**ORIGINAL PAPER**

# The role of tri-*n*-butyltin(IV) *n*-butoxide/aluminum(III) tri-*s*-butoxide mixed initiators in the non-isothermal ring-opening polymerization of *ε*-caprolactone: from small-scale to larger-scale polymerization

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## Abstract

The solvent-free ring-opening polymerization (ROP) of *ε*-caprolactone (*ε*-CL) with the tri-*n*-butyltin(IV) *n*-butoxide/aluminum(III) tri-*s*-butoxide mixed initiators [$n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$] was successfully studied by the non-isothermal differential scanning calorimetry for the first time. The $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators were completely dissolved in *ε*-CL and could be utilized to produce high molecular weight poly(*ε*-caprolactone) (PCL). The presence of the Al(O$s$Bu)$_3$ in the mixed initiators did not interfere with the initiation temperature and could increase the propagation rate of *ε*-CL. The activation energies ($E_a$) obtained from the peak methods of Kissinger and Ozawa for the ROP of *ε*-CL initiated by the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:2.0 mol%) (74.2–78.6 kJ/mol) were lower than $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:1.0 mol%) (75.8–80.3 kJ/mol) and the single $n$Bu$_3$SnO$n$Bu initiator (78.3–82.8 kJ/mol), respectively. From the proton-nuclear magnetic resonance spectroscopy ($^1$H-NMR), the polymerization mechanism was proposed through the classic coordination–insertion mechanism that comprised: (i) the coordination of *ε*-CL and $n$Bu$_3$SnO$n$Bu with Al(O$s$Bu)$_3$ and (ii) the nucleophilic attacked of *n*-butoxy group (–O$n$Bu) from $n$Bu$_3$SnO$n$Bu to the carbonyl carbon of *ε*-CL. From the small-scale synthesis (4 g) of PCL, our $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators could control the polymerization of *ε*-CL by adjusting the concentration of Al(O$s$Bu)$_3$. The number and weight average molecular weights ($M_n$ and $M_w$) of PCL increased with decreasing concentration of mixed initiator. The $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators produced PCL with $M_n$, $M_w$, dispersity (*Đ*), and %yield in the range of $1.3 \times 10^4$–$4.0 \times 10^4$ g/mol, $2.9 \times 10^4$–$6.5 \times 10^4$ g/mol, 1.65–2.26 and 50–95%, respectively. The larger-scale polymerization (250 g) of *ε*-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators was preliminary conducted at 150 °C for 48 h. PCL with higher $M_n$ ($7.3 \times 10^4$ g/mol) and $M_w$ ($1.2 \times 10^5$ g/mol) was synthesized. The $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators acted as an effective candidate for the production of the high molecular weight PCL via solvent-free polymerization.

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## Graphical abstract
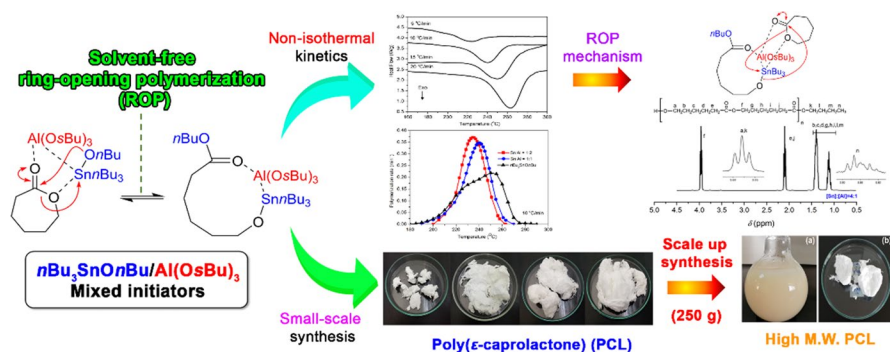
## Introduction

In present days, effective initiating systems or catalysts are considered as an important factor to achieve the controlled synthesis of biodegradable polyesters such as polylactides, polylactones, and copolyesters [1–3]. These polymers are recently utilized in a wide range of applications such as packaging, electronic, agricultural, automotive, and biomedical materials due to their various physical, chemical, biological, and mechanical properties [4–6]. Recently, biodegradable polyesters with good properties can be effectively prepared via the ring-opening polymerization (ROP) of cyclic esters. For better control of this reaction, many metal-containing initiators/catalysts have been developed and utilized under solvent-free or solution polymerization [7–9]. The organometallic initiators are powerful in the synthesis of biodegradable polyesters and can be divided into various types such as metal carboxylate (MCOOR) [10–12], metal alkoxides (MOR) [3, 7, 9], and metal halides (MX) [13–15]. Among these, tin-containing compounds impact our attention due to: (i) high reactivity, (ii) high polymer productivity, (iii) good control of ROP, and (iv) high molecular weight of the polymer can be obtained.

Interestingly, most of the experimental and theoretical works mainly focused on the ROP of cyclic esters with the single metal-containing initiator as described in the following. Recently, Kricheldorf and Weidner [11] reported on the ROP of L-lactide (LL) and $\varepsilon$-caprolactone ($\varepsilon$-CL) initiated by tin(II) acetate (SnAc$_2$), tin(IV) acetate (SnAc$_4$), di-$n$-butyltin(IV)-bis-acetate ($n$Bu$_2$SnAc$_2$) and di-$n$-octyltin(IV)-bis-acetate (Oct$_2$SnAc$_2$). They found that the SnAc$_2$ could produce a wide range of weight average molecular weight ($M_w$) for cyclic poly(L-lactide) (PLL) ($M_w$ of $2.0 \times 10^4$–$2.5 \times 10^5$ g/mol). Moreover, the polymer synthesized from SnAc$_2$ initiator contained one carboxyl and one acetyl end group that has not been found before in the one-step polymerization. Our previous work has focused on the behavior of

tin chloride initiators such as tin(II) chloride (SnCl$_2$), di-$n$-butyltin(IV) chloride ($n$Bu$_2$SnCl$_2$), and tri-$n$-butyltin(IV) chloride ($n$Bu$_3$SnCl) in the solvent-free ROP of $\varepsilon$-CL [15]. From a kinetics study by non-isothermal differential scanning calorimetry (DSC), the reactivity of SnCl$_2$ was higher than $n$Bu$_2$SnCl$_2$ and $n$Bu$_3$SnCl, respectively. From small-scale synthesis, it was found that the SnCl$_2$ initiator could produce high molecular weight poly($\varepsilon$-caprolactone) (PCL) in a short time. Phetsuk et al. [4] showed the performance of liquid tin(II) $n$-butoxide [Sn(O$n$Bu)$_2$] in the synthesis of poly(L-lactide-$co$-$\varepsilon$-caprolactone) (PLC) via solvent-free polymerization. They found that the Sn(O$n$Bu)$_2$ produced statistical PLC copolymer from the one-step polymerization and PLC block copolymer from the two-step polymerization. The synthesized Sn(O$n$Bu)$_2$ initiator could produce a high molecular weight PLC with the number average molecular weight ($M_n$) of $7.59 \times 10^4$–$2.08 \times 10^5$ g/mol.

