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ORIGINAL PAPER

Dibutyltin(IV) maleate as a new effective initiator for the ring-opening polymerization of ε-caprolactone: the non-isothermal kinetics, mechanism, and initiator's performance in polymer synthesis

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Abstract

Dibutyltin(IV) maleate (DBTML) was successfully used as a new initiator in the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) under solvent-free condition for the first time. The performance of DBTML in the ROP of ε-CL was powerfully and rapidly determined by the non-isothermal differential scanning calorimetry technique. The effect of DBTML concentration on the non-isothermal ROP of ε-CL was studied and described. The values of activation energy (E_a) were completely determined by the peak method of Kissinger and the isoconversional method of Kissinger–Akahira–Sunose (KAS). The E_a values for the ROP of ε-CL decreased with increasing DBTML concentration. The frequency factor (A) values for the ROP of ε-CL with 3.0 and 4.0 mol% of DBTML were 7.4×10^6 and 7.3×10^5 min^{-1}, respectively. From mechanistic investigation by proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR), the ROP of ε-CL with DBTML was purposed via the coordination-insertion mechanism. From bulk polymerization, DBTML could produce poly(ε-caprolactone) (PCL) with the weight average molecular weight (M_w) and polydispersity index (PDI) in the range of 1.49×10^4–5.15×10^4 g/mol and 1.52–1.98, respectively.

Keywords Dibutyltin(IV) maleate · Kinetics · ε-Caprolactone · Polycaprolactone · Ring-opening polymerization

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Introduction

Ring-opening polymerization (ROP) has become a potential route for the preparation of the biodegradable polyesters such as polylactides, polylactones, and copolyesters with well-controlled properties [1–3]. These polymers can be used in a variety of applications from packaging materials to biomedical polymers [4, 5]. They are traditionally synthesized from the ROP of cyclic esters with effective organometallic initiators or catalysts. Many organometallic compounds with various metal (M) active centers (M; Al [6], Sn [7, 8], Ti [9], Y [10], Zr [11], etc.) are utilized in ROP of cyclic esters. Focusing on tin(IV) compounds, they can be used in various forms such as non-cyclic and cyclic structures as shown in the following information. Kricheldorf and Saunders [12] reported that tetrabutyltin(IV) (Bu_4Sn) was used as initiator for the ROP of ε-CL. The ROP of ε-CL was catalyzed by Bu_4Sn at 100 °C and could be further accelerated by benzyl alcohol. The initiation process depended on the formation of reactive covalent Sn–O bond as dibutyltin(IV) oxide (Bu_2SnO). Bu_2SnO initiated polymerization of ε-CL by two routes: (i) the presence of alcohol, dibutyltin(IV) alkoxides ($Bu_2Sn(OR)_2$) was formed. These alkoxides could initiate polymerization by coordination insertion mechanism and (ii) lactones may undergo a direct insertion into the stannoxane bonds of Bu_2SnO resulting in the formation of a cyclic initiator. Our previous works also focused on the catalytic performance of the noncyclic tin(IV) compounds such as tributyltin(IV) *n*-butoxide (nBu$_3$SnOnBu) in the ROP of ε-CL [8]. The results found that the polymerization of ε-CL could be controlled by the nBu$_3$SnOnBu initiator. They also could be used to synthesize PCL with weight average molecular weight (M_w) in the range of 2.0×10^4–3.9×10^4 g/mol. Moreover, the ROP mechanism of ε-CL with nBu$_3$SnOnBu initiator was proposed through the coordination-insertion mechanism. For cyclic tin(IV) catalysts, Kricheldorf and Lee [13] studied the macrocyclic polymerization of ε-CL and β-*D,L*-butyrolactone (β-BL) by a spirocyclic tin(IV) initiator. The molecular weight of PCL increased with the [M]/[I] ratio and high molecular weight ($M_w = 2.2\times10^4$–1.64×10^5 g/mol) of PCL was obtained. This spirocyclic tin(IV) initiator with dimeric form initiated polymerization by the coordination insertion mechanism similar to many tin alkoxide compounds. In recent years, Kricheldorf and Weidner [14] successfully prepared new cyclic tin(IV) bisphenoxides (SnBi and SnNa) that could be used in the ring expansion polymerization (REP) of lactide. These initiators were easily synthesized from commercial chemicals and could produce cyclic polylactide with M_w of 1.2×10^4–1.4×10^5 g/mol. From obtained results, these tin(IV) initiators were found to be capable of upscaling in the preparation of cyclic polylactide.

