



Solvent-free ring-opening polymerization of ϵ -caprolactone initiated by Mg(II), Sn(II), Zn(II), Al(III), and Sn(IV) derivatives: a comparative study

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Abstract

Metal chlorides with different metal active centers such as Mg(II), Sn(II), Zn(II), Al(III), and Sn(IV) were successfully utilized as the initiator in the solvent-free ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL). Their reactivity in the ROP of ϵ -CL was effectively compared by differential scanning calorimetry (DSC). The DSC kinetics information demonstrated that the reactivity of those metal chlorides in the solvent-free ROP of ϵ -CL was determined in the following: aluminum(III) chloride (AlCl_3) > tin(II) chloride (SnCl_2) > *n*-butyltin(IV) trichloride ($n\text{BuSnCl}_3$) > di-*n*-butyltin(IV) dichloride ($n\text{Bu}_2\text{SnCl}_2$) > zinc(II) chloride (ZnCl_2) > tri-*n*-butyltin(IV) chloride ($n\text{Bu}_3\text{SnCl}$). The polymerization mechanism for the solvent-free ROP of ϵ -CL with all metal chlorides was proposed through the coordination-insertion mechanism. The effectiveness of all metal chlorides in the synthesis of poly(ϵ -caprolactone) (PCL) was benchmarked by conducting the 4 g scale of bulk polymerization. The highest number average molecular weight of PCL ($M_n = 1.1 \times 10^5$ g/mol) was rapidly obtained from the reactive SnCl_2 system. For the tin(IV) derivatives, the $n\text{Bu}_2\text{SnCl}_2$ produced the highest molecular weight of PCL ($M_n = 5.6 \times 10^4$ g/mol). The slow $n\text{Bu}_3\text{SnCl}$ initiator could not produce PCL under the conditions used in this work. From the results, the Sn-containing initiator

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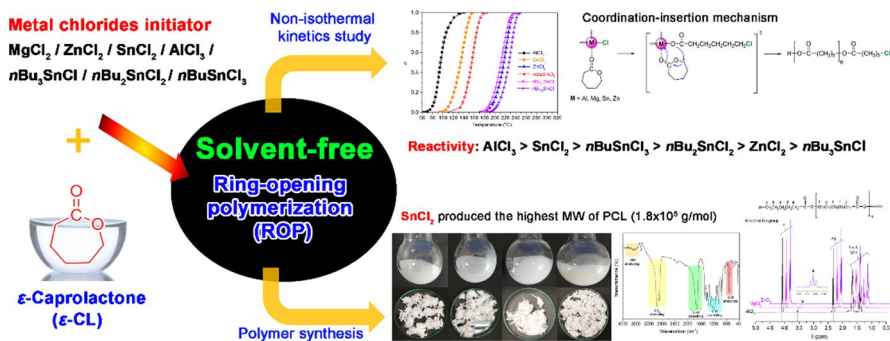
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seemed to be a more powerful initiator than Al, Mg, and Zn-derivatives in the synthesis of PCL under solvent-free conditions. From kinetics study and polymer synthesis, the number of chloride and *n*-butyl groups played an important role in the reactivity of metal chloride and the molecular weight of PCL.

Graphical abstract



Keywords Metal chloride · Ring-opening polymerization · Coordination-insertion · Biodegradable polymer · ε-Caprolactone

Introduction

Recently, the initiators or catalysts have been considered as an important factor to achieve the controlled synthesis of biodegradable polyesters such as poly(ϵ -caprolactone) (PCL) and poly(L-lactide) (PLLA) [1–3]. PCL is one of the most studied biodegradable polyesters that can be utilized in a wide range of applications, especially biomedical materials such as absorbable sutures [4], bone tissue engineering [5], nerve guides [6], membranes [7], etc. This PCL can be potentially synthesized from the ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL) in the presence of an effective initiator that contains different metal active centers such as Sn(II) [8, 9], Zn(II) [10], Al(III) [11], Sm(III) [12], Ge(IV) [13], Sn(IV) [14, 15], and Ti(IV) [16]. These metal-containing initiators have been developed for the synthesis of PCL from the past until now. Among these, Sn(II)-containing compound, namely tin(II) 2-ethyl hexanoate ($Sn(Oct)_2$), is the well-known initiating system for the production of biodegradable polyesters for a long time [2, 17, 18]. In recent years, tin(II) compound that contains nontoxic anion such tin(II) chloride ($SnCl_2$) has been utilized as low-toxic initiator in the control synthesis of high molecular weight PLL [19]. This $SnCl_2$ can be used as a food stabilizer because the chloride ion can be found in human metabolism [19].

From the literature survey, there are several works reported about the ROP of ϵ -CL with metal chlorides initiator in the presence and absence of organic solvent. Kricheldorf et al. [20] reported the effectiveness of different tributyltin(IV) derivatives such as tri-*n*-butyltin(IV) methoxide (nBu_3SnOMe), tri-*n*-butyltin(IV)