From these, few works have reported polymer synthesis by using the combination of different metal-containing compounds via the ROP method. Silvino et al. [16] used the mixed magnesium(II) and titanium(IV) alkoxide (Catylen S200) initiators in the preparation of PLL/poly(D-lactide) (PDL) stereocomplex. They found that the Catylen S200 initiator could produce PLL/PDL stereocomplex with a crystalline melting temperature ($T_m$) up to 250.1 °C. The Catylen S200 acted as a high-efficiency initiator in the ROP of LL and D-lactide (DL) in toluene at 70 °C. This initiator could produce a polymer with $M_n$ in the range of $8.30 \times 10^3$–$5.05 \times 10^4$ g/mol. Moreover, Catylen S200 can be considered as a potential initiator for producing the biomedical polymer. Silvino et al. [17] also reported the utilization of the Catylen S200 initiator in the copolymerization of LL with trimethylene carbonate (TMC). From their results, this Catylen S200 initiator could produce low molecular weight PLL and poly(trimethylene carbonate) (TMC) with $M_n$ of $4.7 \times 10^3$–$8.4 \times 10^3$ g/mol. They also synthesized poly(L-lactide-$co$-trimethylene carbonate) (PLTMC) at different monomer feed ratios of LL to TMC of 50:50, 70:30, and 90:10. The lactidyl block length seemed to be higher than the theoretical length. The presence of more TMC in copolymer increased the amount of intermolecular transesterification. Wanna et al. [18] reported the utilization of aluminum (Al) and calcium (Ca)-incorporated MCM-41-type silica to support titanium(IV) $i$-propoxide [Ti(O$i$Pr)$_4$] in the ROP of LL and $\varepsilon$-CL under solvent-free polymerization. They found that the incorporation of Al and Ca into silica could increase the molecular weight of the polymer but decrease the polymerization rate. The prepared heterogeneous initiating systems seemed to be more effective than the homogeneous Ti(O$i$Pr)$_4$ as indicated by the higher molecular weight of the obtained polymers. They found that the more acidic Al-MCM-41 acted as a better supporter for Ti(O$i$Pr)$_4$ than the more basic Ca-MCM-41.

From literature survey, it is important that the full kinetics of the ROP of cyclic esters with the mixed metal-containing initiating systems has not been studied and investigated before. The kinetics information is valuable and necessary to understand the behavior of mixed initiators/catalysts in the ROP of cyclic esters. The obtained kinetics data can be used to predict and design the effective synthesis process for high molecular weight biodegradable polymers by using mixed initiators. Furthermore, there are lots of metal-containing initiators that have been developed for controlling the ROP of cyclic esters. Therefore, the mixing of two or more

metal-containing initiators can be an effective route for preparing and synthesizing well-defined biodegradable polyesters with the control of molecular weight. This idea can impact the attention of researchers to develop new mixed metal-containing initiators with high performance in the synthesis of biodegradable polyesters in the future.

The goal of this present work is to firstly investigate the performance of the tri-*n*-butyltin(IV) *n*-butoxide/aluminum(III) tri-*s*-butoxide mixed initiators [$n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$] in the ROP of $\varepsilon$-CL under solvent-free conditions. The control ROP of $\varepsilon$-CL by the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is also analyzed by the non-isothermal DSC technique. The coordination–insertion mechanism for the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is also described by using the proton-nuclear magnetic resonance spectroscopy ($^1$H-NMR) technique. The effect of the Al(O$s$Bu)$_3$ content in the mixed initiators on the small-scale synthesis of PCL is clarified via solvent-free polymerization at different temperatures and times. The controllability of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators in the ROP of $\varepsilon$-CL is studied and discussed. By using the results obtained from small-scale synthesis, the larger-scale ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is preliminarily studied and designed to test the effectiveness of these mixed initiators in the scale-up of the synthesis of PCL. The results from this work can be used as the template for designing other mix-metal-containing initiators or cyclic esters. Furthermore, the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators will be applied to the larger-scale synthesis of other biodegradable polyesters in our laboratory that will be reported and described soon.

## Experimental

### Materials preparation

$\varepsilon$-Caprolactone ($\varepsilon$-CL) (Sigma-Aldrich, 97.0%) was dried with calcium hydride (CaH$_2$), purified by vacuum distillation using a high vacuum pump, and kept in 250 mL round bottom flask under vacuum condition before being used. Tri-*n*-butyltin(IV) *n*-butoxide ($n$Bu$_3$SnO$n$Bu) was synthesized and purified by the method reported in our previous work [9]. Aluminum tri-*s*-butoxide (Al(O$s$Bu)$_3$) (Sigma-Aldrich, 97.0%), chloroform (LabScan (AR), 99.5%), methanol (Qrec, 99.0%), and chloroform-*d* (Sigma-Aldrich, 99.8%) were used as received.

### Kinetics study by the non-isothermal DSC technique

The polymerization mixture of purified $\varepsilon$-CL (2 g) with the mixture of 1.0/1.0 mol% of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1:1) and 1.0/2.0 mol% of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1:2) was prepared in the dried vial and stirred for 5 min. After obtaining the homogeneous polymerization mixture, the samples of 7 mg were carefully weighed into an aluminum pan and sealed with an aluminum cover. The polymerization kinetics of $\varepsilon$-CL with those initiating systems was investigated by the non-isothermal DSC

experiments using the Perkin-Elmer DSC-7. The samples were heated from 20 to 300 °C at the heating rates of 5, 10, 15, and 20 °C/min without sample mass loss and the data was analyzed by the Pyris DSC-7 program [9]. The obtained crude poly($\varepsilon$-caprolactone) (PCL) from the non-isothermal DSC polymerization was used to investigate the polymerization mechanism by using the [1] H-NMR technique on a Bruker Avance 400 NMR Spectrometer with $CDCl_3$ solvent.