From the literature surveyed, the development of Sn(IV) initiator in the ROP of cyclic esters still interests many researchers. Dibutyltin(IV) maleate (DBTML), a cyclic tin(IV) compound, impacts our attention due to: (i) it is commercially available, (ii) easy to use, and (iii) stable to air. DBTML has not been utilized as an initiator or catalyst in the ROP of cyclic esters before. The clarification and understanding of DBTML behavior and the kinetics of ROP are necessary

for achieving control of cyclic esters polymerization. From our previous work [8], the non-isothermal differential scanning calorimetry (DSC) technique was effectively employed to follow the ROP of ε-CL with the nBu$_3$SnOnBu initiator. The important kinetic parameters of this reaction could be determined in a short period of time. From obtained kinetic parameters, the synthesized nBu$_3$SnOnBu acted as a slow initiator. After obtaining the kinetics information, the condition for polymer synthesis could be conveniently designed and predicted.

This work aims to firstly utilize DBTML as an initiator for the ROP of ε-CL under solvent-free polymerization. The effectiveness of DBTML in the ROP of ε-CL will also be studied and investigated by the non-isothermal DSC technique. The effect of heating rate and DBTML concentration in the non-isothermal ROP of ε-CL will be described. Moreover, the polymerization mechanism of the ROP of ε-CL with DBTML is studied by proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR) and proposed. The performance of DBTML in the synthesis of PCL will be investigated via solvent-free polymerization at different temperatures and times.

Experimental

Materials preparation

Dibutyltin(IV) maleate (DBTML) (Sigma-Aldrich, 95%) was used as received. The chemical structure of this tin(IV) initiator was displayed in Fig. 1. ε-Caprolactone ($C_6H_{10}O_2$, ε-CL) (Sigma-Aldrich, 97.0%) was purified by vacuum distillation and kept in 250 mL round bottom flask under vacuum before utilized. Methanol (Qrec, 99.0%), chloroform (LabScan, 99.5%), and chloroform-*d* (Sigma-Aldrich, 99.8%) were used as received.

Non-isothermal DSC measurement for the ring-opening polymerization of ε-CL with DBTML initiator

ε-CL (2.000 g) with 3.0 and 4.0 mol% of DBTML initiator were carefully mixed in the dried vial using a magnetic stirrer for 10 min. The polymerization mixture (7–8 mg) was accurately weighed into an aluminum pan and sealed. All DSC measurement was performed on a Mettler Toledo DSC-3+. All samples were heated from 20 to 240 °C at heating rates of 4, 6, 8, and 10 °C/min. The obtained crude polymer from DSC heating was dissolved in $CDCl_3$ and further analyzed by 500 MHz proton-nuclear magnetic resonance spectroscopy (500 MHz ^{1}H-NMR, Bruker AVANCE NEO).

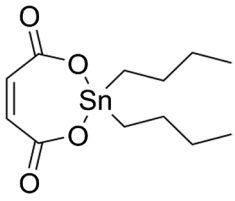

Fig. 1 Chemical structure of dibutyltin(IV) maleate (DBTML) initiator

Theoretical consideration for the non-isothermal DSC kinetics study

Generally, the polymerization reaction is considered as an exothermic process due to chemical bond formation between monomer molecules. Therefore, it is possible to follow the ROP of cyclic ester from the released heat during polymerization. Recently, the thermoanalytical technique, namely DSC is frequently used to study the kinetics and thermodynamics of cyclic esters polymerization under isothermal or non-isothermal mode [8]. The non-isothermal DSC technique is fast method for extracting the kinetics parameters of the ROP of cyclic esters in which the ROP occurred under a constant heating rate. By using the released heat from the ROP of cyclic ester, the fraction of monomer conversion (α) can be determined from Eq. (1) [15, 16].

$$\alpha = \frac{\Delta H_t}{\Delta H_{rxn}} \tag{1}$$

where ΔH_t and ΔH_{rxn} are the heat released at any time and heat of polymerization, respectively. In the non-isothermal DSC experiment, the measured heat flow is directly proportional to the polymerization rate ($d\alpha/dt$). By taking the heating rate (β) into account, the polymerization rate can be expressed as Eq. (2).

$$\beta \frac{d\alpha}{dT} = k(T) f(\alpha) \tag{2}$$

where $k(T)$ and $f(\alpha)$ are the temperature-dependent rate constant and monomer conversion function, respectively. When the $k(T)$ is replaced by the Arrhenius equation, Eq. (2) can be rewritten as Eq. (3) [17]:

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{3}$$

where A is the frequency factor, E_a is the activation energy, and R is the universal gas constant. The value of E_a can be determined by the peak method by Kissinger [18–20]. This Kissinger method is based on the linear relationship of the heating rate (β) and the temperature at maximum rate of polymerization (T_m) as shown in Eq. (4). Therefore, the value of E_a can be extracted from the slope of the plot of $\ln(\beta/T_m^2)$ against $1/T_m$.

