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Synthesis of high-molecular-weight poly(ϵ -caprolactone) catalyzed by highly active bis(amidinate) tin(II) complexes†

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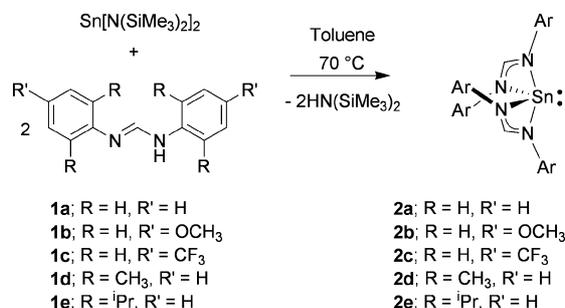
A series of bis(amidinate) tin(II) complexes is synthesized and shown to rapidly polymerize ϵ -caprolactone (ϵ -CL) in the presence and absence of benzyl alcohol giving high-molecular-weight poly(ϵ -CL) (M_n up to 160,600 Da). Ligands having electron donating groups were found to accelerate the polymerization by making the complex more nucleophilic.

There has been increasing attention towards biodegradable and biocompatible polymers during the past decade. Polyesters such as polyglycolide, polylactide (PLA), poly(ϵ -caprolactone) (PCL) and their copolymers have received significant attention.¹ Their properties such as tensile strength, degradation rate, and compatibility in the body are undoubtedly determined by the stereochemistry, composition, molecular weight, and dispersity of the polymers. Such polyesters have been successfully synthesized using various metal alkoxide complexes.² While electropositive metal complexes such as Zn, Mg, and Ca have been found to be highly active, the less active tin(II) complex specifically tin(II) bis(2-ethylhexanoate), Sn(Oct)₂, has been used industrially.^{2,3} This is due to its high solubility and thermal stability in the molten monomers, thus allowing the melt polymerization in the absence of solvents. In addition, several well-defined tin(II) complexes have been shown to be active for the polymerization of cyclic esters giving high-molecular-weight polymers with narrow polydispersity index.^{2,4} For organocatalysts, N-heterocyclic carbenes (NHCs) were reported to be efficient catalysts for high molecular weight linear PLA,⁵ and recently, for linear PCL.⁶ However, in the absence of suitable initiators, Culkin *et al.* later reported the NHC catalysts to generate cyclic PLA in THF.⁷

Following the success of carbene initiators, we hypothesized that, being three rows below carbon in the periodic table, the stannylene⁸ could be an efficient initiator for the polymerization of cyclic esters as well. Herein, we reported the synthesis of highly active bis(amidinate) tin(II) complexes and their application in the solvent-free polymerization of ϵ -caprolactone (ϵ -CL) leading to high-molecular-weight PCL.

Amidine ligands were chosen in this work due to the ease of ligand preparation and modification. The substituents on the aryl groups can be modified systematically to maximize the catalyst activity. Ligands **1a–1e** were prepared from the

reaction of triethyl orthoformate with the corresponding anilines. Reactions of 2 equiv of ligands **1a–1e** with Sn[N(SiMe₃)₂]₂ gave the bis(amidinate) tin(II) complexes **2a–2e**, respectively (Scheme 1). All complexes were isolated in moderate to high yields. Although related bis(amidinate) tin(II) complexes have been reported,⁹ they have never been used as a catalyst for the polymerization of ϵ -CL.



Scheme 1 Synthesis of bis(amidinate) tin(II) complexes.

Complex **2e** was characterized crystallographically (see ESI†) indicating a four-coordinate tin complex having a distorted square pyramidal geometry where Sn is at the top of the pyramid and the four nitrogen atoms are at the base similar to the related bis(amidinate) tin(II) complexes reported earlier.⁹ The position of the lone-pair electrons above Sn atom is clearly evidenced.

