# Mechanistic Study of Sn(Oct)<sub>2</sub>-Catalyzed ε-Caprolactone Polymerization Using Sn(Oct)<sub>2</sub>/BF<sub>3</sub> Dual Catalyst

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**ABSTRACT:** A novel method was used to investigate the mechanism of  $Sn(Oct)_2$ -catalyzed  $\varepsilon$ -caprolactone polymerization by using  $Sn(Oct)_2/BF_3$  dual catalyst. The bulk polymerization was conducted at 110 and 130°C with different  $Sn(Oct)_2/BF_3$  ratios. The polymerization kinetics was followed using gel permeation chromatography, and the molecular structures of the low-molecular weight polymers were examined using <sup>1</sup>H-nuclear magnetic resonance (NMR). A polymerization induction period was observed in polymerizations containing the  $Sn(Oct)_2$  catalyst, but it was not observed in the system containing only  $BF_3$ . After the induction period,  $BF_3$  and  $Sn(Oct)_2$  initiated the polymerization

separately. For Sn(Oct)<sub>2</sub> catalyst with no purposely added alcohol, the actual initiation species is a tin hydroxide species formed *in situ* by the reaction of Sn(Oct)<sub>2</sub> and adventitious water. For BF<sub>3</sub> catalyst, the active species is the protonic acid formed by the reaction of BF<sub>3</sub> with the adventitious water. When mixed, the Sn(Oct)<sub>2</sub> reacts with the adventitious water faster than the BF<sub>3</sub>, preventing the BF<sub>3</sub> catalyzing any polymerizations during the induction period. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 658–662, 2009

**Key words:** stannous octoate; boron trifluordie; εcaprolactone

### INTRODUCTION

Aliphatic polyesters from ring-opening polymerization of cyclic esters such as ε-caprolactone, glycolide, lactide, and p-dioxanone have found increasing application in medical care and agriculture. Sn(Oct)<sub>2</sub> is the most widely used catalyst for the production of these polymers. Boron trifluoride (BF<sub>3</sub>) is a cationic catalyst, which can be used to prepare aliphatic polyesters, but these tend to be of lower molecular weight than those produced with Sn(Oct)<sub>2</sub>. However, it has also been demonstrated that low concentrations of  $BF_3$  in poly( $\varepsilon$ -caprolactone) (PCL) can act as a degradation catalyst providing a novel way to tune the degradation rate of the polymer.<sup>1,2</sup> It is therefore possible to produce PCL with a high molecular weight but also with a predetermined degradation rate by having both catalysts present during polymerization. However, there is a need to understand the polymerization mechanism for both catalysts and the effect the presence of BF<sub>3</sub> has on the

more efficient  $Sn(Oct)_2$  catalyst to engineer polymers with defined structures and tunable degradation rates.

The polymerization mechanism of Sn(Oct)<sub>2</sub>-catalyzed cyclic ester polymerization has become more and more clear by the pioneering research of Penczek and coworkers.<sup>3–7</sup> It is shown that the monomer is inserted into the Sn-alkoxide (Sn-OR) bond, which is derived in situ from an exchange reaction of an octoate group of  $Sn(Oct)_2$  with an alkoxide (-OR) or alternatively a hydroxyl group (-OH) from purposely added alcohols or adventitious water, respectively. The mechanism is also true for other similar catalysts such as zinc octoate (Zn(Oct)<sub>2</sub>) and aluminum acetylacetonate (Al(Acac)<sub>3</sub>).<sup>8</sup> Two main pieces of evidence support this mechanism. The first is the characteristics of the polymerization kinetics. The reaction is first order with respect to monomer concentration. When the molar ratio of the purposely added monoalcohol to Sn(Oct)2 was below two, the reaction rate increased with an increase of the alcohol. However, the rate did not increase further when this ratio was greater than two. Furthermore, the addition of octanoic acid slowed down the polymerization rate significantly.3 The second piece of evidence is that Sn atoms bonded through alkoxide groups to macromolecules, Oct-Sn-O-(CL)n-Bu (in which CL is a *ɛ*-caprolactone repeat unit), were detected using MALDI-TOF mass spectrometry when butanol was used as the initiator.<sup>6</sup> BF<sub>3</sub> usually

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**Figure 1** Polymerization time-conversion relationships of  $\varepsilon$ -caprolactone polymerization under the catalysis of BF<sub>3</sub>/Sn(Oct)<sub>2</sub> dual catalyst with various BF<sub>3</sub> concentrations in the reaction mixture. Sn(Oct)<sub>2</sub>/monomer = 1/1000 (molar ratio). The polymerization/temperature was 110°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

catalyzes cationic polymerizations, however, the initiation mechanism is not clear. It may either activate monomer directly<sup>9,10</sup> or through the conversion into a protonic acid.<sup>11</sup> Through investigation of the polymerization kinetics of  $\epsilon$ -caprolactone initiated by Sn(Oct)<sub>2</sub>/BF<sub>3</sub> catalysts, an insight into both the mechanisms for Sn(Oct)<sub>2</sub>- and BF<sub>3</sub>-catalyzed polymerization has been achieved.