## Synthesis of poly($\varepsilon$-caprolactone) using the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators via solvent-free polymerization

For small-scale synthesis (4 g), the mixture of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ at the different molar ratios of 4:1, 2:1, 1:1, 1:2, or 1:4 by mol with initial $n$Bu$_3$SnO$n$Bu concentration ([$n$Bu$_3$SnO$n$Bu]$_0$) of 0.125 mol% was firstly weighed into dried round 10 mL round bottom flask. Then, 4 g of the purified $\varepsilon$-CL was introduced into these prepared flasks under $N_2$ atmosphere in the controlled atmosphere glove box (LABCONCO). The flasks were immersed into the pre-heated silicone oil bath at the temperature of 120 °C for 72 h and 150 °C for 24 h. After complete polymerization, the crude PCLs were purified by dissolving in chloroform and precipitated in cold methanol. The obtained white solid polymers were dried at 45 °C under vacuum conditions until constant weight is achieved. The molecular weights average and dispersity (Đ) of all synthesized PCLs were determined from the gel permeation chromatography (GPC) on a Waters 2414 refractive index (RI) detector equipped with Styragel HR5E 7.8×300 mm column (molecular weight resolving range = 2000–4,000,000). Tetrahydrofuran (THF) was used as eluent with a flow rate of 1.0 mL/min at 40 °C and calibrated with polystyrene standards. After obtaining knowledge about the performance of the mixed initiators in the synthesis of PCL, the initial $n$Bu$_3$SnO$n$Bu concentration was reduced to 0.0625 mol% to test the effectiveness of mixed initiators in the synthesis of the higher molecular weight PCL. The molar ratios of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ were similar to the previous part. The ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators ([$n$Bu$_3$SnO$n$Bu]$_0$) of 0.0625 mol%) was conducted at 150 °C for 24 h. The obtained PCLs were characterized that similar to the method described earlier.

For larger-scale synthesis (250 g), the condition used in this part was predicted and modified from the best synthesis condition obtained from the small-scale polymerization. Similar to the small-scaled synthesis, the mixture of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ at the molar ratio of $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ at 4:1 ([$n$Bu$_3$SnO$n$Bu]$_0$ of 0.0625 and 0.0156 mol%) was prepared in the dry 250 mL round bottom flask. Then, 250 g of $\varepsilon$-CL was weighed into this flask and the flask was closed with a stopcock for desiccator. After that, the pressure of the flask was reduced for 10 min at room temperature by using a vacuum pump and refilled with $N_2$ gas. The prepared flask was immersed into a pre-heated silicone oil bath in 1000 mL beaker at 150 °C for 48 h. The PCL sample was taken out from the molten crude PCL and purified by the method described in the small-scale polymerization.

## Theoretical consideration for non-isothermal DSC kinetics analysis

Generally, the reaction rate ($d\alpha/dt$) investigated by thermal analysis technique, especially DSC is proportional to the heat flow rate ($dH/dt$). The $d\alpha/dt$ can be expressed in terms of rate constant and function of monomer conversion as shown in Eq. (1) [19].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is the temperature dependence rate constant of the reaction and $f(\alpha)$ is the function of monomer conversion. Under non-isothermal conditions, the heating rate ($\beta = dT/dt$) must be concerned and taken into account. Then, replacing the $k(T)$ by the Arrhenius equation yields the new rate equation as shown in Eq. (2) [20].

$$\beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{2}$$

where $A$, $E_a$, and $R$ are the pre-exponential factor, the activation energy, and the universal gas constant, respectively. The $E_a$ can be determined by the methods of Kissinger [21, 22] and Ozawa [23, 24]. The Kissinger method is based on the relationship between the heating rate ($\beta$) and the temperature at the maximum rate of polymerization ($T_p$) and derived by using the Murray and White mathematics approximation as shown in Eq. (3) [21, 22].

$$\frac{d[ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R} \tag{3}$$

Therefore, the value of $E_a$ can be obtained from the slope of a plot of $\ln(\beta/T_p^2)$ against $1/T_p$, where $R$ is the gas constant. The Ozawa method employed Doyle's approximation of $\log p(x) \cong -2.315 - 0.457E_a/RT$ for $x = E_a/RT > 20$ resulting in the linear relationship of $\log\beta$ and $1/T_p$ as shown in Eq. (4) [23, 24].

$$\log\beta = \text{constant} - 0.457\frac{E_a}{RT_p} \tag{4}$$

## Results and discussion

### Initiating performance of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators in the ROP of $\varepsilon$-CL by the non-isothermal DSC

Recently, the non-isothermal DSC has been frequently and effectively used to investigate and compare the performance of metal-containing initiators in the ROP of cyclic esters [9, 12, 15]. In this technique, the polymerization process can be

observed by the presence of the exothermic peak in the DSC curve. From this, the heat flow rate obtained at each heating rate from the non-isothermal DSC is directly proportional to the rate of reaction. Moreover, the temperature position of the DSC exotherm can reveal the effectiveness of the initiator such as the lower polymerization temperature range obtained from the fast initiator. Therefore, the data obtained from the milligram-scale polymerization in DSC seems to be very useful for predicting the condition used in the larger-scale polymerization. The non-isothermal DSC can be considered as the fast method to compare the reactivity of the initiator in the ROP of cyclic esters [9, 12, 15, 25].

From our previous works [9, 26], the initiating behavior of $n$Bu$_3$SnO$n$Bu and Al(O$s$Bu)$_3$ in the ROP of $\varepsilon$-CL was successfully investigated by the non-isothermal DSC technique. From the results, it was found that the $n$Bu$_3$SnO$n$Bu initiator could be used to control the ROP of $\varepsilon$-CL by adjusting $n$Bu$_3$SnO$n$Bu concentration. Furthermore, both of $n$Bu$_3$SnO$n$Bu and Al(O$s$Bu)$_3$ seemed to act as the slow initiator due to their steric hindrance around Sn–O and Al–O active centers. The polymerization temperatures of the ROP of $\varepsilon$-CL with 1.0 mol% of $n$Bu$_3$SnO$n$Bu and 2.0 mol% of Al(O$s$Bu)$_3$ were observed at 190–295 °C [9] and 220–300 °C [26]. It is important that Al(O$s$Bu)$_3$, the high steric hindrance initiator, cannot initiate the ROP of $\varepsilon$-CL at a similar concentration to $n$Bu$_3$SnO$n$Bu. These clearly suggest that the Al(O$s$Bu)$_3$ initiator shows a lower polymerization rate of $\varepsilon$-CL than $n$Bu$_3$SnO$n$Bu. In this present work, we try to improve the performance of $n$Bu$_3$SnO$n$Bu by mixing with Al(O$s$Bu)$_3$ resulting in the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators. First of all, the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is conducted and surveyed by the non-isothermal DSC technique at a heating rate of 10 °C/min. It is found that the shape of the polymerization exotherm of the ROP of $\varepsilon$-CL obtained from the mixed initiators is different from the single $n$Bu$_3$SnO$n$Bu initiator. The beginning temperature of polymerization seems to be equal for both initiating systems (around 197 °C). Interestingly, the exotherm obtained from the mixed initiators is sharper than the reported single $n$Bu$_3$SnO$n$Bu initiator [9] which may be related to the higher propagation rate. Furthermore, it possibly relates to the difference in the polymerization mechanism of $\varepsilon$-CL with the single and the mixed initiators. From the obtained heat of polymerization, the fractional monomer conversion can be determined. The results show that the monomer conversion of $\varepsilon$-CL in the presence of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators approaches 1 at a lower temperature range than the single $n$Bu$_3$SnO$n$Bu initiator. The maximum polymerization rate for the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is also higher than the single $n$Bu$_3$SnO$n$Bu initiator. From preliminary investigation, it implies that the reactivity of the mixed initiators is higher than the single initiator. After obtaining this information, the effect of Al(O$s$Bu)$_3$ concentration in the mixed initiators is investigated and the kinetics of the ROP of $\varepsilon$-CL with mixed initiators is studied at different heating rates and the results are illustrated in Fig. 1.