Complex **2e** was tested for the solvent-free polymerization of ϵ -CL using a low ϵ -CL:**2e** molar ratio of 10:1 at 110 °C for 1 min (>99% conversion by ¹H NMR) in order to study the polymer structure by mass spectrometry and NMR. MALDI-TOF spectrum of the resulting polymer is shown in Fig. 1 (top). Interestingly, the repeating mass is assigned to [ϵ -CL]_n + Na⁺. The mass of the end group is clearly missing. This is in agreement

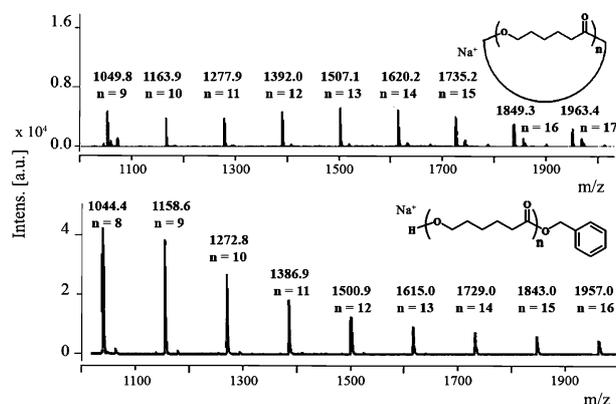


Fig. 1 MALDI-TOF spectra of PCL synthesized without addition of BnOH (top) and with addition of 1 equiv of BnOH (bottom).

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† Electronic supplementary information (ESI) available: Synthesis and characterization of **2a–e**, polymerization procedure, ORTEP drawing of **2e**, water contact angles of PCL, and GPC traces. CCDC reference number 795658. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01050b

with the ^1H NMR spectrum of the resulting polymer as shown in Fig. 2(a) where a triplet peak of the HOCH_2 - end group at 3.6 ppm is not observed. These results suggest that the majority, if not entirely, of the low-molecular-weight polymer is cyclic PCL.¹⁰ The peaks with much lower intensities observed at 1600–2200 Da (e.g. 1753.3, 1867.2, 1981.4, 2098.5) are assigned to linear $\text{H}[\text{CL}]_n\text{OH}+\text{Na}^+$. This minor linear polymer having H_2O end group may arise during polymer precipitation and purification. For comparison, a polymerization using $\epsilon\text{-CL}:\mathbf{2e}$ molar ratio of 10:1 was performed under the same condition but with the addition of 1 equiv of benzyl alcohol (>99% conversion by ^1H NMR). MALDI-TOF spectrum of the resulting polymer is shown in Fig. 1 (bottom). The repeating mass is assigned to $\text{H}[\epsilon\text{-CL}]_n\text{OBn} + \text{Na}^+$. The ^1H NMR spectra of the resulting polymer shown in Fig. 2(b) clearly reveals a triplet peak of the HOCH_2 - end group at 3.6 ppm confirming the linear structure of the polymer. At higher $\epsilon\text{-CL}:\mathbf{2e}$ molar ratio, the NMR signal of the end group is too small to be observed. The polymerization mechanism accounted for the observed linear and cyclic PCL is still under investigation. A similar mechanism to the NHC catalyst system is possible by using the lone-pair electrons to attack the ester group of monomer.⁷ However, a polymerization initiated by anionic ligand followed by intramolecular transesterification leading to cyclic PCL cannot be ruled out at this point.

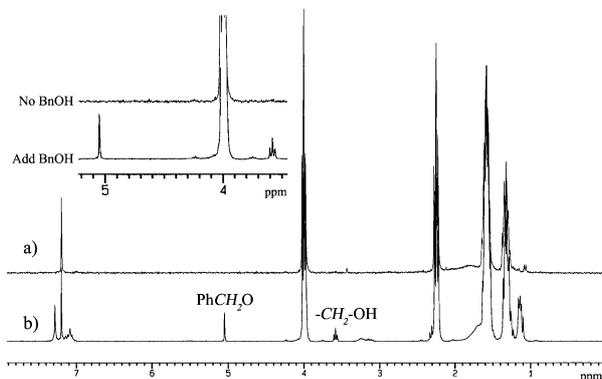


Fig. 2 ^1H NMR spectra of PCL synthesized from $\epsilon\text{-CL}:\mathbf{2e}$ ratio = 10:1 (a) without addition of BnOH and (b) with addition of 1 equiv of BnOH.

