

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

G. Jiang,\* I. A. Jones, C. D. Rudd, G. S. Walker

School of Mechanical, Materials, and Manufacturing Engineering, University of Nottingham, Nottingham NG7 2RD, United Kingdom

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**ABSTRACT:** A novel method was used to investigate the mechanism of Sn(Oct)<sub>2</sub>-catalyzed  $\epsilon$ -caprolactone polymerization by using Sn(Oct)<sub>2</sub>/BF<sub>3</sub> dual catalyst. The bulk polymerization was conducted at 110 and 130°C with different Sn(Oct)<sub>2</sub>/BF<sub>3</sub> 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)<sub>2</sub> catalyst, but it was not observed in the system containing only BF<sub>3</sub>. After the induction period, BF<sub>3</sub> and Sn(Oct)<sub>2</sub> 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 trifluoride;  $\epsilon$ -caprolactone

## INTRODUCTION

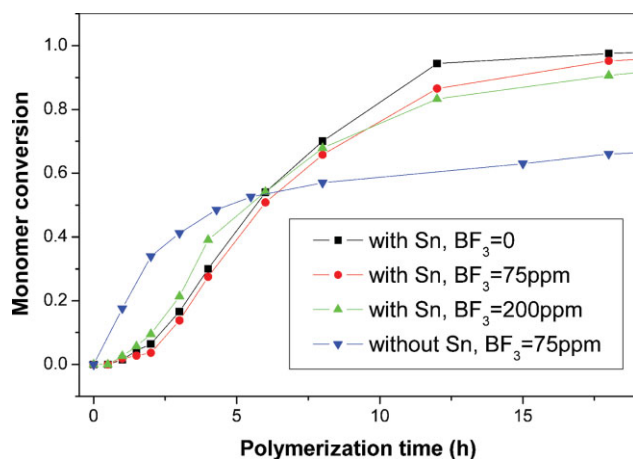
Aliphatic polyesters from ring-opening polymerization of cyclic esters such as  $\epsilon$ -caprolactone, glycolide, lactide, and *p*-dioxanone have found increasing application in medical care and agriculture. Sn(Oct)<sub>2</sub> is the most widely used catalyst for the production of these polymers. 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<sub>3</sub> in poly( $\epsilon$ -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)<sub>2</sub> 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)<sub>2</sub> 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)<sub>2</sub> 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.<sup>3</sup> The second piece of evidence is that Sn atoms bonded through alkoxide groups to macromolecules, Oct–Sn–O–(CL)<sub>*n*</sub>–Bu (in which CL is a  $\epsilon$ -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

\*Present address: Chemical Engineering and Applied Chemistry, School of Engineering and Applied Science, Aston University, Birmingham B4 7ET, UK.

Correspondence to: G. S. Walker (gavin.walker@nottingham.ac.uk).



**Figure 1** Polymerization time-conversion relationships of  $\epsilon$ -caprolactone polymerization under the catalysis of  $\text{BF}_3/\text{Sn}(\text{Oct})_2$  dual catalyst with various  $\text{BF}_3$  concentrations in the reaction mixture.  $\text{Sn}(\text{Oct})_2/\text{monomer} = 1/1000$  (molar ratio). The polymerization/temperature was  $110^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://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  $\text{Sn}(\text{Oct})_2/\text{BF}_3$  catalysts, an insight into both the mechanisms for  $\text{Sn}(\text{Oct})_2$ - and  $\text{BF}_3$ -catalyzed polymerization has been achieved.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactone, PCL, calcium hydride ( $\text{CaH}_2$ ),  $\text{Sn}(\text{Oct})_2$ , and  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  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 $\epsilon$ -caprolactone

All glasswares for the preparation of reaction mixtures and reaction vials were dried overnight in a high vacuum oven at  $140^\circ\text{C}$  before use. The reaction mixture of  $\epsilon$ -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  $\text{Sn}(\text{Oct})_2$  and  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  was prepared and injected into 12  $2\text{-cm}^3$  reaction vials under the protection of dry nitrogen. The reaction vials were then sealed and placed in an oven at a predetermined temperature for reac-

tion. At appropriate time intervals, a reaction vial was removed from the oven for analysis.