## **EXPERIMENTAL**

# Materials

 $\epsilon$ -Caprolactone, PCL, calcium hydride (CaH<sub>2</sub>), Sn(Oct)<sub>2</sub>, and BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> were all obtained from Sigma-Aldrich (Dorset, UK).  $\epsilon$ -Caprolactone was freshly distilled under reduced pressure over calcium hydride just before use. The other compounds were used as received.

### **Polymerization of ε-caprolactone**

All glasswares for the preparation of reaction mixtures and reaction vials were dried overnight in a high vacuum oven at 140°C before use. The reaction mixture of  $\varepsilon$ -caprolactone and catalysts was prepared under a blanket of dry nitrogen with vigorous stirring for 5 min. A reaction mixture containing a predetermined concentration of Sn(Oct)<sub>2</sub> and BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> was prepared and injected into 12 2cm<sup>3</sup> reaction vials under the protection of dry nitrogen. The reaction vials were then sealed and placed in an oven at a predetermined temperature for reaction. At appropriate time intervals, a reaction vial was removed from the oven for analysis.

#### Measurements

Monomer conversion and molecular weights of the polymer were determined using gel permeation chromatography (GPC). The GPC system (Polymer Labs) consisted of two 5-µm PLgel columns, a guard column, and a refractive index (RI) detector. Chloroform (HPLC grade) was used as the mobile phase at a flow rate of 1 cm<sup>3</sup>/min at 35°C, and polystyrene standards (Polymer Labs PS2 narrow standard) were used to calibrate the system.

A sample was taken from the reaction vial and then was dissolved into chloroform to obtain a solution of about 0.2 wt %. The solution was then filtered through a 0.45-µm nylon filter into a 2-cm<sup>3</sup> sample vial for GPC analysis to determine the monomer conversion and molecular weights. For measuring the monomer conversion, the GPC system was calibrated using a series of solutions containing different concentrations of monomer and polymer. The number-average molecular weight ( $M_n$ ), weightaverage molecular weight ( $M_w$ ), and the ratio of  $M_w$ to  $M_n$  were reported.

The molecular structure of the polymer was analyzed by means of a Bruker 200 MHz <sup>1</sup>H-nuclear magnetic resonance (<sup>1</sup>H-NMR) apparatus. The concentration of the polymer was about 50 mg in 0.5 mL in deuterated chloroform. The number of scans was 16, and the decay time was 3 s.

The sample used in NMR analysis was purified by double precipitation from a polymer/toluene solution in hexane.



**Figure 2** Polymerization time–conversion relationships of  $\varepsilon$ -caprolactone polymerization under the catalysis of BF<sub>3</sub>/Sn(Oct)<sub>2</sub> dual catalyst with various BF<sub>3</sub> concentrations in the reaction mixture. Sn(Oct)<sub>2</sub>/monomer = 1/1000 (molar ratio). The polymerization temperature was 130°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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**Figure 3** <sup>1</sup>H-NMR spectrum of the PCL prepared using neat  $Sn(Oct)_2$  catalyst. The polymerization temperature was  $110^{\circ}C$ ; polymerization time was 1 h. The molar ratio of  $Sn(Oct)_2$  to  $\varepsilon$ -caprolactone was 1/1000.

#### **RESULTS AND DISCUSSION**

The polymerization was conducted at 110 and 130°C with neat Sn(Oct)<sub>2</sub>, neat BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub>, and Sn(Oct)<sub>2</sub>/ BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> dual catalyst. When Sn(Oct)<sub>2</sub>/ BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> was used as the catalyst, the concentration of BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> was either 75 ppm (vol) or 200 ppm (vol) in the reaction mixture. 75 ppm (vol) of BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> was equivalent to 0.0090% (w/w) or the molar ratio of BF<sub>3</sub> to monomer was 1/11058. 200 ppm (vol) of BF<sub>3</sub>·O(CH<sub>3</sub>)<sub>2</sub> was equivalent to 0.024% (w/w) or the molar ratio of BF<sub>3</sub> to monomer was 1/4147. The concentration of Sn(Oct)<sub>2</sub> in these



**Figure 4** <sup>1</sup>H-NMR spectrum of the PCL prepared using  $Sn(Oct)_2/BF_3$  dual catalyst. The polymerization temperature was 110°C; polymerization time was 1 h. The molar ratio of  $Sn(Oct)_2$  to  $\varepsilon$ -caprolactone was 1/1000, and the BF<sub>3</sub> concentration in the reaction mixture was 75 ppm (vol).

experiments was kept at a molar ratio of  $Sn(Oct)_2$  to monomer at 1/1000, which was equivalent to 0.355% (w/w) or 2926 ppm (vol) in the reaction mixture. No alcohols were added deliberately. Adventitious water in the reaction mixture was used as the initiator. The relationship between monomer conversion and time is shown in Figures 1 and 2 for the polymerizations at 110°C and 130°C, respectively.