tert-butoxide ($n\text{Bu}_3\text{SnOtBu}$), tri-*n*-butyltin(IV) phenoxide ($n\text{Bu}_3\text{SnOPh}$), tri-*n*-butyltin(IV) chloride ($n\text{Bu}_3\text{SnCl}$), tri-*n*-butyltin(IV) bromide ($n\text{Bu}_3\text{SnBr}$), tri-*n*-butyltin(IV) acetate ($n\text{Bu}_3\text{SnOAc}$), and tri-*n*-butyltin(IV) thioacetate ($n\text{Bu}_3\text{SnSAc}$) in the bulk and solution polymerization of ϵ -CL. The kinetics result showed that the reactivity of $n\text{Bu}_3\text{SnOMe}$ in the solvent-free ROP of ϵ -CL at 100 °C was higher than $n\text{Bu}_3\text{SnCl}$, $n\text{Bu}_3\text{SnOAc}$, and $n\text{Bu}_3\text{SnSAc}$. From the bulk polymerization of ϵ -CL at 100 °C for 24 h and 100 h, those initiators could produce PCL with molecular weight lower than 2.6×10^4 g/mol. The ROP of ϵ -CL in toluene in the presence of di-*n*-butyltin(IV) dichloride ($n\text{Bu}_2\text{SnCl}_2$) and *n*-propanol ($n\text{PrOH}$) was studied by Deshayes et al. [21]. From a mechanistic study, $n\text{Bu}_2\text{SnCl}_2$ acted as catalysts and $n\text{PrOH}$ was the initiator. The results showed that this initiating system produced a low molecular weight PCL. Limwanich et al. [22] reported the steric interference from the *n*-butyl group ($n\text{Bu}$) around the tin active center of different tin chlorides on their reactivity in solvent-free ROP of ϵ -CL. The higher number of the $n\text{Bu}$ group in the tin chlorides, the lower polymerization rate was obtained. From non-isothermal kinetics results, the reactivity of $\text{SnCl}_2 > n\text{Bu}_2\text{SnCl}_2 > n\text{Bu}_3\text{SnCl}$. From the synthesis of PCL via solvent-free polymerization, PCL could not be obtained by using the slow $n\text{Bu}_3\text{SnCl}$ initiator. Moreover, the highly reactive SnCl_2 produced PCL with a very high number average molecular weight ($M_n = 1.1 \times 10^5$ g/mol) in a short synthesis time of 2 h at 150 °C without utilizing a solvent. Recently, the performance of SnCl_2 and zinc(II) chloride (ZnCl_2) in the solvent-free ROP of ϵ -CL was reported by Punyodom et al. [23]. From the differential scanning calorimetry (DSC) analysis, the activation energy (E_a) for the ROP of ϵ -CL initiated by SnCl_2 was lower than ZnCl_2 . Furthermore, the activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger) for the ROP of ϵ -CL initiated by SnCl_2 was also lower than ZnCl_2 . These indicated that the reactivity of SnCl_2 was higher than ZnCl_2 in the ROP of ϵ -CL under non-isothermal conditions. From PCL synthesis by solvent-free polymerization, ZnCl_2 produced a lower molecular weight of PCL than SnCl_2 at similar synthesis conditions. Interestingly, the molecular weight of PCL seemed to increase with increasing synthesis temperature when ZnCl_2 was used as an initiator for the ROP of ϵ -CL.

From these, it has been revealed that the understanding of the initiator's performance in the ROP of ϵ -CL is still important for the production of PCL. In this work, metal chlorides with various metal counterparts such as Mg(II), Sn(II), Zn(II), Al(III), and Sn(IV) will be utilized as the initiator for the solvent-free ROP of ϵ -CL. Their reactivity will be powerfully compared by using the DSC technique. After understanding the reactivity of metal chlorides, their effectiveness in the synthesis of PCL will be investigated and compared by solvent-free polymerization. The synthesized PCLs are characterized by the methods of gel permeation chromatography (GPC), proton-nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), and Fourier-transform infrared spectroscopy (FT-IR). Furthermore, the polymerization mechanism of ϵ -CL with those metal chlorides will also be studied and described.

Experimental

Chemicals and monomer preparation

Magnesium(II) chloride (MgCl_2 , Sigma, 95.0%), anhydrous tin(II) chloride (SnCl_2 , Sigma, 95.0%), zinc(II) chloride (ZnCl_2 , Sigma, 97.0%), aluminum(III) chloride (AlCl_3 , Sigma, 95.0%), tri-*n*-butyltin(IV) chloride ($n\text{Bu}_3\text{SnCl}$, Sigma-Aldrich, 95.0%), di-*n*-butyltin(IV) dichloride ($n\text{Bu}_2\text{SnCl}_2$, Sigma-Aldrich, 96.0%), *n*-butyltin(IV) trichloride ($n\text{BuSnCl}_3$, Sigma-Aldrich, 97.0%), methanol (MeOH, Qrec, 99.0%), and chloroform (CH_3Cl , LabScan, 99.5%) were used as received. ϵ -Caprolactone (ϵ -CL, Sigma, 97.0%) with pale-yellow color was purified by vacuum distillation at 60 °C. The colorless liquid of purified ϵ -CL was carefully kept in a round bottom flask under vacuum conditions before being used.

Comparison of the reactivity of metal chlorides in the ROP of ϵ -CL by using differential scanning calorimetry

The polymerization mixture was prepared by mixing the purified ϵ -CL (2 g) with 1.0 mol% of metal chlorides initiator in a dry 10 mL round bottom flask. The reaction mixture was then stirred by using a magnetic stirrer until a homogeneous mixture was obtained. The sample mass of 7–8 mg was placed into an aluminum pan and sealed. The sample was heated from 20 to 260 °C at a heating rate of 5 °C/min without sample mass loss by using a Mettler Toledo DSC3+ under a flowing atmosphere of N_2 at 20 mL/min. The obtained polymerization exotherms were used for comparing the reactivity of metal chlorides in the ROP of ϵ -CL. After completing first heating, the sample was quenched to 20 °C and then reheated to 80 °C at a heating rate of 10 °C/min to confirm the formation of PCL after complete dynamic DSC heating [23, 24].