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E_a}{R} \tag{4}$$

To support the results obtained from the Kissinger method, the isoconversional method of Kissinger–Akahira–Sunose (KAS) is utilized [21]. This method is considered as the accurate method for determination of E_a values under the non-isothermal condition [17]. By using this method, the reactivity of initiator in the ROP of cyclic esters can be investigated by using the E_a values for the whole stages of polymerization. Moreover, it can be used to observe the variation of E_a values with fractional monomer conversion. The integrated isoconversional method of KAS

bases on the Murray and White mathematic approximation [22]. Therefore, the KAS isoconversional method bases on the linear relationship between $\ln(\beta/T^2)$ and $1/T$ as shown in Eq. (5).

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{-RAf'(\alpha)}{E_a}\right) - \frac{E_a}{RT} \tag{5}$$

The value of E_a at each stage of polymerization can be determined from slope of the plot of $\ln(\beta/T^2)$ and $1/T$ at the arbitrary monomer conversion. In this method, the knowledge of $f'(\alpha)$ is not necessary and it only assumes that the polymerization occurred under the same mechanism at a given conversion.

Poly(ε-caprolactone) synthesis via solvent-free polymerization using DBTML as initiator

For small-scale synthesis, ε-CL (4.000 g) with different concentrations (0.050–1.000 mol%) of DBTML initiator were carefully prepared in a dried 10 mL round bottom flask under nitrogen atmosphere. The reaction flasks were immersed in a pre-heated silicone oil bath at 150 °C for 24 and 48 h. The obtained poly(ε-caprolactone) (PCL) was dissolved in $CHCl_3$ and re-precipitated in cold methanol. The purified PCLs were dried at 47 °C in a hot air oven until the constant weight was reached**.** The molecular weight averages and polydispersity index (PDI) of these PCLs were further characterized by the Water e2695 gel permeation chromatography (GPC*)* technique using polystyrene (PS) as standard. GPC analysis was performed at 35 °C with refractive index and viscosity detectors. Tetrahydrofuran (THF) was used as eluent with a flowing rate of 1.0 mL/min.

Results and discussion

Kinetics and mechanistic studies of the ring-opening polymerization of ε-CL with DBTML initiator

The non-isothermal DSC technique is recently and effectively used to follow the change of the heat from ROP of cyclic esters with various initiating systems [8, 18, 22–25]. The position of the obtained DSC polymerization exotherms corresponds to the reactivity of the initiator/catalyst. In this work, the polymerizability of ε-CL with DBTML is firstly investigated by the non-isothermal DSC technique. The non-isothermal DSC curves for the ROP of ε-CL with DBTML at different heating rates are illustrated in Fig. 2a, b. From these figures, the polymerization exotherms shift to a higher temperature range as the heating rate increases. Moreover, the exothermic curves seem to be broad and sharp at a high heating rate. These obtained results are generally observed in the non-isothermal DSC technique as reported in the literature [22, 24]. Furthermore, the polymerization exotherms are obtained at a lower temperature range as DBTML concentration increases. These obtained results are similar to the non-isothermal ROP of ε-CL with $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator [8]. This indicates

that DBTML concentration affects the polymerizability of ε-CL. From the obtained heat of polymerization (Fig. 2a, b), fractional monomer conversion (α) can be determined by the ratio of the heat released at each time divided by the heat of polymerization. Plots of monomer conversion against temperature are depicted in Fig. 2c, d.

From Fig. 2c, d, it is found that the monomer conversion for the ROP of ε-CL initiated by 3.0 mol% of DBTML reaches 1 at a higher temperature range than 4.0 mol% indicating the higher reactivity of DBTML is obtained at higher concentration. To clarify this, an example of the plots of monomer conversion and polymerization rate against temperature for the ROP of ε-CL with 3.0 and 4.0 mol% of DBTML at a low heating rate of 4 °C/min are displayed in Fig. 3a, b, respectively.

From Fig. 3a, the monomer conversion for ROP of ε-CL initiated by 4.0 mol% of DBTML reaches 1 at a lower temperature than 3.0 mol%. Figure 3b demonstrates that the polymerization rate for the ROP of ε-CL initiated by 4.0 mol% of DBTML is higher than 3.0 mol% at a lower temperature range. These demonstrate that the initiative efficiency of DBTML increases with increasing its concentration. To support these obtained results, the values of half-life ($t_{1/2}$), activation energy (E_a), and frequency factor (A) are utilized. As mentioned in the experimental part, the method of Kissinger (Eq. (4)) is used to determine the values of E_a for the ROP of ε-CL with DBTML. The Kissinger plots plot for the ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML are depicted in Fig. 4.