From Fig. 1a, b, the polymerization exotherms for the ROP of $\varepsilon$-CL with the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:2.0 mol% occur at a lower temperature range than the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:1.0 mol% at all heating rates. Furthermore, the monomer conversions of $\varepsilon$-CL close to 1 at a higher temperature range as heating rates increase similar to many works [9, 15, 27]. It is important that the
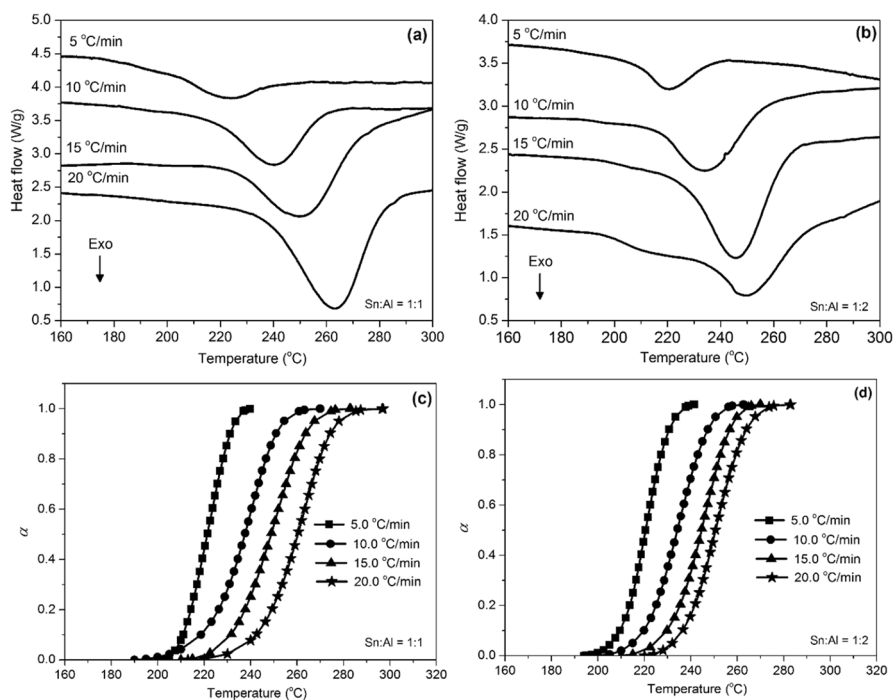
**Fig. 1** The non-isothermal DSC curves and plots of monomer conversion ($\alpha$) against temperature for the ROP of $\varepsilon$-CL with different molar ratios of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at heating rates of 5, 10, 15, and 20 °C/min: [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] = 1.0:1.0 mol% (**a**, **c**) and 1.0:2.0 mol% (**b**, **d**)

polymerization exotherms for the ROP of $\varepsilon$-CL with both mixed initiators occur at a lower temperature range than the single initiating system of $n$Bu$_3$SnO$n$Bu or Al(O$s$Bu)$_3$. From the obtained $\alpha$, the value of polymerization rate (d$\alpha$/d$t$) for the ROP of $\varepsilon$-CL with different initiators can be determined by dividing the difference of $\alpha$ with time or temperature, and the polymerization rates are compared in Fig. 2.

It is found that the ROP of $\varepsilon$-CL with the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:2.0 mol% shows a higher polymerization rate than the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:1.0 mol% and the single $n$Bu$_3$SnO$n$Bu initiator, respectively. This clearly demonstrates that the polymerization rate of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu initiator can be increased by the addition of the Al(O$s$Bu)$_3$ without the interference of initiation temperature. To support these obtained results, the peak temperatures ($T_p$) of the ROP of $\varepsilon$-CL with different initiators are compared and summarized in Table 1.

From Table 1, the values of $T_p$ of the ROP of $\varepsilon$-CL increase with increasing heating rates for all initiators. The ROP of $\varepsilon$-CL with the mixed initiators at [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:2.0 mol% shows the lowest value of $T_p$ than the rest initiators. To support this obtained result, the values of activation energy ($E_a$) are utilized. The values of $E_a$ for the ROP of $\varepsilon$-CL with the mixed initiators are effectively determined from the peak methods of Kissinger [21, 22] and Ozawa [23, 24] as illustrated in Fig. 3.
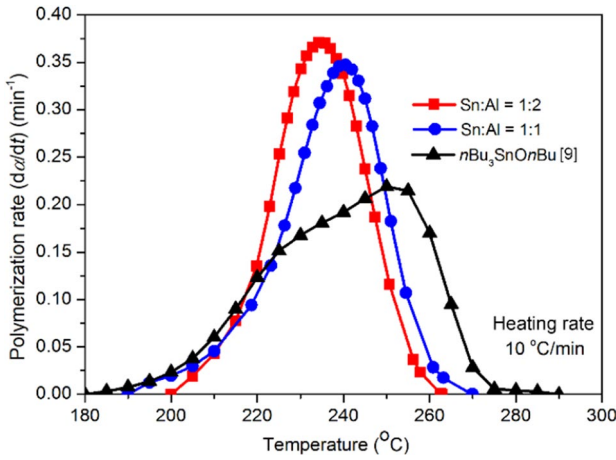
**Fig. 2** Plots of polymerization rate against temperature for the ROP of $\varepsilon$-CL with different initiators at a heating rate of 10 °C/min

**Table 1** The peak temperatures ($T_p$) of the ROP of $\varepsilon$-CL with different initiators at the heating rates of 5, 10, 15, and 20 °C/min

| Initiator concentration (mol%) | | | Heating rate (°C/min) | $T_p^{\text{b}}$ (°C) |
|---|---|---|---|---|
| $n\mathrm{Bu_3SnO}n\mathrm{Bu}$ | $\mathrm{Al(O}s\mathrm{Bu)_3}$ | [Sn]/[Al] | | |
| $1.0^{\text{a}}$ | – | – | 5 | 235.7 |
| | | | 10 | 251.0 |
| | | | 15 | 258.5 |
| | | | 20 | 273.3 |
| 1.0 | 1.0 | 1:1 | 5 | 225.0 |
| | | | 10 | 240.5 |
| | | | 15 | 251.5 |
| | | | 20 | 261.7 |
| 1.0 | 2.0 | 1:2 | 5 | 218.3 |
| | | | 10 | 233.8 |
| | | | 15 | 247.8 |
| | | | 20 | 253.0 |

[a]The values reported in our previous work [9]

[b]The temperature at the maximum rate of polymerization

From Fig. 3, the Kissinger and Ozawa plots show the linear behavior with $R^2 > 0.98$ indicating the suitability of these two methods in the determination of the $E_a$ values for the polymerization of $\varepsilon$-CL with those $n\mathrm{Bu_3SnO}n\mathrm{Bu}/\mathrm{Al(O}s\mathrm{Bu)_3}$ mixed initiators. The obtained $E_a$ values from the Kissinger and Ozawa plots for the ROP of $\varepsilon$-CL with the $n\mathrm{Bu_3SnO}n\mathrm{Bu}/\mathrm{Al(O}s\mathrm{Bu)_3}$ mixed initiators are summarized in Table 2.

