE_a) and the pre-exponential factor (A) were 58.0 kJ mol⁻¹ and 4.58E+9, respectively. The value of the activation energy was lower than that reported in literature by using a Haake Rheocord mixer as the polymerization reactor. This result indicated that less energy was needed for the ROP of L-lactide using the tubular static mixing reactor. It is suggested that the tubular static mixing reactor is a promising apparatus for ring-opening polymerization of L-lactide with low energy consumption.

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