Polymer synthesis via solvent-free polymerization using metal chlorides as initiator and polymer characterization

The reaction mixture between purified ϵ -CL (4 g) and various concentrations of AlCl_3 , MgCl_2 , SnCl_2 , ZnCl_2 , $n\text{Bu}_3\text{SnCl}_2$, $n\text{Bu}_2\text{SnCl}_2$, and $n\text{BuSnCl}_3$ was carefully weighed and prepared in dry 10 mL round bottom flask with a magnetic bar. All reaction flasks were then closed by a glass stopcock with a ground joint (B13/24) and the pressure in the flask was reduced by a vacuum pump for 5 min. These flasks were refilled with the high-purity N_2 gas and the polymerization was conducted under N_2 atmosphere. After that, the prepared flasks were further immersed into the preheated silicone oil bath at a synthesis temperature of 150 °C for 24 and 48 h similar to the literature [23–25]. When the polymerization reached the designed reaction time, the flasks were taken out from the oil bath, left at room temperature, cooled down by an ice bath, and kept in the refrigerator. All synthesized PCLs were

purified by dissolving them in CHCl_3 and precipitating them in the cold MeOH. The white solids of PCLs were filtered by vacuum filtration and dried in the hot air oven at $45\text{ }^\circ\text{C}$ until their constant weight [23–25].

For the characterization of the obtained PCLs, the chemical structure of PCL was identified by the 400 MHz proton-nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) on a Bruker Avance-400 NMR spectrometer (using CDCl_3 and TMS as a solvent and internal standard). The functional groups of PCL were also identified by the Fourier transform infrared spectroscopy (FT-IR) on a Shimadzu Tracer-800 FT-IR using the KBr disc technique. The FT-IR spectrum was recorded from 400 to 4000 cm^{-1} at $4\text{ cm}^{-1}/\text{min}$ and calibrated with polyethylene (PE) film. The gel permeation chromatography (GPC) was performed by a Waters 2414 refractive index (RI) detector equipped with Styragel HR5E $7.8 \times 300\text{ mm}$ column. The polymer sample was eluted with tetrahydrofuran (THF) at $40\text{ }^\circ\text{C}$ with a flowing rate of $1.0\text{ mL}/\text{min}$. Polystyrene (PS) was used as a calibration standard with a molecular weight resolving range of $2 \times 10^3 - 4 \times 10^6\text{ g}/\text{mol}$.

Results and discussion

Comparison for the reactivity of metal chlorides in the ROP of $\epsilon\text{-CL}$ by using differential scanning calorimetry

As mentioned in the literature [14–16, 22–24], the non-isothermal DSC can be considered as a powerful and fast technique for comparing the reactivity of initiators in the solvent-free ROP of cyclic esters. In the dynamic DSC measurement, positions of the polymerization exotherms from the ROP of $\epsilon\text{-CL}$ relate to the effectiveness and reactivity of initiators [15, 22, 23]. In the case of the highly reactive initiator, polymerization exotherms for the ROP of $\epsilon\text{-CL}$ will occur at a lower temperature range than the slow initiator. Moreover, the high steric hindrance initiator will give the polymerization exotherms for the ROP of $\epsilon\text{-CL}$ at a higher temperature range in the DSC curve. Therefore, it is possible and convenient to compare the reactivity of different metal chlorides initiator in the solvent-free ROP of $\epsilon\text{-CL}$ by utilizing the non-isothermal DSC technique. The polymerization exotherms obtained from the ROP of $\epsilon\text{-CL}$ initiated by 1.0 mol% of all metal chlorides at a slow heating rate of $5\text{ }^\circ\text{C}/\text{min}$ are illustrated in Fig. 1. From Fig. 1, it is found that the exotherm obtained from the AlCl_3 initiator occurred at a lower temperature range than SnCl_2 , ZnCl_2 , $n\text{BuSnCl}_3$, $n\text{Bu}_2\text{SnCl}_2$, and $n\text{Bu}_3\text{SnCl}$. In the case of MgCl_2 , the polymerization exotherm is not shown because it is partially soluble in $\epsilon\text{-CL}$ resulting in a heterogeneous mixture that is not suitable for DSC kinetics analysis.

When the polymerization exotherms are obtained, the conversion of monomer (α) is determined by dividing the released heat at the arbitrary time by the heat of polymerization ($\alpha = \Delta H_t / \Delta H_p$) [14, 26, 27]. At 50% of monomer conversion, the half-life ($t_{1/2}$) of polymerization can be determined. Plots of α against temperature and the values of $t_{1/2}$ for the ROP of $\epsilon\text{-CL}$ with each initiating system at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ are depicted in Fig. 2.

