초임계유체에서 L-Lactide 중합의 반응속도와 메커니즘에 관한 연구

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Kinetic and Mechanistic Studies of L-Lactide Polymerization in Supercritical Fluid

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Introduction

Numerous studies have been devoted to the syntheses, processing of biodegradable thermoplastics such as poly(ε-caprolactone), poly(L-lactide) and poly(3-hydroxybutyrate). More recently, the synthesis of biodegradable polymers in supercritical CO_2 (sc CO_2) has attracted more attention. Supercritical CO_2 is an adequate reaction medium because of its low toxicity, low cost and nonflammability. In coordination-insertion polymerization of L-lactide(L-LA) promoted by Al, Zn and Sn compounds as catalyst in bulk, in solution and in sc CO_2, the structure of the active species, the reactivity of the initiators including a hydroxyl group bearing reagents and their contribution to propagation and side reactions (e.g. intra- and intermolecular transesterifications) are known. However, nothing is known about the mechanism and kinetics of homogeneous ring-opening polymerization of L-LA promoted by tin octoate in supercritical HCFC-22. This paper reports preliminary results about the ring-opening polymerization of L-LA initiated by 1-dodecanol/tin octoate in supercritical HCFC-22.

Experimental Section

Materials. L-Lactide was purchased from Purac Biochem BV (Gorinchem, The Netherland). They were recrystallized from ethyl acetate and dried in vacuum (0.2 mmHg) over P_4O_{10}. Tin(II)bis(2-ethylhexanoate) ($Sn(Oct)_2$) (Sigma Chemical Co., St. Louis, MO, 99%) and 1-dodecanol (Aldrich, 99.5%) were purified by distillation under reduced pressure and dissolved in dry toluene. HCFC-22 was purchased from Solvey Gas Co. (USA), and its certified purity was 99.99 wt %. It was used as received without further purification. Toluene was dried by refluxing over benzophenone-Na complex and distilled under nitrogen atmosphere just prior to use. $CDCl_3$ (Aldrich, 99.5 atom % D) was used as received.

Polymerization Procedure in Supercritical HCFC-22 (Typical Example). The high-pressure schematized in Figure 1. Polymerization was conducted in a 52 mL stainless steel high-pressure cell equipped with a magnetic stirring bar and an electrically heating mantle. L-LA (2.85 g), initiator solution (0.3 mL of a 0.11 M solution in toluene; 1.54×10^{-3} mol of 1-dodecanol) and catalyst solution (0.4 mL of a 0.12 M solution in toluene; 2.37×10^{-3} mol of $Sn(Oct)_2$) were added into the cell. The toluene was removed under vacuum for a few minutes. The cell was then connected to the nitrogen purge and HCFC-22 feed system. The reactor was heated to 50 °C and purged with nitrogen for 5 min. While cooling to room temperature, it was evacuated for a few hours via a trap cooled by liquid nitrogen. And then it was purged with nitrogen for an additional 10 min. The cell was filled with liquid HCFC-22 to ca. 30 bar at 50 °C by an air-driven gas compressor (Maximator Schmidt Kranz & Co. GMBH) and then gradually heated to 110 °C to achieve a pressure of 200-205 bar. Polymerization was allowed to proceed for 32 min. The reactor was then cooled to 25 °C, and the HCFC-22 was vented through a needle valve. M_n was determined by ^1H NMR.

Polymer Characterization. NMR spectra were recorded at 25 °C using Varian Unity Plus 300 MHz spectrometer in $CDCl_3$ for ^1H NMR. Conversion of the polymer was calculated from the relative intensities of the monomer and polymer methine quartet at 5.03 and 5.16 ppm or the methyl doublets at 1.59 and 1.69 ppm. A tetramethylsilane (TMS) signal was taken as the zero chemical shift.