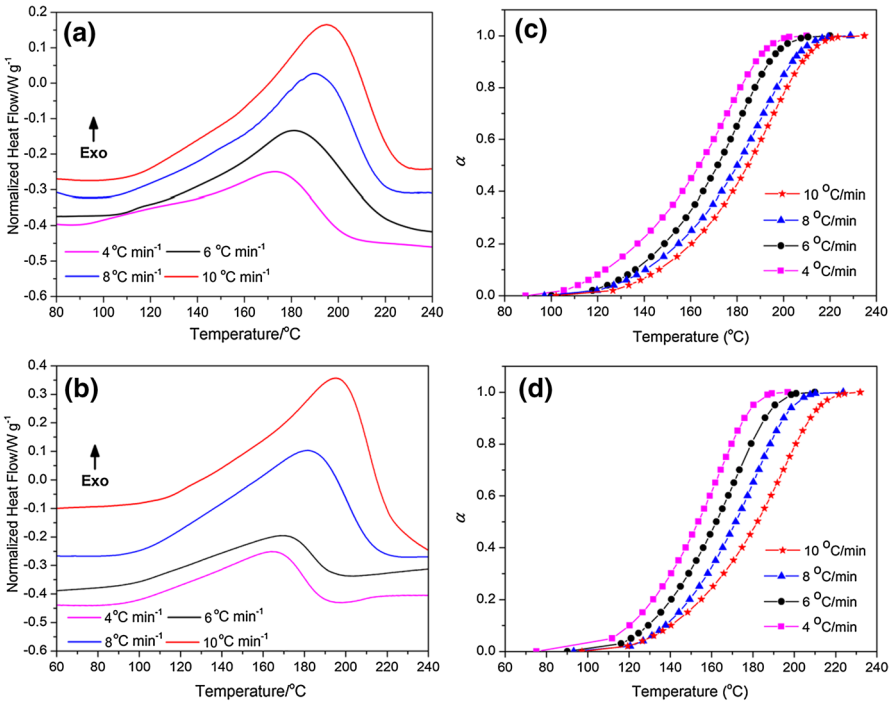

Fig. 2 **a**, **b** DSC curves and **c**, **d** plots of monomer conversion against temperature for the non-isothermal ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML at heating rates of 4, 6, 8, and 10 °C/min

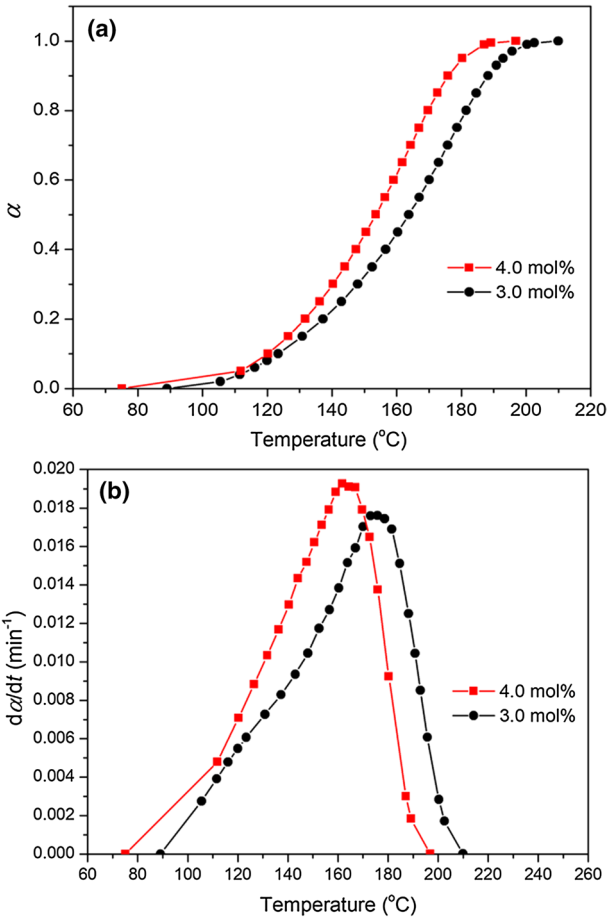

Fig. 3 **a** Plots of monomer conversion and **b** polymerization rate ($d\alpha/dt$) against temperature for the non-isothermal ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML at a heating rate of 4 °C/min

Figure 4 shows a good linear behavior ($R^2 > 0.98$) of the Kissinger plots. The values of E_a can be extracted from the slope of these plots. To support the Kissinger plots, the integrated isoconversional method of KAS is applied to the non-isothermal DSC data. The KAS plots for the ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML at monomer conversion of 0.2 to 0.8 are displayed in Fig. 5. From Fig. 5, it is found that the KAS plots resemble the linear behavior. The values of A are determined from the intercept of those KAS plots by using the first-order reaction model ($f'(\alpha) = 1 - \alpha$) because the ROP of cyclic ester is the first-order reaction with respect to monomer concentration [8]. From Fig. 5, the plots of E_a values for the ROP of ε-CL initiated by DBTML at different monomer conversions are illustrated in Fig. 6.