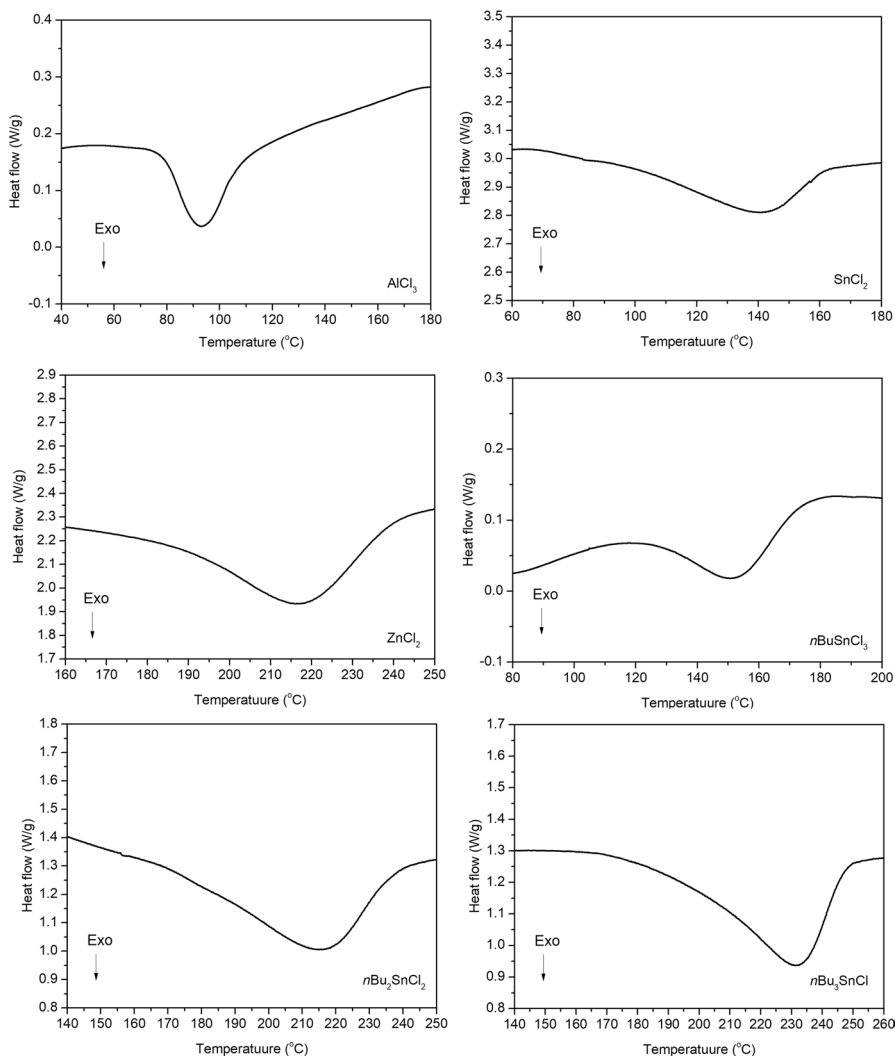


Fig. 1 The non-isothermal DSC curves for the ROP of ϵ -CL initiated by 1.0 mol% of different metal chlorides at a heating rate of 5 °C/min

From Fig. 2, the α value for the ROP of ϵ -CL with AlCl_3 approaches 1 faster than other metal chlorides with the lowest $t_{1/2}$ value. After complete heating of the polymerization mixture by DSC, the obtained crude PCL is characterized by performing the DSC 2nd heating in which the sample is heated from 20 to 80 °C at a heating rate of 10 °C/min, and the 2nd heating curves are displayed in Fig. 3.

Fig. 3 shows the crystalline melting temperatures (T_m) of PCL around 40 to 63 °C which are close to the value of PCL reported in the literature [28]. The double melting peaks in T_m of PCL relate to the difference in crystal sizes. The first melting peak is observed at a lower temperature range corresponding to the smaller PCL crystal. The

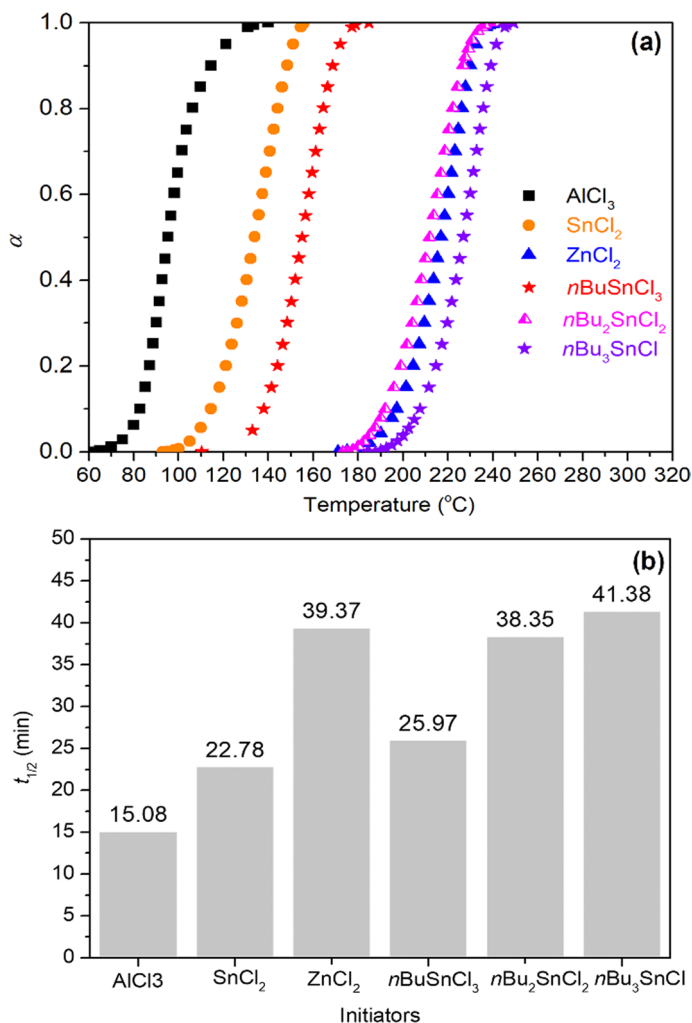


Fig. 2 a Plots of α vs temperature and b half-life for the ROP of ϵ -CL initiated by 1.0 mol% of different metal chlorides at a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$

second melting peak observed at a higher temperature range relates to the larger PCL crystal [28]. From these, it is strongly confirmed that PCL was synthesized from the dynamic DSC heating of ϵ -CL with metal chlorides initiator at a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$. According to the non-isothermal DSC polymerization, the reactivity of metal chlorides in the solvent-free ROP of ϵ -CL can be ordered as: $\text{AlCl}_3 > \text{SnCl}_2 > n\text{BuSnCl}_3 > n\text{Bu}_2\text{SnCl}_2 > \text{ZnCl}_2 > n\text{Bu}_3\text{SnCl}$. When comparing the AlCl_3 , SnCl_2 , and ZnCl_2 systems, the reactivity of AlCl_3 is higher than SnCl_2 , and ZnCl_2 . This relates to the stronger Lewis acidity of AlCl_3 than SnCl_2 , and ZnCl_2 . When comparing the reactivity of tin(II) and tin(IV) derivatives, SnCl_2 is more reactive than $n\text{BuSnCl}_3$, $n\text{Bu}_2\text{SnCl}_2$, and $n\text{Bu}_3\text{SnCl}$. This finding indicates that the presence of the $n\text{Bu}$ around the Sn-Cl