From Table 2, the value of $E_a$ for the ROP of $\varepsilon$-CL with the mixed initiators at $[n\mathrm{Bu_3SnO}n\mathrm{Bu}]/[\mathrm{Al(O}s\mathrm{Bu)_3}]$ of 1.0:2.0 mol% is lower than the mixed initiators at $[n\mathrm{Bu_3SnO}n\mathrm{Bu}]/[\mathrm{Al(O}s\mathrm{Bu)_3}]$ of 1.0:1.0 mol% and the single $n\mathrm{Bu_3SnO}n\mathrm{Bu}$
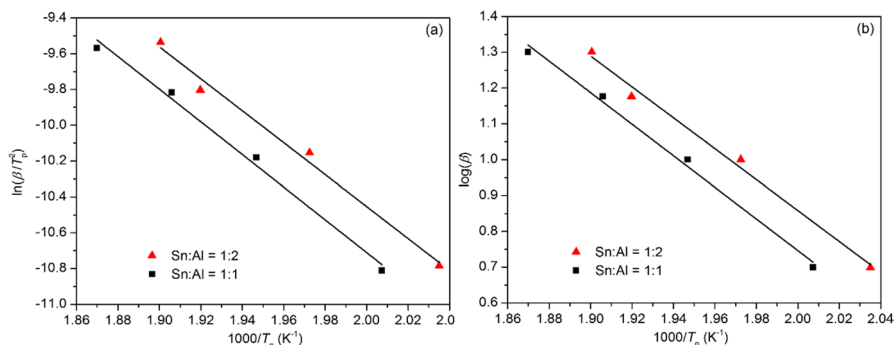
**Fig. 3** Kissinger (**a**) and Ozawa (**b**) plots for the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 1.0:1.0 mol% and 1.0:2.0 mol%

**Table 2** The $E_a$ values for the ROP of $\varepsilon$-CL with different initiators obtained from the peak methods of Kissinger and Ozawa

| Initiators | [I]$_0$[a] (mol%) | [Sn]/[Al] | $E_a$ (K)[b] (kJ/mol) | $E_a$ (O)[c] (kJ/mol) | $R^2$ |
|---|---|---|---|---|---|
| $n$Bu$_3$SnO$n$Bu | 1.0 | 1:0 | 78.3[d] | 82.8[d] | > 0.98 |
| $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ | 1.0:1.0 | 1:1 | 75.8 | 80.3 | > 0.99 |
| $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ | 1.0:2.0 | 1:2 | 74.2 | 78.6 | > 0.99 |

[a]The initial concentration of the initiator

[b]Determined from Eq. (3)

[c]Determined from Eq. (4)

[d]The values reported in our previous work [9]

initiator, respectively. From non-isothermal DSC analysis, the reactivity of the initiating systems used in this work in the ROP of $\varepsilon$-CL is arranged in the following order: $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:2.0 mol%) > $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:1.0 mol%) > $n$Bu$_3$SnO$n$Bu (1.0 mol%). The addition of Al(O$s$Bu)$_3$ into $n$Bu$_3$SnO$n$Bu can increase the polymerization rate of $\varepsilon$-CL. The obtained results are interesting that have not been investigated and studied before.

To confirm the formation of poly($\varepsilon$-caprolactone) (PCL) from non-isothermal DSC heating of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:2.0 mol%) mixed initiators, the obtained sample from the complete 1st heating at 5 °C/min is cooled down to 20 °C at a cooling rate of 20 °C/min. Then, the sample is reheated to 270 °C (2nd heating) at a heating rate of 10 °C/min. The non-isothermal DSC curves for proofing the formation of PCL after complete DSC heating of $\varepsilon$-CL with the mixed initiators are depicted in Fig. 4.

From Fig. 4, it is found that the crystalline melting temperature ($T_m$) of PCL is found around 50 °C with the heat of melting ($\Delta H_m$) of 76.4 J/g which is close to the literature [28, 29]. When comparing $\Delta H_m$ of PCL with the theoretical heat of melting of 100% crystallized PCL ($\Delta H^*_m = 135$ J/g) [30], the percentage of crystallinity (%$X_c$) of our synthesized PCL from the non-isothermal heating is
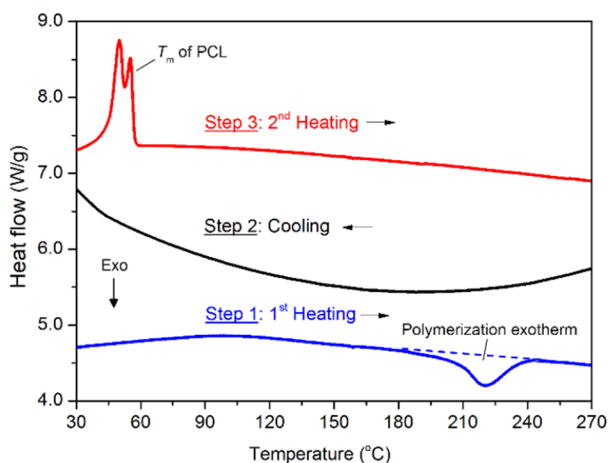
**Fig. 4** The non-isothermal DSC curves for confirming the formation of PCL after complete heating of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators (1.0:2.0 mol%) at a heating rate of 5 °C/min

found to be 56.6% indicating the semi-crystalline property of PCL. From this, it clearly demonstrated that PCL is completely synthesized from the 1st heating of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators (1.0:2.0 mol%) at a heating rate of 5 °C/min.

## Synthesis of poly($\varepsilon$-caprolactone) using the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators via small-scale polymerization

From the previous section, the behavior of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators in the ROP of $\varepsilon$-CL is investigated. In this section, the performance of this $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators in the synthesis of PCL is firstly investigated at 150 °C for 24 and 48 h. The obtained crude PCLs are purified by dissolving in CHCl$_3$ and precipitating in cold methanol [9, 15]. The GPC analysis for the purified PCLs is summarized in Table 3.