From Fig. 6, the E_a values for the ROP of ε-CL initiated by 4.0 mol% of DBTML are lower than 3.0 mol% for the whole stage of polymerization. This clearly demonstrates that the reactivity of DBTML in the ROP of ε-CL increases with increasing

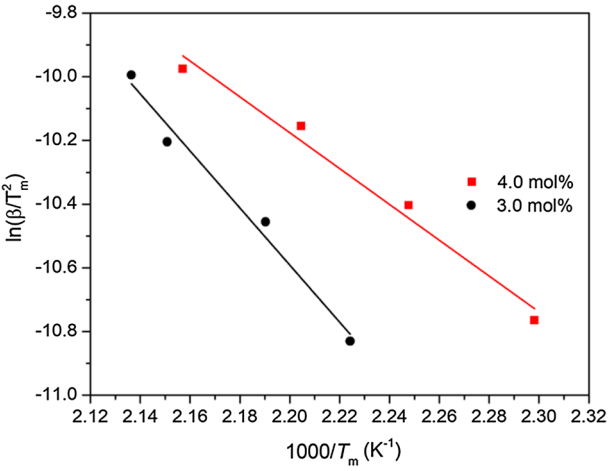

Fig. 4 Plots of $\ln(\beta/T_m^2)$ against $1000/T_m$ based on the Kissinger method for the ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML

DBTML concentration due to the higher amount of Sn–O active center presented in reaction mixture. The kinetic parameters for the ROP of ε-CL initiated by DBTML obtained from the peak method of Kissinger and the isoconversional method of KAS are summarized in Table 1.

From Table 1, it is found that the values of polymerization half-life ($t_{1/2}$) decrease with increasing heating rates and DBTML concentration. Furthermore, the values of E_a and A for the ROP of ε-CL initiated by 3.0 mol% of DBTML are higher than 4.0 mol%. The obtained results demonstrate that the rate ε-CL polymerization increases with increasing DBTML concentration [8]. Moreover, the ROP of ε-CL seems to be controlled by DBTML concentration. This may be implied that the DBTML initiator can be used to control the polymerization of ε-CL under solvent-free condition. The non-isothermal kinetics results from DSC may be useful for designing the effective synthesis process of poly(ε-caprolactone) (PCL) that will be described in the polymer synthesis part.

After understanding the polymerization kinetics by non-isothermal DSC, the mechanism of the ROP of ε-CL initiated by DBTML is also investigated and studied for the first time. To investigate the polymerization mechanism, the crude PCL sample obtained from the non-isothermal DSC polymerization of ε-CL with 3.0 mol% of DBTML at a heating rate of 6 °C/min is analyzed by 500 MHz ^{1}H-NMR technique and the obtained spectrum is illustrated in Fig. 7. From Fig. 7, the assignments for ^{1}H-NMR spectrum are summarized as following: (i) the multiplet signal from methyl ($–CH_3$) end groups at 0.90 ppm (a,h) [8], (ii) the multiplet signal from methylene proton ($–CH_2–$) at 1.25–1.65 ppm (b, c, d, e, f, g, j, k, l, o, p, q, v, w, x, a_1, b_1, c_1) [23], (iii) the triplet signal from methylene proton ($–CH_2–CO–$) connected to carbonyl carbon of PCL chain at 2.30 ppm (m,r,u,z) [25], (iv) the triplet signal from methylene proton ($–CH_2–O–Sn–$) adjacent to Sn–O bond at 3.65 ppm (i,d_1) [26, 27], (v) the triplet signal from methylene

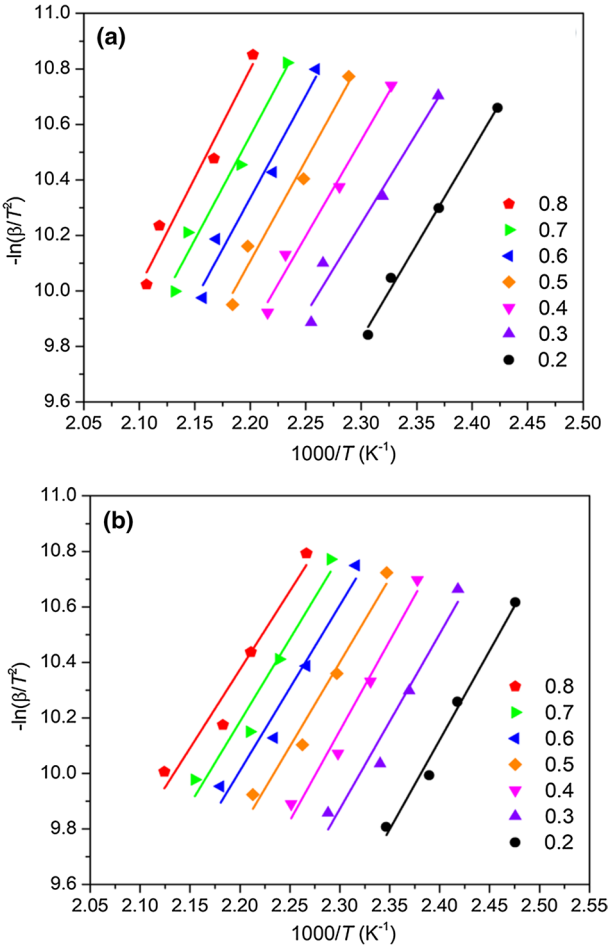

Fig. 5 KAS plots of $\ln(\beta/T^2)$ against $1000/T$ for the ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML at different stages of polymerization