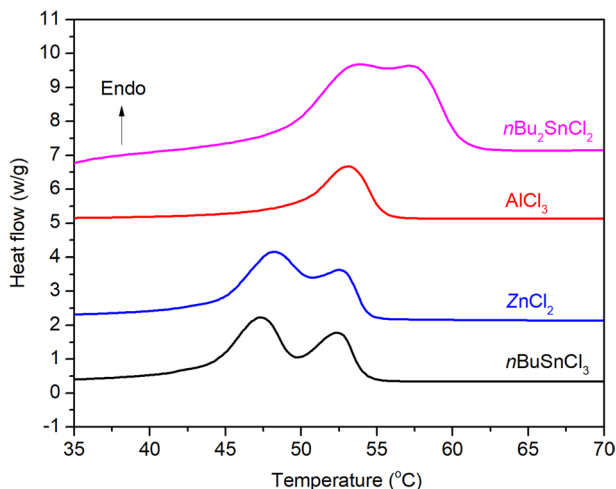


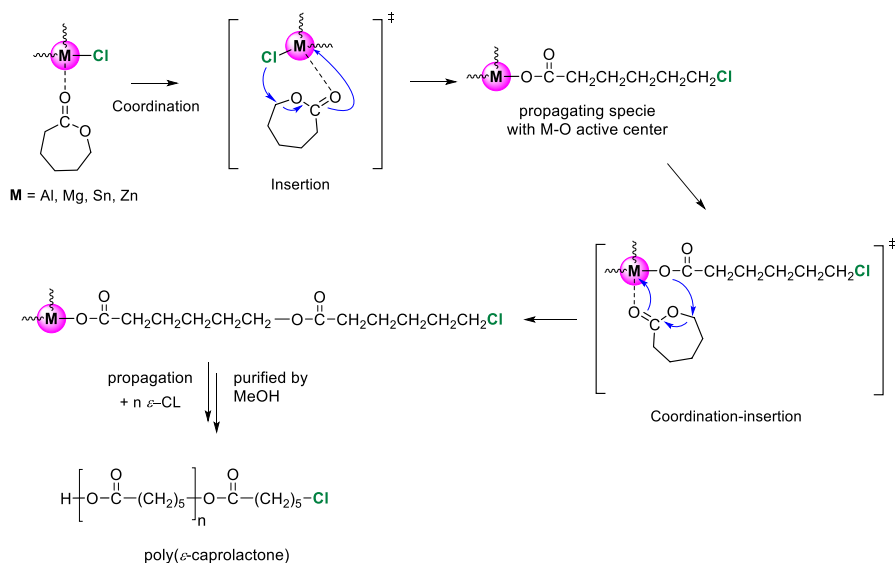
Fig. 3 DSC 2nd heating curves for the crude PCL synthesized from the non-isothermal ROP of ϵ -CL initiated by 1.0 mol% of AlCl_3 , ZnCl_2 , $n\text{Bu}_2\text{SnCl}_2$, and $n\text{BuSnCl}_3$ at a heating rate of 10 °C/min

active center causes steric hindrance in reacting with the ϵ -CL monomer. The higher number of $n\text{Bu}$ groups, the lower initiation rate of ϵ -CL is obtained. Furthermore, the number of chloride groups seems to affect the reactivity of metal chloride initiators. The higher number of chloride groups in metal chloride, the higher initiation rate of ϵ -CL is observed. This suggests that the Lewis acidity of metal chloride increases with increasing chloride groups resulting in the increment of its reactivity to react with ϵ -CL. However, a very fast initiating system does not ensure that the good property of the polymer can be obtained. This will be proved and described in the polymer synthesis part.

For the consideration of the polymerization mechanism, the data reported in the literature [29] is utilized to study the ROP mechanism of ϵ -CL with metal chlorides used in this work. The ROP of ϵ -CL with metal chlorides proceeds via the coordination-insertion mechanism as proposed in Scheme 1. For the initiation step, the metal chloride will coordinate with the carbonyl group of ϵ -CL. Then, the Cl atom attacks the alkyl-oxygen resulting in the breaking the alkyl-oxygen bond in ϵ -CL. The opened monomer ring will insert into the metal-chloride bond and change the reactive propagating specie that contains the metal-oxygen bond. When another ϵ -CL approaches this new active metal-oxygen bond, the growth of the PCL chain will occur through the same mechanism as the initiation step. At this stage, the insertion process occurs by the attacking of the O atom connected to the metal active center to the alkyl-oxygen bond of ϵ -CL. When ϵ -CL is completely consumed, the long PCL chain will be obtained.

PCL synthesis via the solvent-free polymerization of ϵ -CL using metal chlorides as initiator and polymer characterization

From in “Comparison for the reactivity of metal chlorides in the ROP of ϵ -CL by using differential scanning calorimetry” Section, the reactivity of all metal chlorides



Scheme 1 The proposed coordination-insertion mechanism for the solvent-free ROP of ϵ -CL with metal chlorides initiator

in the milligram-scale (7–8 mg) ROP of ϵ -CL under solvent-free and non-isothermal conditions is understood. In this part, the potential of all metal chlorides in the larger-scale (4 g) polymerization of ϵ -CL is investigated under the isothermal condition (150 °C). The PCLs synthesized from the ROP of ϵ -CL initiated by metal chlorides are firstly characterized by the GPC technique and the results are summarized in Tables 1 and 2.