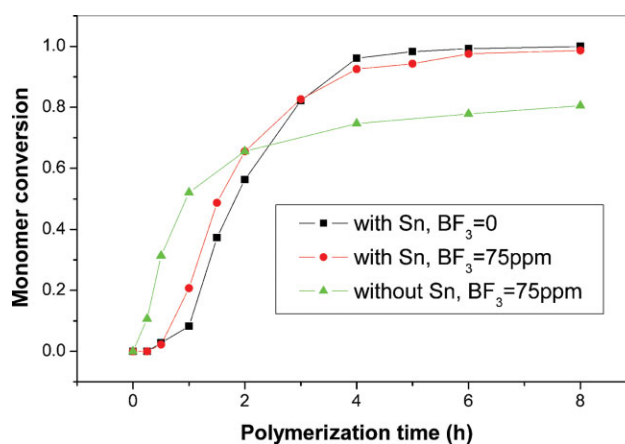
### Measurements

Monomer conversion and molecular weights of the polymer were determined using gel permeation chromatography (GPC). The GPC system (Polymer Labs) consisted of two  $5\text{-}\mu\text{m}$  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  $1\text{ cm}^3/\text{min}$  at  $35^\circ\text{C}$ , and polystyrene standards (Polymer Labs PS2 narrow standard) were used to calibrate the system.

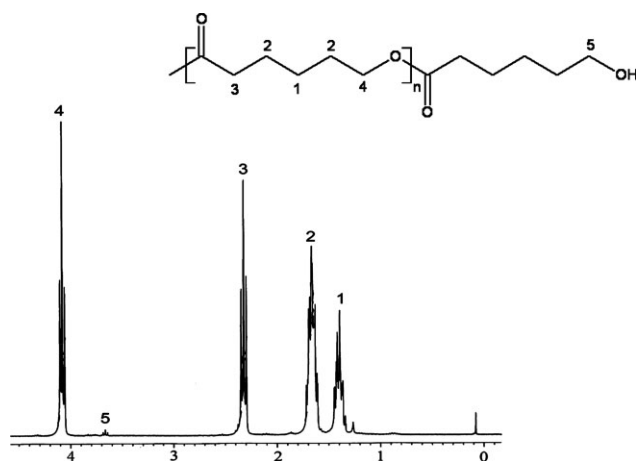
A sample was taken from the reaction vial and then was dissolved into chloroform to obtain a solution of about 0.2 wt %. The solution was then filtered through a  $0.45\text{-}\mu\text{m}$  nylon filter into a  $2\text{-cm}^3$  sample vial for GPC analysis to determine the monomer conversion and molecular 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 ( $M_n$ ), weight-average 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  $^1\text{H}$ -nuclear magnetic resonance ( $^1\text{H-NMR}$ ) 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.

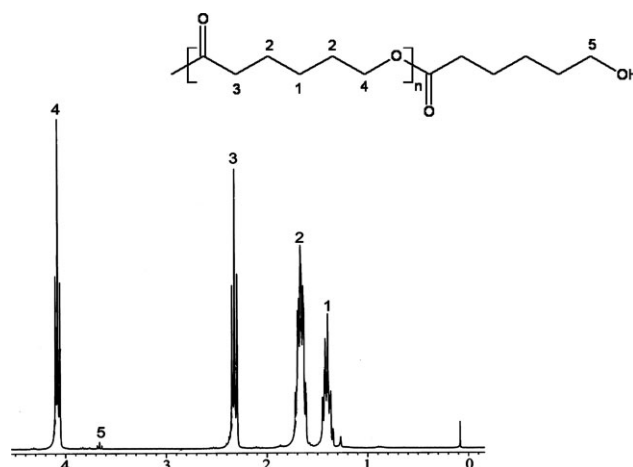
The sample used in NMR analysis was purified by double precipitation from a polymer/toluene solution in hexane.



**Figure 2** Polymerization time-conversion relationships of  $\epsilon$ -caprolactone polymerization under the catalysis of  $\text{BF}_3/\text{Sn}(\text{Oct})_2$  dual catalyst with various  $\text{BF}_3$  concentrations in the reaction mixture.  $\text{Sn}(\text{Oct})_2/\text{monomer} = 1/1000$  (molar ratio). The polymerization temperature was  $130^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



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



**Figure 4**  $^1\text{H-NMR}$  spectrum of the PCL prepared using  $\text{Sn}(\text{Oct})_2/\text{BF}_3$  dual catalyst. The polymerization temperature was  $110^\circ\text{C}$ ; polymerization time was 1 h. The molar ratio of  $\text{Sn}(\text{Oct})_2$  to  $\epsilon$ -caprolactone was 1/1000, and the  $\text{BF}_3$  concentration in the reaction mixture was 75 ppm (vol).