From Table 3, it is important that the molecular weight of PCL is controlled by the concentration of Al(O$s$Bu)$_3$ in the mixed initiators at a constant concentration of $n$Bu$_3$SnO$n$Bu and the examples of the GPC curve are depicted in Fig. 5. The dependency of the position of GPC curves with the molecular weight of the polymer is similar to the literature [31]. When decreasing the concentration of $n$Bu$_3$SnO$n$Bu, the molecular weight of PCL seems to slightly increase. This indicates that our mixed initiators can be used to synthesize PCL at a very low concentration of $n$Bu$_3$SnO$n$Bu and Al(O$s$Bu)$_3$. The highest molecular weight of PCL (entry 6) is obtained at 150 °C for 24 h with the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 0.0625:0.2500 mol% (1:4). The low %yield of PCL in entry 5 may be related to the occurrence of the intramolecular transesterification that causes the decreasing of PCL molecular weight (as indicated by the high $Đ$ value) [32]. The high concentration of $n$Bu$_3$SnO$n$Bu can induce and accelerate this unwanted side

**Table 3** The molecular weight average, dispersity, and %yield of the synthesized PCL from the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at 150 and 160 °C at different polymerization times

| Entry | $[I]_0^a$ (mol%) | | | $T$ (°C) | $t$ (h) | $M_n^b$ (g/mol) | $M_w^b$ (g/mol) | $Đ^b$ | %Yield$^c$ |
|---|---|---|---|---|---|---|---|---|---|
| | $n$Bu$_3$SnO$n$Bu | Al(O$s$Bu)$_3$ | [Sn]/[Al] | | | | | | |
| 1 | 0.125 | 0.0313 | 4:1 | 150 | 24 | $3.6 \times 10^4$ | $5.3 \times 10^4$ | 1.74 | 93 |
| 2 | | 0.0625 | 2:1 | 150 | 24 | $2.5 \times 10^4$ | $5.6 \times 10^4$ | 2.19 | 93 |
| 3 | | 0.1250 | 1:1 | 150 | 24 | $2.4 \times 10^4$ | $5.4 \times 10^4$ | 2.26 | 91 |
| 4 | | 0.2500 | 1:2 | 150 | 24 | $1.9 \times 10^4$ | $4.0 \times 10^4$ | 2.11 | 89 |
| 5 | | 0.5000 | 1:4 | 150 | 24 | $1.3 \times 10^4$ | $2.9 \times 10^4$ | 2.15 | 50 |
| 6 | 0.0625 | 0.0156 | 4:1 | 150 | 24 | $3.4 \times 10^4$ | $6.3 \times 10^4$ | 1.84 | 72 |
| 7 | | 0.0313 | 2:1 | 150 | 24 | $3.2 \times 10^4$ | $6.0 \times 10^4$ | 1.87 | 89 |
| 8 | | 0.0625 | 1:1 | 150 | 24 | $3.1 \times 10^4$ | $6.1 \times 10^4$ | 1.98 | 93 |
| 9 | | 0.1250 | 1:2 | 150 | 24 | $2.7 \times 10^4$ | $5.4 \times 10^4$ | 2.03 | 95 |
| 10 | | 0.2500 | 1:4 | 150 | 24 | $1.9 \times 10^4$ | $3.9 \times 10^4$ | 2.12 | 89 |
| 11 | 0.0625 | 0.0156 | 4:1 | 150 | 48 | $2.9 \times 10^4$ | $5.5 \times 10^4$ | 1.89 | 88 |
| 12 | 0.0500 | 0.0125 | 4:1 | 160 | 24 | $4.0 \times 10^4$ | $6.5 \times 10^4$ | 1.65 | 93 |
| 13 | 0.0313 | 0.0313 | 1:1 | 160 | 24 | $3.5 \times 10^4$ | $6.1 \times 10^4$ | 1.74 | 92 |

$^a$The initial concentration of the initiator

$^b$Determined from GPC technique using THF as eluent at 40 °C

$^c$Determined from the ratio of the mass of purified PCL divided by the mass of $\varepsilon$-CL
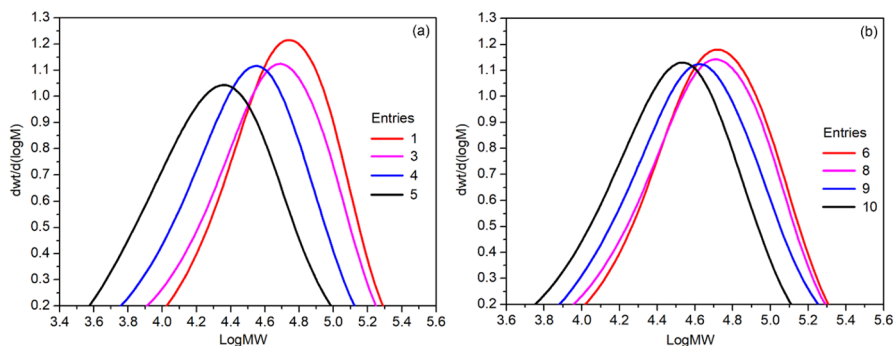


**Fig. 5** GPC curves for the synthesized PCLs (entries 1–10) from the ROP of $\varepsilon$-CL with the $n$Bu$_3$S-nO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at 150 °C for 24 h

reaction that causes the formation of more PCL oligomers or short PLC chains. In the filtration process, they cannot be filtered because they are very short PCL chains which occurred as a very fine and very small powder resulting in a low %yield of PCL. In the case of entry 6, the concentration of $n$Bu$_3$SnO$n$Bu is decreased to 50% (from 0.125 to 0.0625 mol%) of entries 1–5 and the reactivity of $n$Bu$_3$SnO$n$Bu is also decreased. Therefore, it seems to require a higher amount of Al(O$s$Bu)$_3$ to drive and accelerate the ROP of $\varepsilon$-CL under the high

viscosity condition (solvent-free). From this, the low %yield of PCL in entry 6 may be related to the insufficient Al(O$s$Bu)$_3$ concentration. At the identical ratio of [Sn]:[Al], the decreasing of $n$Bu$_3$SnO$n$Bu content in the mixed initiators can increase the molecular weight of the synthesized PCL.

From entry 6, we try to increase polymerization time to 48 h (entry 11). It is found that the molecular weight of PCL decreases and the %yield increases. This indicates that the long polymerization time is not suitable for producing high molecular weight PCL by using the mix-metal alkoxides initiating system. The physical appearances of the synthesized PCL are displayed in Fig. 6. From Fig. 6, most of the PCLs synthesized from the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators are in the fiber form that relates to moderate to the high molecular weight of PCL.

From the results obtained from entries 1–10, we try to reduce the concentration of the mixed initiators in combination with increasing the polymerization temperature to test the production possibility of the high molecular weight PCL at a low initiator concentration (entries 12 and 13). It is found that the higher molecular weight of PCL can be obtained from a low concentrations of mixed initiators. The highest values of $M_n$ and $M_w$ of PCL obtained from the condition used in this work are $4.0 \times 10^4$ g/mol and $6.5 \times 10^4$ g/mol, respectively. The physical appearances of PCL from entries 12 and 13 are depicted in Fig. 7.