From Table 1, the highly reactive AlCl_3 can produce PCL with the highest number average molecular weight (M_n) of 3.2×10^4 g/mol with dispersity (D) and %yield of 1.80 and 90%. The control of PCL molecular weight seems to be difficult because AlCl_3 may react with H_2O trace forming the aluminum hydroxide ($\text{Al}(\text{OH})_3$) that can interfere the polymerization. In the case of MgCl_2 , it can produce only the low molecular weight PCL at a long reaction time of 48 h. When MgCl_2 concentration is increased to 0.1000 mol%, it cannot completely dissolve in ϵ -CL which results in the uncontrollable of active species in the polymerization system. For the SnCl_2 system, SnCl_2 acts as a powerful initiator in the synthesis of PCL. As reported in our previous work, SnCl_2 could produce PCL with M_n of 1.1×10^5 g/mol in a short synthesis time of 2 h [22]. The increasing of synthesis time to 24 h seems to be not suitable for the reactive SnCl_2 initiator that causes the reduction of PCL molecular weight. ZnCl_2 , a slow initiator, produces low molecular weight PCL with M_n in the range of $1.2 \times 10^4 - 2.1 \times 10^4$ g/mol. Similar to SnCl_2 , the increasing synthesis time also causes the reduction of PCL molecular weight.

For tin(IV) derivatives (Table 2), the slow $n\text{Bu}_3\text{SnCl}$ initiator cannot produce PCL at 150 °C for 24 h. This means that the high concentration of $n\text{Bu}_3\text{SnCl}$ should be used in the synthesis of PCL via the solvent-free conditions and high molecular weight PCL seems to cannot be obtained from this slow $n\text{Bu}_3\text{SnCl}$ initiator. In

Table 1 GPC analysis for the purified PCLs obtained from the solvent-free ROP of ϵ -CL initiated by metal chlorides at 150 °C for different polymerization times

Entries	Initiators	Time (h)	$[I]_0^a$ (mol%)	M_n^b (g/mol)	M_w^b (g/mol)	\bar{D}^b	%Yield ^c (%)
1	AlCl ₃	24	0.0500	2.1×10^4	3.6×10^4	1.74	66
2	AlCl ₃	24	0.0750	2.3×10^4	4.3×10^4	1.88	74
3	AlCl ₃	24	0.1000	2.5×10^4	4.8×10^4	1.89	74
4	AlCl ₃	24	0.5000	1.5×10^4	2.8×10^4	1.90	63
5	AlCl ₃	48	0.0250	8.9×10^3	1.2×10^4	1.40	55
6	AlCl ₃	48	0.0500	3.2×10^4	5.7×10^4	1.80	90
7	AlCl ₃	48	0.1000	1.9×10^4	5.8×10^4	3.07	84
8	AlCl ₃	48	1.0000	8.7×10^3	1.6×10^4	1.79	55
9	MgCl ₂	48	0.0500	1.4×10^4	2.5×10^4	1.76	82
10	MgCl ₂	48	0.1000	1.2×10^4	2.0×10^4	1.65	75 ^f
11	SnCl ₂ ^d	2	0.0100	1.1×10^5	1.8×10^5	1.71	58
12	SnCl ₂ ^d	24	0.0500	2.3×10^4	4.1×10^4	1.80	90
13	ZnCl ₂ ^e	24	0.0500	1.6×10^4	2.3×10^4	1.45	72
14	ZnCl ₂ ^e	24	0.1000	2.1×10^4	3.9×10^4	1.85	89
15	ZnCl ₂	48	0.0250	1.2×10^4	2.0×10^4	1.73	77
16	ZnCl ₂	48	0.1000	2.0×10^4	3.6×10^4	1.85	84
17	ZnCl ₂	48	0.2000	1.3×10^4	2.4×10^4	1.81	81

^aThe initial concentration of metal chlorides

^bThe values obtained from the GPC technique: measurement temperature of 40 °C using THF and PS as eluent and standard

^cDetermined by the mass ratio between the purified PCL and the initial ϵ -CL monomer

^{d,e}The values reported in references number [22] and [23]

^fMgCl₂ initiator cannot be completely soluble in ϵ -CL monomer

the case of $n\text{Bu}_2\text{SnCl}_2$, it is more reactive than $n\text{Bu}_3\text{SnCl}$ and can produce high molecular weight PCL with M_n , \bar{D} , and %yield of 5.6×10^4 g/mol, 1.51, and 83%. The molecular weight of PCL seems to decrease with increasing $n\text{Bu}_2\text{SnCl}_2$ concentration. For the reactive $n\text{BuSnCl}_3$ system, the molecular weight of PCL increases with decreasing $n\text{BuSnCl}_3$ concentration at a synthesis time of 24 h. The highest weight average molecular weight ($M_w = 6.2 \times 10^4$ g/mol) of PCL is obtained at low concentration of $n\text{BuSnCl}_3$ (0.0100 mol%). Interestingly, the high %yields (90–93%) of PCL are obtained from this effective $n\text{BuSnCl}_3$ initiator. When the synthesis time is increased to 48 h, it is found that the low molecular weight PCL is obtained. At 150 °C and 24 h, the molecular weight of PCL obtained from $n\text{Bu}_2\text{SnCl}_2$ is higher than $n\text{BuSnCl}_3$ and $n\text{Bu}_3\text{SnCl}$. From these, it is important to note that a suitable synthesis condition is necessary for each initiating system. The fast or slow initiators can produce a polymer with the desired property under their suitable synthesis conditions.