As can be seen from Figure 1, after the reaction vials were placed in the  $110^{\circ}$ C oven for half an hour, there was no detectable polymerization reactions for both neat Sn(Oct)<sub>2</sub> catalyst and Sn(Oct)<sub>2</sub>/BF<sub>3</sub> dual



**Figure 5** <sup>1</sup>H-NMR spectrum of the PCL prepared using neat  $BF_3$  catalyst. The polymerization temperature was  $110^{\circ}C$ ; polymerization time was 1 h. The  $BF_3$  concentration was 75 ppm (vol) in the reaction mixture.



Scheme 1 Reaction between  $BF_3$  and adventitious water in the reaction system produce protonic acid.

catalyst, while there was 8.5% monomer conversion for the polymerization using neat BF<sub>3</sub> catalyst. After 1 h, the conversion reached 17.6% for the latter, whereas the conversion for the former (for both the higher and lower BF<sub>3</sub> concentrations) was only about 2%. With the increase of polymerization time, monomer conversion in the presence of neat BF<sub>3</sub> became much slower than those using neat Sn(Oct)<sub>2</sub> catalyst and the dual catalyst. A similar phenomenon was observed when the polymerization was conducted at  $130^\circ C$  as shown in Figure 2. At  $130^\circ C,$  there was no detectable polymerization in the first 15 min when  $Sn(Oct)_2$  was present in the reaction mixture, but the monomer conversion reached 11% during this period in the presence of neat BF<sub>3</sub>. It is clear that there was an induction period when  $Sn(Oct)_2$  was present in the reaction mixture. Because there was no induction period for neat BF<sub>3</sub> catalyst, the polymerization induction period could not be attributed to merely heat transfer.

Another interesting result was that the polymerization with the dual catalyst and the neat  $Sn(Oct)_2$ catalyst had almost the same length of induction period. At both temperatures, the polymerization rates in the earlier stages were slightly higher for the dual catalyst than for the neat  $Sn(Oct)_2$  catalyst. The higher the concentration of BF<sub>3</sub>, the higher was the polymerization rate after the induction period. The conversion of the last few percent of the monomer, however, took much longer time when using the dual catalyst than using neat  $Sn(Oct)_2$  catalyst.

Figures 3–5 show the <sup>1</sup>H-NMR spectra of the lowmolecular weight polymer isolated from the polymerization using neat Sn(Oct)<sub>2</sub>, the dual catalyst, and neat BF<sub>3</sub>, respectively, after 1-h polymerization. The spectra of the polymer using dual catalyst and neat Sn(Oct)<sub>2</sub> are very similar. They all have a triplet in the vicinity of  $\delta = 3.7$  ppm, which is due to a --CH<sub>2</sub>OH end, and the multiplets centered at  $\delta =$ 1.4, 1.65, 2.3, 4.05 ppm, which correspond to the main chain protons of PCL.<sup>12,13</sup> The spectrum of the polymer using neat BF<sub>3</sub> catalyst has a triplet at  $\delta =$ 



**Scheme 2** Reaction between BF<sub>3</sub> and a hydroxyl end of a polymer molecule.

3.4 ppm, which is due to an ether bond formed by the reaction between two hydroxyl end groups.<sup>14</sup>

The presence of hydroxyl end groups in the polymer molecules indicated by the NMR spectra is the imprint of water initiator. The reaction system containing neat BF<sub>3</sub> catalyst had no induction period, whereas there was an induction period when BF<sub>3</sub> and Sn(Oct)<sub>2</sub> coexisted in the system. This indicates that BF<sub>3</sub> cannot initiate polymerization alone and it must be converted into protonic acid by reacting with the adventitious water first (Scheme 1). All the adventitious water in the system containing Sn(Oct)<sub>2</sub> must have been trapped by Sn(Oct)<sub>2</sub> so that no water was left to be used by BF<sub>3</sub> to initiate polymerization. Also, the reaction between Sn(Oct)<sub>2</sub> and water must be much faster than the reaction between BF3 and water, otherwise some water would have reacted with the BF<sub>3</sub> to initiate polymerization and the induction period would not appear. However, the fast-reaction products between Sn(Oct)<sub>2</sub> and water have no catalytic; activity due to the induction period for  $Sn(Oct)_2$  catalyst, and this complex must further react to form the actual catalyst; although the work presented here is unable to shed light on these species, other researchers suggest that the active species is Oct–Sn–OH.<sup>3</sup>