**Fig. 6** Physical appearances of the synthesized PCLs (entries 1–11) from the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at 150 °C for 24 and 48 h
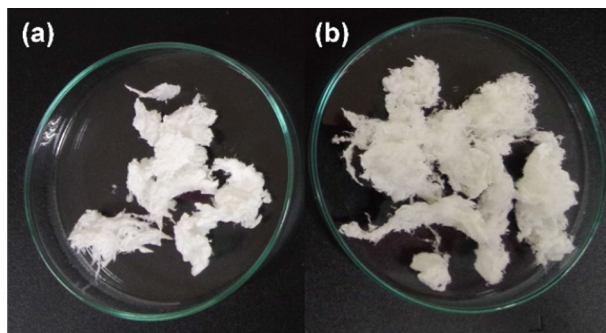
**Fig. 7** Physical appearances of the synthesized PCLs (entries 12 and 13) from the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators at 160 °C for 24 h: [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 0.0500:0.0125 mol% (4:1) (**a**) and 0.0313:0.0313 mol% (1:1) (**b**)

## Mechanistic study for the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators

After understanding the ROP kinetics of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators, the reaction mechanism is further clarified. The mechanism of the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators is proposed through the classic coordination–insertion mechanism as illustrated in Fig. 8 [2, 3, 9, 15].

From Fig. 8, $\varepsilon$-CL is coordinated with Al(O$s$Bu)$_3$ resulting in the more electrophilic property of the carbonyl group. Al(O$s$Bu)$_3$ will also be coordinated with $n$Bu$_3$SnO$n$Bu via the Sn atom yielding the more electronegative of the $n$-butoxy group (–O$n$Bu). After the increasing of the nucleophilicity of the –O$n$Bu group, it
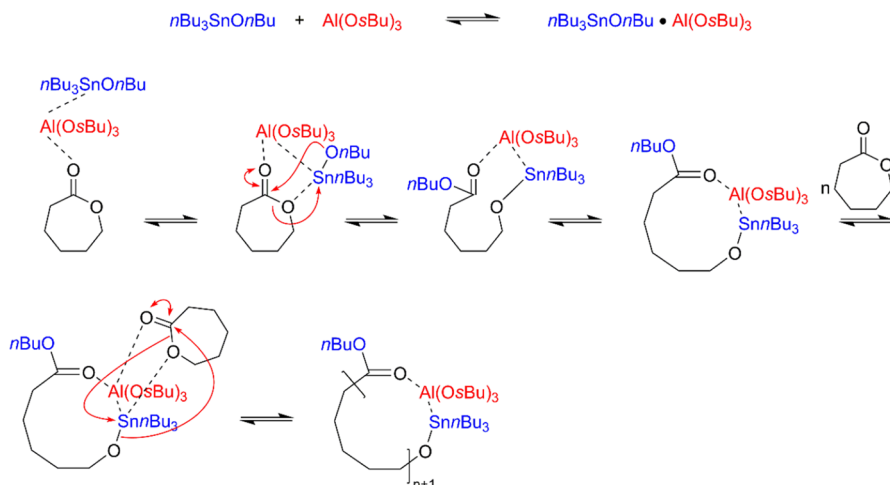


**Fig. 8** The plausible coordination–insertion mechanism for the ROP of $\varepsilon$-CL with the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators under solvent-free conditions

will attack the reactive carbonyl carbon of $\varepsilon$-CL resulting in the ring-opening of $\varepsilon$-CL via acyl–oxygen bond cleavage. After this step, the molecules of $\varepsilon$-CL, $n$Bu$_3$SnO$n$Bu, and Al(O$s$Bu)$_3$ are converted to the propagating species that still contain the Sn–O active center [9, 26]. Then, new $\varepsilon$-CL molecules will coordinate with this propagating species via the same mechanism converting to PCL. To confirm this mechanism, the 400 MHz $^1$H-NMR spectra of the purified PCL (entries 6–8) are used as shown in Fig. 9.

From Fig. 9, the assignments for the $^1$H-NMR spectra of the synthesized PCL are as follows: (i) the multiplet signals from methyl end group (–CH$_3$) and methylene proton (–CH$_2$–) of PCL chain are found at 0.85 [9] and 1.20–1.60 ppm [9, 33, 34], respectively, (ii) the triplet signals of methylene proton (–CH$_2$–) connected to carbonyl carbon (–$\underline{C}$O–) and hydroxyl end group (–OH) of PCL chain are observed around 2.30 [9] and 3.65 ppm [35, 36], respectively, (iii) the triplet signal of methylene proton (–CH$_2$–) connected to carbonyl oxygen (–CO–O–) of PCL chain is found at 4.00 ppm which are close to literature data [26, 33, 34, 37]. The obtained spectrum is fitted with the chemical structure of the synthesized PCLs and close to the $^1$H-NMR spectrum of PCL synthesized from the single $n$Bu$_3$SnO$n$Bu initiator reported in the literature [9]. It is important to note that the obtained $^1$H-NMR spectrum of the synthesized PCL does not show the signal from the Al(O$s$Bu)$_3$. This indicates that the Al(O$s$Bu)$_3$ is not incorporated into the PCL chain. If the Al(O$s$Bu)$_3$ incorporates in the PCL chain, the multiplet signal from the methine proton of the $s$-butoxide group (–O$\underline{C}$H(CH$_3$)CH$_2$CH$_3$) must be found at 4.85 ppm as reported in our previous work [26]. From this, the obtained $^1$H-NMR spectrum can be used to support the proposed polymerization mechanism shown in Fig. 8. The obtained $^1$H-NMR spectra confirm that the Al(O$s$Bu)$_3$ did not incorporate into the chain of the synthesized PCL because the signal around 4.85 ppm is not observed. As shown in Fig. 8, Al(O$s$Bu)$_3$ acts as the catalyst that can increase the performance of $n$Bu$_3$SnO$n$Bu initiator in the ROP of $\varepsilon$-CL under solvent-free conditions.

## Preliminary investigation on the scale-up of the synthesis of poly($\varepsilon$-caprolactone) using the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators via solvent-free polymerization

After complete understanding the effectiveness of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators in the small-scale polymerization of $\varepsilon$-CL, we try to scale up the ROP of $\varepsilon$-CL from 4 to 250 g by using the condition of entry 6 in Table 3 (150 °C and 24 h). It is found that the polymerization is not complete after 24 h and very low reaction mixture viscosity is obtained. This indicates that the larger-scale polymerization needs a longer time to complete the reaction similar to the work of Stjerndahl et al. [38]. They found that the time to complete the reaction of L-lactide (LL) with cyclic tin(IV) alkoxide initiator at different synthesis scales is in the following order: 50 g > 20 g > 5 g. By using our designed apparatus, we increase the polymerization time from 24 to 48 h. The physical appearances of crude and purified PCLs obtained from this condition are shown in Fig. 10.