From the GPC analysis shown in Tables 1 and 2, examples of the physical appearance of the synthesized PCLs are displayed in Figs. S1–S3. From Fig. S1, the crude

Table 2 GPC analysis for the purified PCLs obtained from the solvent-free ROP of ϵ -CL initiated by tin(IV) derivatives at 150 °C for different polymerization times

Entries	Initiator	Time (h)	$[I]_0^a$ (mol%)	M_n^b (g/mol)	M_w^b (g/mol)	\bar{D}^b	%Yield ^c (%)
18	<i>n</i> Bu ₃ SnCl ^d	24	0.0100	n.d	n.d	n.d ^e	n.d
19	<i>n</i> Bu ₃ SnCl ^d	24	0.1000	n.d	n.d	n.d	n.d
20	<i>n</i> Bu ₂ SnCl ₂ ^d	2	0.0100	n.d	n.d	n.d	n.d
21	<i>n</i> Bu ₂ SnCl ₂ ^d	2	0.1000	n.d	n.d	n.d	n.d
22	<i>n</i> Bu ₂ SnCl ₂ ^d	24	0.0100	5.6×10^4	8.6×10^4	1.51	83
23	<i>n</i> Bu ₂ SnCl ₂ ^d	24	0.1000	3.7×10^4	5.8×10^4	1.57	82
24	<i>n</i> BuSnCl ₃	24	0.0050	3.2×10^4	5.6×10^4	1.77	93
25	<i>n</i> BuSnCl ₃	24	0.0100	3.6×10^4	6.2×10^4	1.71	92
26	<i>n</i> BuSnCl ₃	24	0.0250	3.3×10^4	5.9×10^4	1.79	92
27	<i>n</i> BuSnCl ₃	24	0.1000	2.3×10^4	4.4×10^4	1.91	90
28	<i>n</i> BuSnCl ₃	48	0.0050	8.5×10^3	1.1×10^4	1.27	25
29	<i>n</i> BuSnCl ₃	48	0.0100	1.6×10^4	2.5×10^4	1.58	66
30	<i>n</i> BuSnCl ₃	48	0.0250	2.2×10^4	4.5×10^4	2.01	89

^aThe initial concentration of metal chlorides

^bThe values obtained from the GPC technique: measurement temperature of 4035 °C using THF and PS as eluent and standard

^cDetermined by the mass ratio between the purified PCL and the initial ϵ -CL monomer

^dThe values reported in reference number[22]

^en.d. refers to “cannot be determined”

PCLs obtained from the ROP of ϵ -CL initiated by AlCl₃ are pale yellow solid. After purification, the purified PCLs are in the form of white powder. From Fig. S2, the crude and purified PCLs obtained from the ROP of ϵ -CL initiated by *n*BuSnCl₃ are white solid and white fiber. This confirms that *n*BuSnCl₃ produces a higher molecular weight of PCL than AlCl₃ under a similar synthesis condition. From Fig. S3, the MgCl₂ and ZnCl₂ initiators produce low molecular weight PCL which is observed in the white powder form. From this point, it is found that the physical appearance of the synthesized PCLs depends strongly on their molecular weight similar to the literature [22, 23]. From the obtained results, the chemical structure of PCL is further investigated by the ¹H-NMR technique. Examples of 400 MHz ¹H-NMR spectra of the synthesized PCL are illustrated in Fig. 4.

It is important that all spectra show similar signals such as: (i) the triplet signal of CH₂ next to the carbonyl oxygen of PCL chain is found at a chemical shift (δ) of 4.10 ppm (f), (ii) the triplet signal of CH₂ closes to the hydroxyl or chloride end groups at δ of 3.67 ppm (a), (iii) the triplet signal from CH₂ connected to the carbonyl carbon of PCL chain at 2.30 ppm (e, j), and (iv) the multiplet signal of CH₂ groups presented in the PCL chain around 1.30–1.60 ppm (b,c,d,g,h,i).

To support the ¹H-NMR analysis, the functional groups presented in the synthesized PCLs are investigated by the FT-IR technique. Examples of FT-IR spectra of the synthesized PCLs by different metal chlorides are depicted in Fig. 5. From Fig. 5, it is important that the spectra show the similar FT-IR peaks that consist of: (i) the

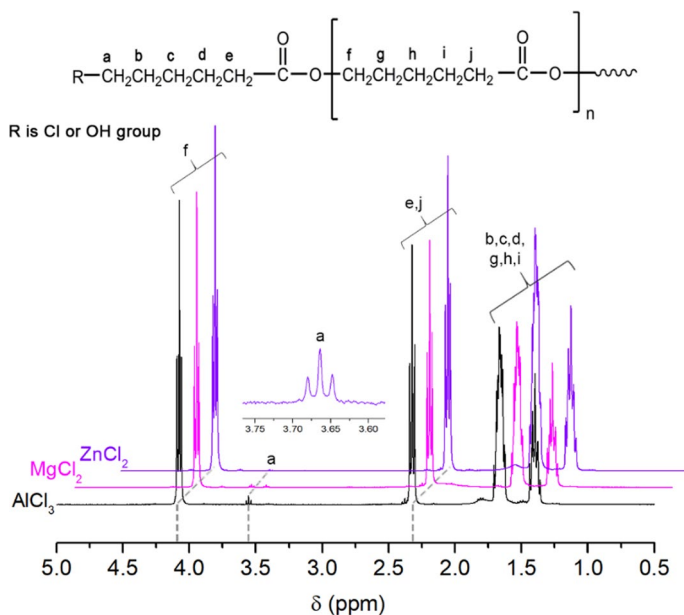


Fig. 4 400 MHz $^1\text{H-NMR}$ spectra of the synthesized PCLs obtained from the ROP of $\epsilon\text{-CL}$ initiated by AlCl_3 (entry 8), MgCl_2 (entry 10), and ZnCl_2 (entry 13) at $150\text{ }^\circ\text{C}$ for 48 h