proton ($-CH_2-$) connected to carbonyl oxygen ($-CH_2-O-CO-$) at 4.05 ppm (n,y) [25], and (vi) the doublet signal from alkenyl proton (–CH=CH–) at 5.35 ppm (s,t). From these assignments, it is found that the signals from the ^{1}H-NMR spectrum correspond, and fit the chemical structure of crude PCL. From these results, the mechanism for the ROP of ε-CL with DBTML under bulk condition is proposed through the coordination-insertion mechanism as depicted in Fig. 8.

From Fig. 8, the polymerization starts with the coordination of the carbonyl group of the ε-CL ring with the –Sn–O– bond in DBTML resulting in more reactive carbonyl carbon of ε-CL [1–3, 28]. Then, the insertion process occurs by the nucleophilic attack of oxygen of Sn–O to this carbonyl carbon causing the ring-opening by acyl-oxygen bond cleavage. From this step, the ε-CL will insert

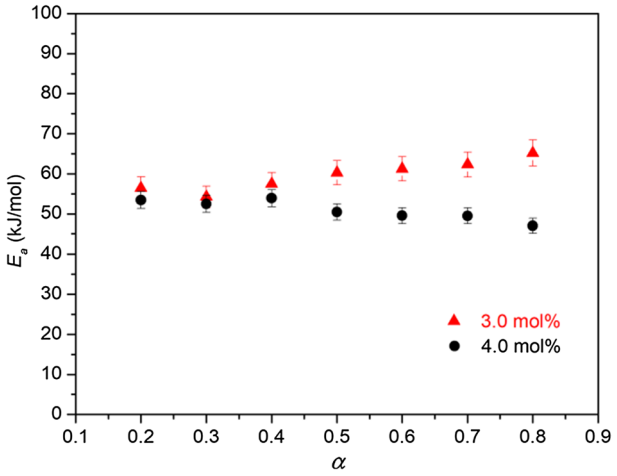

Fig. 6 Plots of E_a against α for the ROP of ε-CL initiated by 3.0 and 4.0 mol% of DBTML at different monomer conversions

Table 1 Kinetic parameters obtained from the non-isothermal DSC polymerization of ε-CL with 3.0 and 4.0 mol% of DBTML

[DBTML] (mol%)	β (°C/min)	T_m (°C)	$t_{1/2}$ [a] (min)	E_a [b] (kJ/mol)	E_a [c] (kJ/mol)	A [d] (min^{-1})
3.0	4	176.5	36.0	74.7	59.6	7.4×10^6
	6	183.4	25.3			
	8	191.8	20.4			
	10	194.9	16.5			
4.0	4	162.0	33.4	46.8	50.9	7.3×10^5
	6	171.7	23.7			
	8	180.4	18.5			
	10	190.4	16.0			

[a] $t_{1/2}$ is the time required to reach 50% of polymerization

[b] Determined from the peak method of Kissinger

[c] The average value of E_a obtained from the KAS isoconversional method

[d] The average values obtained from Eq. (5) and using first-order reaction model ($f(\alpha)=1-\alpha$)

into the DBTML molecule yielding the propagating species with a reactive Sn–O bond. This bond can further react with carbonyl carbon of another ε-CL molecule via the same mechanism. For the propagation process, other ε-CL molecules are coordinated and inserted into this propagating species resulting in the formation of long cyclic PCL. After the purification process, this cyclic PCL will be converted to a linear PCL. After a complete understanding of the kinetics and mechanism of ROP of ε-CL with DBTML initiator, the potential of DBTML in the