In the study of the bulk polymerization of  $\varepsilon$ -caprolactone using Sn(Oct)<sub>2</sub> as the catalyst, Storey et al.<sup>15</sup> also observed the existence of an induction period when ethylene glycol or 1,3-dipropanediol was added as the initiator. They attributed the induction period to both heat transfer effect and the formation of more stable, less reactive stannous alkoxides compounds when compared with stannous alkoxides derived from the polymer chain end. The fact that there was an induction period for the dual catalyst but not for neat BF<sub>3</sub> catalyst shows that heat transfer was not the cause of the induction period. The reason for an induction period must result from the slow formation of an active catalyst species from the initial water/Sn(Oct)<sub>2</sub> complex.



**Scheme 3** The polymerization of ε-caprolactone (CL) by catalysis from both Sn(Oct)<sub>2</sub> and BF<sub>3</sub>.



**Figure 6** Molecular weight distribution index  $(M_w/M_n)$  changes with BF<sub>3</sub> concentration in the dual catalyst polymerization. The polymerization temperature was 110°C. The molar ratio of Sn(Oct)<sub>2</sub> to ε-caprolactone was 1/1000.

For the dual catalyst system, it was surprising that polymerization also needed an induction period, as Figures 1 and 2 show that polymerization catalyzed by BF<sub>3</sub> on its own had no induction period. Therefore, BF<sub>3</sub> must also need adventitious water to form an active catalyst, i.e., forming a protonic acid. For the dual catalyst system, although BF<sub>3</sub> initially did not catalyze any polymerizations, with the appearance of the alcohol end groups on the propagating chains (see Fig. 4),  $BF_3$  can catalyze the polymerization through the protonic acid formed by the reaction between BF<sub>3</sub> and end hydroxyls (Scheme 2). The faster polymerization rate for the dual catalyst system in comparison with the Sn(Oct)<sub>2</sub> was likely due to catalysis from both catalysts (Scheme 3). BF<sub>3</sub> can also catalyze transesterifications after the conversion into protonic acid.<sup>16</sup> Because the rate of polymerization is the reaction of a polymer and a monomer, which should be much higher than the rate of transesterification between two polymer molecules, the polymerization was dominant at earlier stages. Transesterifications may become significant during latter stages of reaction with the decrease of monomer in the system, and these reactions will lead to two effects. First, the lower polymerization rate of the dual catalyst in the latter stages may be due to monomer formed by transesterifications. Second, the molecular weight distribution for the polymer will become broader (i.e., the  $M_w/M_n$ will become higher). It can be seen that with an increase in BF<sub>3</sub> concentration for the dual catalyst polymerizations, the molecular weight distribution became broader, as shown in Figure 6.

The faster polymerization rate for the dual catalyst after the induction period and the transesterification reaction suggests that there was no interaction between  $BF_3$  and  $Sn(Oct)_2$ . In the course of the polymerization, the two catalysts initiated polymeriza-

tion separately and had a summative effect on the polymerization kinetics (i.e., the rate was faster because there was more catalyst). This indicates that the induction period was not caused by the interaction of  $BF_3$  and  $Sn(Oct)_2$  but by the fast reaction between  $Sn(Oct)_2$  and adventitious water in the reaction mixture.

### CONCLUSIONS

This work investigated the kinetics of  $\varepsilon$ -caprolactone polymerization in the presence of  $Sn(Oct)_2/BF_3$  dual catalyst. There is an induction period for both neat  $Sn(Oct)_2$  catalyst and  $Sn(Oct)_2/BF_3$  dual catalyst, whereas there is no induction period for neat BF<sub>3</sub> catalyst. The length of the induction period for the  $Sn(Oct)_2$ -catalyzed reactions was unaffected by the presence of BF<sub>3</sub>. The following conclusions can be drawn:

- The actual active catalyst for Sn(Oct)<sub>2</sub> catalyzed polymerization was a reaction product of Sn(Oct)<sub>2</sub> and adventitious water. The formation of the active catalyst has two steps. The first step was the fast formation of a complex of Sn(Oct)<sub>2</sub> and water, and the second step was the slow rearrangement/reaction into the active catalyst.
- BF<sub>3</sub> must first react with the adventitious water or an alcohol to form a protonic acid, which can act as the actual catalyst for ε-caprolactone polymerization.

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