## RESULTS AND DISCUSSION

The polymerization was conducted at 110 and  $130^\circ\text{C}$  with neat  $\text{Sn}(\text{Oct})_2$ , neat  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$ , and  $\text{Sn}(\text{Oct})_2/\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  dual catalyst. When  $\text{Sn}(\text{Oct})_2/\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  was used as the catalyst, the concentration of  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  was either 75 ppm (vol) or 200 ppm (vol) in the reaction mixture. 75 ppm (vol) of  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  was equivalent to 0.0090% (w/w) or the molar ratio of  $\text{BF}_3$  to monomer was 1/11058. 200 ppm (vol) of  $\text{BF}_3\cdot\text{O}(\text{CH}_3)_2$  was equivalent to 0.024% (w/w) or the molar ratio of  $\text{BF}_3$  to monomer was 1/4147. The concentration of  $\text{Sn}(\text{Oct})_2$  in these

experiments was kept at a molar ratio of  $\text{Sn}(\text{Oct})_2$  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  $110^\circ\text{C}$  and  $130^\circ\text{C}$ , respectively.

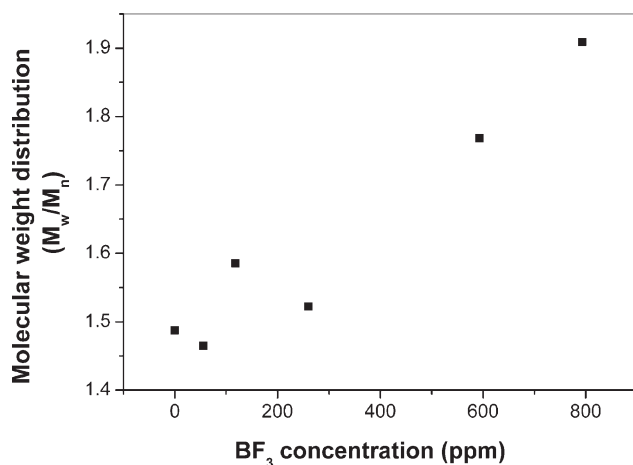
As can be seen from Figure 1, after the reaction vials were placed in the  $110^\circ\text{C}$  oven for half an hour, there was no detectable polymerization reactions for both neat  $\text{Sn}(\text{Oct})_2$  catalyst and  $\text{Sn}(\text{Oct})_2/\text{BF}_3$  dual



**Figure 5**  $^1\text{H-NMR}$  spectrum of the PCL prepared using neat  $\text{BF}_3$  catalyst. The polymerization temperature was  $110^\circ\text{C}$ ; polymerization time was 1 h. The  $\text{BF}_3$  concentration was 75 ppm (vol) in the reaction mixture.







**Figure 6** Molecular weight distribution index ( $M_w/M_n$ ) changes with  $\text{BF}_3$  concentration in the dual catalyst polymerization. The polymerization temperature was  $110^\circ\text{C}$ . The molar ratio of  $\text{Sn}(\text{Oct})_2$  to  $\epsilon$ -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  $\text{BF}_3$  on its own had no induction period. Therefore,  $\text{BF}_3$  must also need adventitious water to form an active catalyst, i.e., forming a protonic acid. For the dual catalyst system, although  $\text{BF}_3$  initially did not catalyze any polymerizations, with the appearance of the alcohol end groups on the propagating chains (see Fig. 4),  $\text{BF}_3$  can catalyze the polymerization through the protonic acid formed by the reaction between  $\text{BF}_3$  and end hydroxyls (Scheme 2). The faster polymerization rate for the dual catalyst system in comparison with the  $\text{Sn}(\text{Oct})_2$  was likely due to catalysis from both catalysts (Scheme 3).  $\text{BF}_3$  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  $\text{BF}_3$  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  $\text{BF}_3$  and  $\text{Sn}(\text{Oct})_2$ . 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  $\text{BF}_3$  and  $\text{Sn}(\text{Oct})_2$  but by the fast reaction between  $\text{Sn}(\text{Oct})_2$  and adventitious water in the reaction mixture.

## CONCLUSIONS

This work investigated the kinetics of  $\epsilon$ -caprolactone polymerization in the presence of  $\text{Sn}(\text{Oct})_2/\text{BF}_3$  dual catalyst. There is an induction period for both neat  $\text{Sn}(\text{Oct})_2$  catalyst and  $\text{Sn}(\text{Oct})_2/\text{BF}_3$  dual catalyst, whereas there is no induction period for neat  $\text{BF}_3$  catalyst. The length of the induction period for the  $\text{Sn}(\text{Oct})_2$ -catalyzed reactions was unaffected by the presence of  $\text{BF}_3$ . The following conclusions can be drawn:

- The actual active catalyst for  $\text{Sn}(\text{Oct})_2$  catalyzed polymerization was a reaction product of  $\text{Sn}(\text{Oct})_2$  and adventitious water. The formation of the active catalyst has two steps. The first step was the fast formation of a complex of  $\text{Sn}(\text{Oct})_2$  and water, and the second step was the slow rearrangement/reaction into the active catalyst.
- $\text{BF}_3$  must first react with the adventitious water or an alcohol to form a protonic acid, which can act as the actual catalyst for  $\epsilon$ -caprolactone polymerization.

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