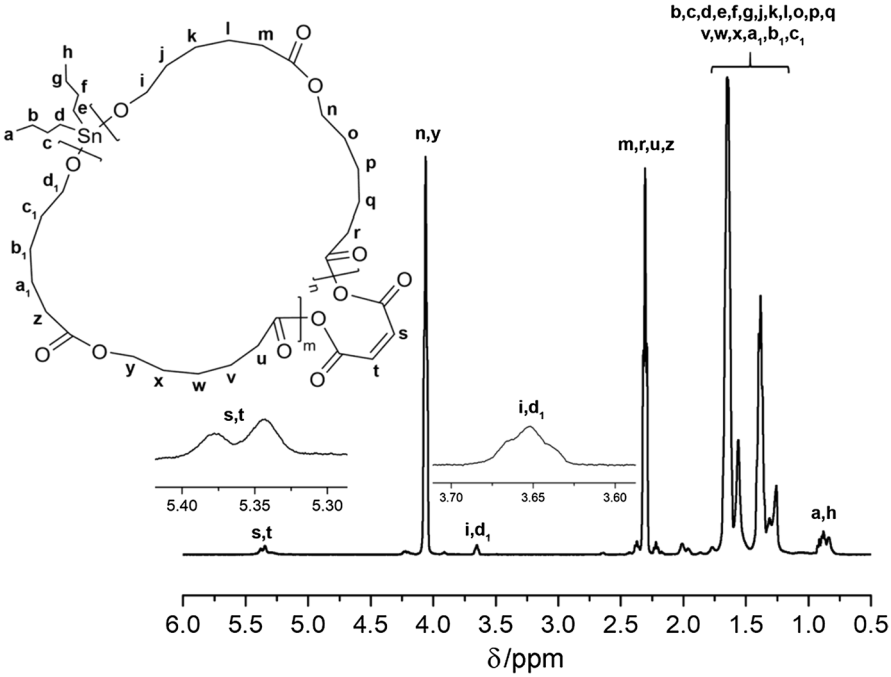

Fig. 7 500 MHz ^{1}H-NMR spectrum of crude PCL obtained from the non-isothermal ROP of ε-CL initiated by 3.0 mol% of DBTML at a heating rate of 6 °C/min

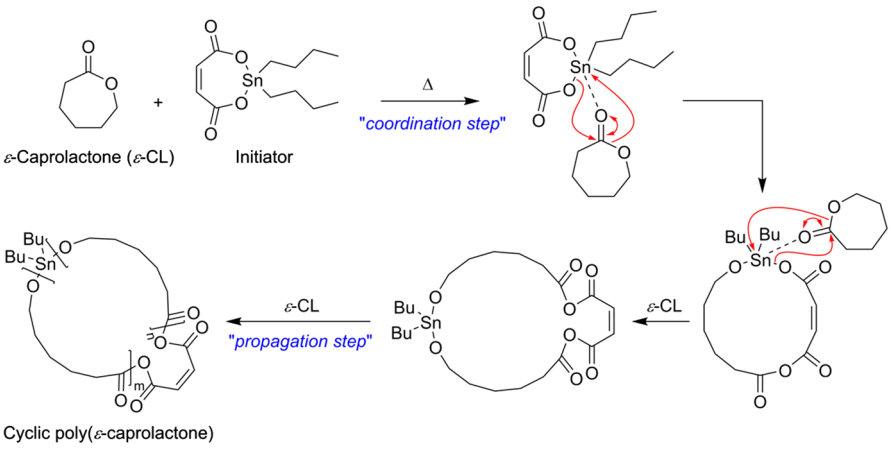

Fig. 8 The coordination-insertion mechanism for the solvent-free ROP of ε-CL initiated by DBTML

synthesis of PCL will be investigated by solvent-free polymerization as shown in the following section.

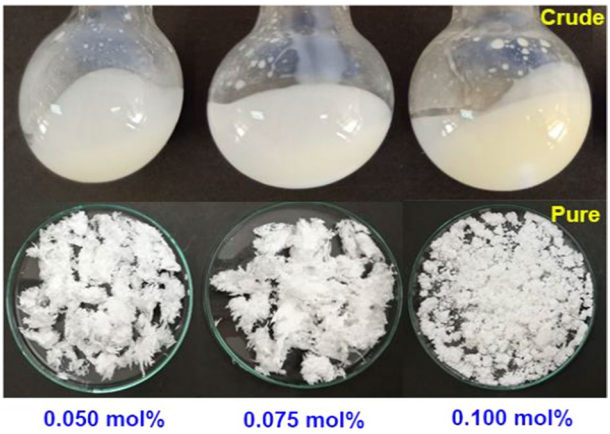

Fig. 9 Physical appearances of crude and pure poly(ε-caprolactone) obtained from solvent-free ROP of ε-CL with different concentrations of DBTML at 150 °C for 24 h

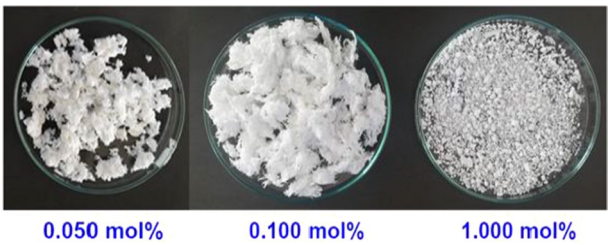

Fig. 10 Physical appearances of crude and pure poly(ε-caprolactone) obtained from solvent-free ROP of ε-CL with different concentrations of DBTML at 150 °C for 48 h

Synthesis of biodegradable poly(ε-caprolactone) via solvent-free polymerization

The efficiency of the DBTML initiator in the synthesis of biodegradable PCL is firstly investigated via solvent-free polymerization. As observed in the kinetics analysis, it is found that DBTML acted as a slow initiator due to its high concentration is required to drive the ROP of ε-CL to occur under the condition used in non-isothermal DSC measurement. This may be caused by the steric interference from two *n*-butyl groups around the Sn–O active center of DBTML. From our previous studies [24], a higher polymerization temperature is needed for a slow initiator. This means that each type of initiator requires a suitable temperature for polymer synthesis. For the synthesis of PCL, the ROP of ε-CL with different concentrations of DBTML is conducted at 150 °C for 24 h. The physical appearance of the obtained crude and purified PCLs is depicted in Fig. 9.