Complexes **2a–e** were used to polymerize $\epsilon\text{-CL}$ under solvent-free condition at 110 °C using $\epsilon\text{-CL}:\text{Sn}:\text{BnOH}$ molar ratio of 500:1:1 and a fixed time at 3 min. The polymerization results were summarized in Table 1, entries 1–5. All catalysts were highly active for the polymerization of $\epsilon\text{-CL}$ giving complete conversion in only 3 min. The polymers have high M_n (42,200–107,400 Da) and broad PDI of 1.65–1.90. The unusually high M_n and broad PDI are indicative of slow initiation compared to the propagation. This is also supported by the observation that the complexes **2a–e** are soluble in $\epsilon\text{-CL}$ only at elevated temperature but not at room temperature. In addition, the broad PDI could be a result of the mass transportation problems due to high viscosity. For comparison, a commercial $\text{Sn}(\text{Oct})_2$ was used as catalyst under identical condition as shown in entry 14. The polymerization was much slower compared to our catalysts giving only 58% conversion in 50 min.

For polymerizations without the addition of alcohol, complexes **2a–e** were used to polymerize $\epsilon\text{-CL}$ under solvent-free condition

Table 1 Solvent-free polymerizations of $\epsilon\text{-CL}$ at 110 °C

Entry	Catalyst	[CL]/[Sn]	Time/min	Conv. ^a (%)	M_n ^b (Dalton)	PDI ^b
1	2a ^c	500	3	>99	69,100	1.70
2	2b ^c	500	3	>99	40,900	1.78
3	2c ^c	500	3	>99	107,400	1.90
4	2d ^c	500	3	>99	42,200	1.84
5	2e ^c	500	3	>99	70,400	1.65
6	2a	500	2	47	66,300	1.55
7	2b	500	2	75	48,600	1.85
8	2c	500	2	30	99,100	1.69
9	2d	500	2	80	46,600	1.85
10	2e	500	2	97	69,800	1.85
11	2e	1,000	5	>99	70,100	1.80
12	2e	5,000	20	82	137,400	1.94
13	2e	10,000	60	94	160,600	2.07
14	$\text{Sn}(\text{Oct})_2$ ^c	500	50	58	30,700	1.32

^a Conversions determined by ^1H NMR spectroscopy. ^b Determined by GPC, calibrated using polystyrene standards. Correction factor of 0.68 was also applied. ^c Polymerization with addition of 1 equiv of BnOH.

at 110 °C using $\epsilon\text{-CL}:\text{Sn}$ molar ratio of 500:1 and a fixed time at 2 min. The polymerization results were summarized in Table 1, entries 6–10. All catalysts were also active for the polymerizations of $\epsilon\text{-CL}$. The order of activity based on conversion is **2e** > **2d** > **2b** > **2a** > **2c**. The polymerization using **2e** is the fastest giving 97% conversion in only 2 min. The polymer has high M_n of 69,800 Da and a PDI of 1.85. Other catalysts were less active producing PCL with M_n (46,600–99,100 Da) and PDI of 1.55–1.85. For complex **2e**, a plot of M_n and PDI versus % conversion is shown in Fig. 3. The polymer has low PDI at low conversion and higher PDI at later stage. The M_n of the polymer also increases with increasing conversion. Interestingly, polymerization in toluene at 70 °C for 25 h using $\epsilon\text{-CL}:\mathbf{2e} = 500:1$ with and without alcohol addition gave no polymer. Blank polymerizations (no catalyst) with and without alcohol addition at 110 °C were also carried out for 2 days giving no polymer.