Result and discussion

In this paper, in-situ observation of the polymerization by ^1H NMR spectroscopy is used for kinetic and mechanistic studies. The polymerization is illustrated in Figure 1. Figure 2 shows the ^1H NMR spectra of the polymerization system during reaction at 110 °C. While the monomer concentration 1.69 and 5.03 ppm, the polymer signals increase as seen from the peaks at 1.59 and 5.16 ppm. The conversion of L-LA can be calculated from (1). Figure 3 shows the logarithm of monomer conversion versus polymerization time for the same system with an increasing concentration of $Sn(Oct)_2$. The linear relation between the logarithm of conversion of monomer $\ln([M]_0/[M])$, and the reaction time at low conversion indicates that the reaction is first order in monomer. The rate constants (k_M) obtained are 3.59×10^{-2}, 2.65×10^{-2}, 1.13×10^{-2} and

7.67×10^{-3} min^{-1} with [I]/[Cat]= 5.4, 10.8, 27.0 and 54.0, respectively. Figure 4 shows the molecular weight growth during polymerization as calculated from (2) or (3). They are in fair agreement at reaction time < 40, but show some deviations at reaction time > 40.

$$\text{conversion (\%)} = I_{a'}/(I_a+I_{a'})\times100 \qquad (1)$$

$$M_{n,NMR} = M_I+(I_{a'}+I_{a''})\times(M_{LA}/2)+(M_{LA}/2+1) \qquad (2)$$

$$M_{n,calc} = M_I+[M]_0/[I]_0\times M_{LA}(1-\exp(-k_M t)) \qquad (3)$$

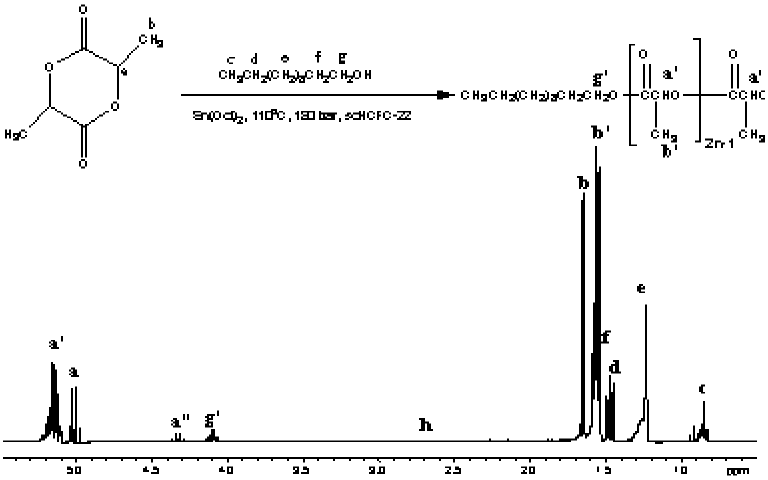

Figure 1. ^{1}H NMR spectrum during polymerization of L-LA initiated by 1-dodecanol/Sn(Oct)$_2$ in supercritical HCFC-22 at 110 °C, 200-205 bar for 42 min. $[LA]_0/[I]_0=9.7$ and $[I]_0/[Cat]_0=5.4$. I = 1-dodecanol as initiator and Cat = Sn(Oct)2 as catalyst.

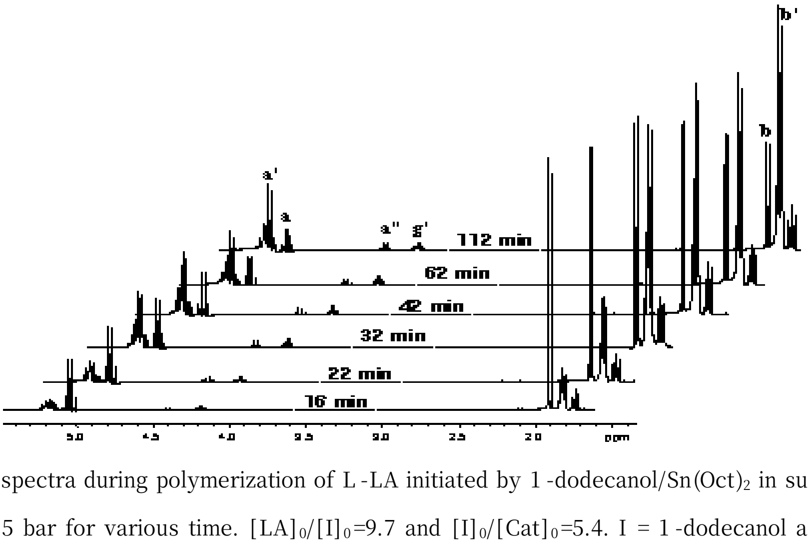

Figure 2. ^{1}H NMR spectra during polymerization of L-LA initiated by 1-dodecanol/Sn(Oct)$_2$ in supercritical HCFC-22 at 110 °C, 200-205 bar for various time. $[LA]_0/[I]_0=9.7$ and $[I]_0/[Cat]_0=5.4$. I = 1-dodecanol as initiator and Cat = Sn(Oct)$_2$ as catalyst.