Interestingly, the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators can produce a high molecular weight of PCL with $M_n$, $M_w$, Đ, and %yield of $7.3 \times 10^4$ g/mol,
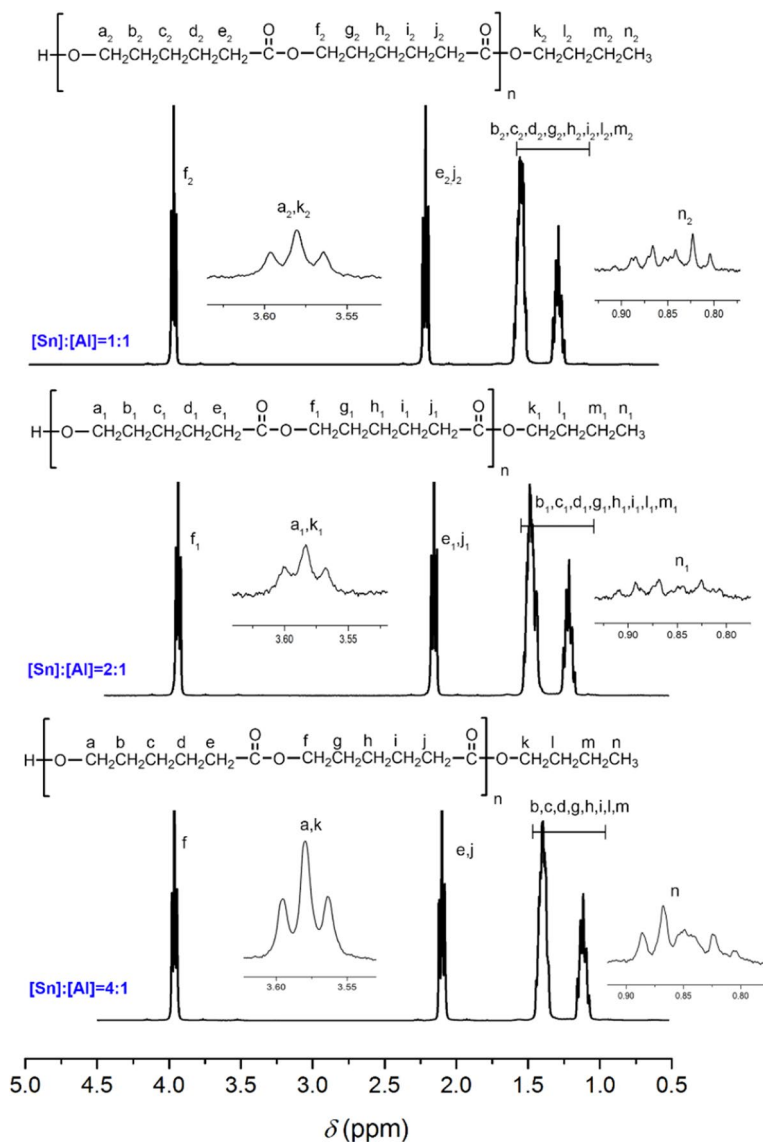
**Fig. 9** 400 MHz $^1$H-NMR spectra of the purified PCL (entries 6-8) from the ROP of $\varepsilon$-CL with the $[n\text{Bu}_3\text{Sn}O n\text{Bu}]/[\text{Al}(O s\text{Bu})_3]$ of 0.0625:0.0625 mol% (1:1), 0.0625:0.0313 mol% (2:1), and 0.0625:0.0156 mol% (4:1) at 150 °C for 24 h

$1.2 \times 10^5$ g/mol, 1.69 and 82%, respectively. These results may indicate that the mixed initiators show higher performance in the larger-scale synthesis of PCL under solvent-free conditions. Mixed initiators work is in progress in our laboratory and the results will be reported soon.
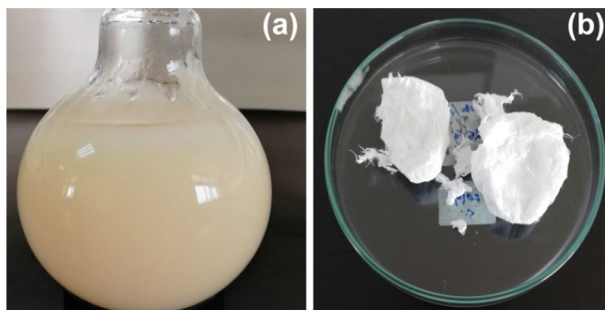
**Fig. 10** Physical appearances of the crude (**a**) and the purified (**b**) PCLs from the ROP of $\varepsilon$-CL (250 g) with the [$n$Bu$_3$SnO$n$Bu]/[Al(O$s$Bu)$_3$] of 0.0625:0.0156 mol% (4:1) at 150 °C for 48 h

## Conclusions

The $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators were successfully utilized in the ROP of $\varepsilon$-CL under solvent-free conditions. From the DSC kinetics study, the polymerization rate of $\varepsilon$-CL increased with increasing Al(O$s$Bu)$_3$ content at a constant $n$Bu$_3$SnO$n$Bu concentration. The $E_a$ values for the ROP of $\varepsilon$-CL initiated with $n$Bu$_3$SnO$n$Bu (1.0 mol%), $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:1.0 mol%), and $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ (1.0:2.0 mol%) were 78.3–82.8, 75.8–80.3 and 74.2–78.6 kJ/mol, respectively. The polymerization mechanism of the ROP of $\varepsilon$-CL with the mixed initiators was proposed through the coordination–insertion mechanism. From the $^1$H-NMR technique, the Al(O$s$Bu)$_3$ did not incorporate into the PCL chain and it could enhance the efficiency of the $n$Bu$_3$SnO$n$Bu initiator in the solvent-free ROP of $\varepsilon$-CL. From small-scale synthesis, the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators could control the $\varepsilon$-CL polymerization and the molecular weight of PCL by varying Al(O$s$Bu)$_3$ concentration. At a constant $n$Bu$_3$SnO$n$Bu concentration, the $M_n$ of PCL increased with decreasing of Al(O$s$Bu)$_3$ concentration because the polymerization rate of $\varepsilon$-CL was lower at low Al(O$s$Bu)$_3$ concentration resulting in the slow increase in the viscosity of the polymerization system. This assisted the coordination of $\varepsilon$-CL with the reactive center of propagating species to form the longer PCL chain. The PCL could be effectively produced by using a very low concentration of the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators. The highest $M_n$ of PCL synthesized from small-scale polymerization was $4.0 \times 10^4$ g/mol with Đ and %yield of 1.65 and 93%. From larger-scale synthesis (250 g) at 150 °C for 48 h, the $n$Bu$_3$SnO$n$Bu/Al(O$s$Bu)$_3$ mixed initiators (0.0625:0.0156 mol%) (4:1) could produce high molecular weight PCL ($M_n = 7.3 \times 10^4$ g/mol, $M_w = 1.2 \times 10^5$ g/mol and Đ = 1.69). The mixed initiators seemed to be suitable for larger-scale polymerization and more information about the larger-scale synthesis of PCL would be described and reported in our future works.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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