$-\text{OH}$ stretching of the PCL end group at $3600\text{--}3700\text{ cm}^{-1}$, (ii) the $-\text{CH}_2$ stretching around $2800\text{--}2900\text{ cm}^{-1}$, (iii) the $\text{C}=\text{O}$ stretching from ester group at 1750 cm^{-1} , (iv) the $-\text{CH}_2$ bending at 1450 cm^{-1} , and (v) the $\text{C}-\text{O}$ stretching at $1100\text{--}1200\text{ cm}^{-1}$, and the characteristic peak of $\text{C}-\text{Cl}$ stretching at 730 cm^{-1} . The obtained wavenumbers in FT-IR spectra are close to values reported elsewhere [30–32].

Conclusions

A comparative study on the reactivity of metal chlorides in the solvent-free ROP of $\epsilon\text{-CL}$ was successfully investigated. From the non-isothermal DSC measurements, the Lewis acidity and steric hindrance around the active center played an important role in the reactivity of metal chlorides in the solvent-free ROP of $\epsilon\text{-CL}$. From the values of α and $t_{1/2}$, the reactivity of AlCl_3 was higher than SnCl_2 , $n\text{BuSnCl}_3$, $n\text{Bu}_2\text{SnCl}_2$, ZnCl_2 , and $n\text{Bu}_3\text{SnCl}$. The mechanism of the solvent-free ROP of $\epsilon\text{-CL}$ with those metal chlorides was proposed through the coordination-insertion mechanism. This mechanism involved the coordination and insertion of monomer with reactive metal-chloride bond to form the new reactive metal–oxygen bond in the propagating specie. The efficiency of all metal chlorides in the larger-scale (4 g) synthesis of PCL was tested and compared via solvent-free polymerization. AlCl_3 acted as a very fast initiator and the control of polymerization seemed to be difficult. The fast SnCl_2 initiator could produce the highest M_n of PCL ($1.1 \times 10^5\text{ g/mol}$) in a short time at $150\text{ }^\circ\text{C}$. The MgCl_2 was not suitable for the ROP of $\epsilon\text{-CL}$ due to its low solubility

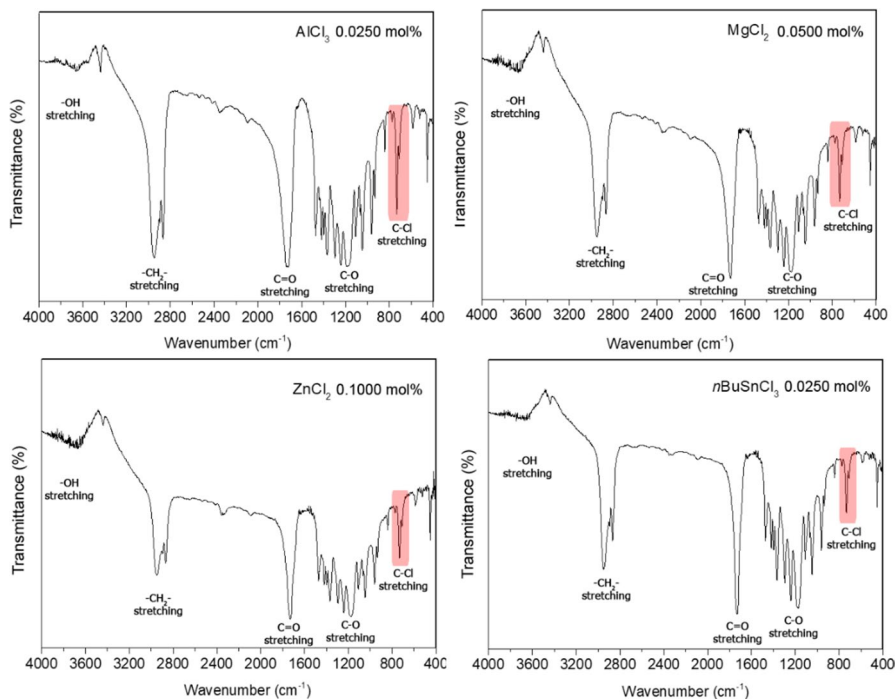


Fig. 5 FT-IR spectra (KBr disc) of the synthesized PCLs obtained from the ROP of ϵ -CL initiated by AlCl_3 (entry 5), MgCl_2 (entry 9), ZnCl_2 (entry 16), and $n\text{BuSnCl}_3$ (entry 30) at 150 °C for 48 h

in the monomer. The $n\text{Bu}_3\text{SnCl}$ could not produce PCL under the condition used in this work. For the series of tin(IV) derivatives, the highest M_n (5.6×10^4 g/mol) of PCL was obtained by using 0.0100 mol% of the $n\text{Bu}_2\text{SnCl}_2$. However, $n\text{BuSnCl}_3$ could produce PCL with M_n in the range of 2.3×10^4 – 3.6×10^4 g/mol with a high %yields of 90–93%. Importantly, the higher amount of Cl groups around the metal active center increased the reactivity of metal chloride in the ROP of ϵ -CL. The long synthesis time at high temperatures was not suitable for all metal chlorides used in this work as confirmed by the decreasing of PCL molecular weight. This may be attributed to the increase of unwanted side reactions. The development of these metal chlorides initiator in the ROP of cyclic esters is still working in our laboratory and will be reported soon.

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