From Fig. 9, the obtained crude PCLs are white to pale yellow solid. After purification by methanol, the pure PCLs are in the form of white powder to fiber. The results significantly show the dependency of PCL physical appearance on the DBTML

Table 2 GPC results and %yield of PCL synthesized from solvent-free ROP of ε-CL with DBTML at 150 °C for 24 and 48 h

T (°C)	t (h)	[DBTML][a] (mol%)	M_n[b] (g/mol)	M_w[b] (g/mol)	PDI[b]	%yield (%)[c]
150	24	0.050	2.60×10^4	5.08×10^4	1.95	93
150	24	0.075	2.72×10^4	5.15×10^4	1.90	94
150	24	0.100	1.90×10^4	3.76×10^4	1.98	84
150	48	0.050	2.81×10^4	5.04×10^4	1.79	93
150	48	0.100	2.67×10^4	4.96×10^4	1.86	92
150	48	1.000	9.81×10^3	1.49×10^4	1.52	68

[a]The initial DBTML concentration

[b]Obtained from GPC technique using THF as eluent and processing temperature of 35 °C

[c]Determined from the weight of purified PCL after purification and drying processes

concentration. This may also be related to the PCL molecular weight that will be described afterward. From Fig. 9, the polymerization time is modified from 24 to 48 h to test the possibility of improving the synthesis process. The physical appearance of the obtained PCLs from the ROP of ε-CL with DBTML at 150 °C for 48 h is depicted in Fig. 10. From Fig. 10, it is found that the physical appearance of pure PCL also varies from white powder to fiber. These results can be implying that the fiber shape of PCL relates to the longer PCL chain (higher PCL molecular weight). From Figs. 9 and 10, the obtained pure PCLs are further analyzed by GPC technique using THF as eluent and the results from GPC analysis are summarized in Table 2.

From Table 2, the molecular weight of PCL seems to be controlled by DBTML concentration. The molecular weight of PCL increases with decreasing DBTML concentration similar to the literature [8, 24]. At a low concentration of DBTML (0.050 mol%) and polymerization time of 24 h, the molecular weight of PCL is lower than 0.075 mol% indicating an insufficient DBTML concentration for producing a higher molecular weight of PCL. At 150 °C and 24 h, high molecular weight ($M_w = 5.15\times10^4$ g/mol) and %yield (94%) of PCL is obtained at DBTML concentration of 0.075 mol%. We try to improve the molecular weight of PCL by increasing the polymerization time from 24 to 48 h. It is found that high molecular weight ($M_w = 5.04\times10^4$ g/mol) PCL can be obtained at a lower DBTML concentration (0.050 mol%) with 93% of yield. This indicates that DBTML can produce high molecular weight PCL at low concentration under suitable synthesis conditions. However, the values of PDI for all synthesized PCLs are in the range of 1.52–1.98. This may be indicated that the transesterification, a side reaction, occurred in our synthesis process.

Conclusions

DBTML was successfully and firstly used as a new initiator for the ROP of ε-CL under solvent-free conditions. The initiating performance of DBTML was completely investigated by the non-isothermal DSC technique. From non-isothermal

DSC measurement, DBTML could effectively control the polymerization of ε-CL. The values of E_a and A for the ROP of ε-CL with 4.0 mol% were lower than 3.0 mol%. This demonstrated that the reactivity of DBTML in the ROP of ε-CL increased with increasing its concentration. From ^{1}H-NMR analysis, the polymerization mechanism for the ROP of ε-CL with this new DBTML initiator was successfully described and proposed by the coordination-insertion mechanism. From biodegradable PCL synthesis, DBTML could produce high molecular weight ($M_w = 5.15 \times 10^4$ g/mol) and high %yield (94%) of PCL at low DBTML concentration. Furthermore, the increasing polymerization time could also improve the molecular weight of PCL at low DBTML concentration. From the overall results, it could be concluded that DBTML was considered as an effective initiator that could control the polymerization rate and molecular weight of the polymer. Moreover, DBTML could also be utilized at low concentrations for synthesizing biodegradable PCL. The obtained results from this work were useful and could be applied to other monomers that still working in our laboratory.

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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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