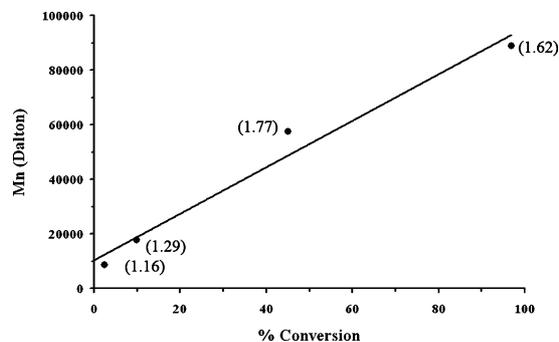


Fig. 3 Molecular weight data (PDI in parenthesis) of PCL obtained at different conversion using $\epsilon\text{-CL}:\mathbf{2e}$ molar ratio of 500:1 at 110 °C.

Complexes **2a–e** can be classified into two groups having different electronic (**2a–c**) and steric (**2a**, **2d**, **2e**) contributions. In term of electronic contribution, the order of reactivity is **2c** ($R' = \text{CF}_3$) < **2a** ($R' = \text{H}$) < **2b** ($R' = \text{OMe}$) in agreement with the increasing electron donation of the aryl groups. Based on the polymerization mechanism for NHC catalyst system,⁷ the metal in complex **2b** is electron-rich and more nucleophilic and hence more susceptible to attack $\epsilon\text{-CL}$. In term of steric hindrance, the order of reactivity is **2a** ($R = \text{H}$) < **2d** ($R = \text{Me}$) < **2e** ($R = \text{iPr}$) in

agreement with the increasing steric hindrance of the *ortho*-alkyl groups. This was surprising at first since more hindered complex gave higher activity. However, these results are not unprecedented because there are reports that sterically demanding substituents enhanced the catalytic activity of the catalysts.¹² In addition, the ³Pr groups in **2e** are more electron donating making the complex more nucleophilic.

For complex **2e**, the polymerizations using higher ϵ -CL:Sn molar ratios of 1000, 5000, and 10000 were performed at 110 °C (Table 1, entries 11–13). Great care was taken to exclude moisture or impurities from the reaction. In entry 13, PCL with $M_n = 160,600$ Da was obtained in 1 h. For 1000:1 and 5000:1 molar ratios, the polymerizations finished in 5 and 20 min having the M_n 's of 70,100 and 137,400 Da, respectively.

The difference between surfaces of PCL synthesized with and without addition of BnOH was also observed by water contact angle analysis.¹³ Polymers having similar molecular weights based on GPC were chosen. The average water contact angle of PCL (Table 1, entry 10, synthesized without addition of alcohol) is $107.4 \pm 2.5^\circ$ while that of entry 5 (with addition of BnOH) is $92.8 \pm 0.6^\circ$.

In conclusion, a series of bis(amidinate) tin(II) complexes were successfully synthesized and characterized. The major advantage is the simplicity of complex preparation and a large number of possible ligand library to fine tune both reactivity and selectivity of the catalysts. The bis(amidinate) tin(II) complexes are active for the polymerization of ϵ -CL in the presence and absence of alcohol giving high-molecular-weight PCL. Although the low-molecular-weight PCL synthesized using a low ϵ -CL:Sn molar ratio of 10:1 in the absence of alcohol was shown to be cyclic based on mass spectrometry and NMR, the exact topology (linear or cyclic) of high-molecular-weight PCL synthesized using higher ϵ -CL:Sn molar ratio is still uncertain due to the lack of access to required instruments (*e.g.* viscometer, light scattering detector) used to prove the cyclic structure.^{7,14} Nonetheless, the bis(amidinate) tin(II) complexes are highly active for the solvent-free polymerization of ϵ -CL in the presence and absence of BnOH giving high-molecular-weight PCL. This catalyst system is much more active than the commercial Sn(Oct)₂ catalyst. Amidinate ligands having electron-donating group were found to accelerate the polymerization by making the complex more nucleophilic. Further attempts to characterize the polymers and to understand the insight mechanism of the polymerization are in progress.

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