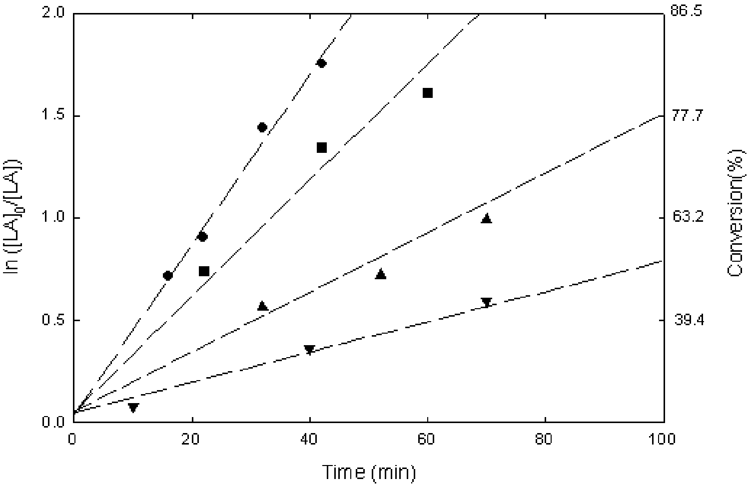

Figure 3. Kinetics of the ring-opening polymerization of L-Lactide(LA) initiated by 1-dodecanol/Sn(Oct)$_2$ in supercritical HCFC-22 at 110 °C and 200-205 bar. $[LA]_0/[I]_0$=9.7. $[I]_0/[Sn(Oct)_2]_0$ was (●) 5.4 (k_M=3.59×10^{-2} min^{-1}), (■) 10.8 (k_M=2.65×10^{-2} min^{-1}) and (▲) 27.0 (k_M=1.13×10^{-2} min^{-1}) and (▼) 54.0 (k_M=7.67×10^{-3} min^{-1})

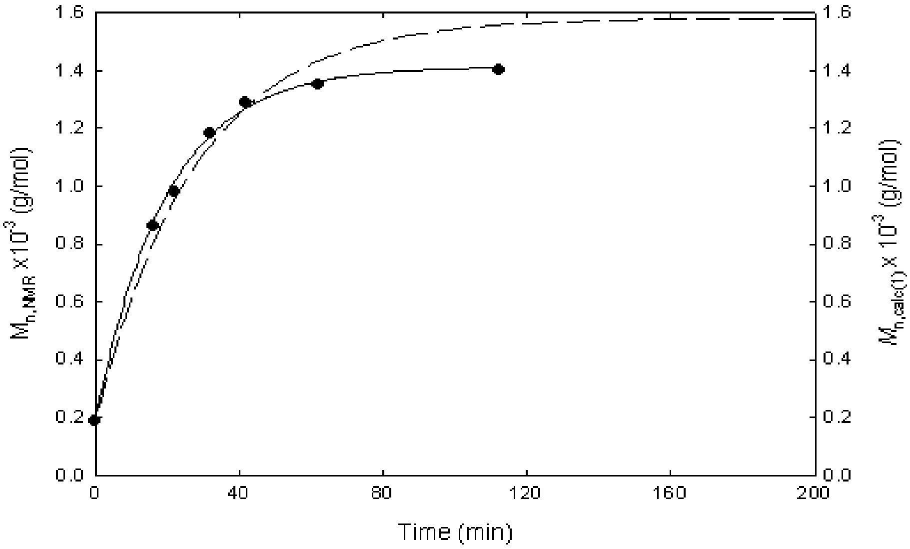

Figure 4. Molecular weight growth during polymerization. The dashed lines are drawn according to the eq. (3). The solid lines are drawn based on ^{1}H NMR spectroscopic data. Polymerization temperature, and pressure were 110 °C and 200-205 bar. $[LA]_0/[I]_0$= 9.7 and $[I]_0/[Sn]_0$=5.4 in (●) sc HCFC-22.

Reference

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