

Kinetics and thermodynamics analysis for ring-opening polymerization of ϵ -caprolactone initiated by tributyltin *n*-butoxide using differential scanning calorimetry

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Abstract The bulk ring-opening polymerizations (ROP) of ϵ -caprolactone (ϵ -CL) initiated by synthesized tributyltin *n*-butoxide ($n\text{Bu}_3\text{SnOnBu}$) initiator were conducted at 120 °C and the molecular mass and polydispersity index of poly(ϵ -CL), PCL, were determined. The coordination-insertion ROP of ϵ -CL was confirmed by $^1\text{H-NMR}$. The molecular mass of PCL was successfully controlled with monomer to initiator concentration ratio. The kinetics and thermodynamics of ROP were investigated by differential scanning calorimetry (DSC) using both non-isothermal and isothermal methods. From the non-isothermal method, the activation energy (E_a) of ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ was derived from the method of Kissinger (78.3, 61.1, and 59.9 kJ mol $^{-1}$) and Ozawa (82.8, 66.2, and 64.9 kJ mol $^{-1}$). For isothermal method, the values of E_a for these three concentrations of $n\text{Bu}_3\text{SnOnBu}$ were 74.2, 65.8, and 62.0 kJ mol $^{-1}$, respectively. The first-order reaction model was employed to determine the apparent rate constant (k_{app}). The degree of aggregation (m) of $n\text{Bu}_3\text{SnOnBu}$ in ϵ -CL was also determined using isothermal method which confirmed its non-aggregated form. In addition, the activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were estimated to be 70.5 kJ mol $^{-1}$ and $-100.3 \text{ J mol}^{-1} \text{ K}^{-1}$ by isothermal DSC. The Friedman, Kissinger–Akahira–Sunose, and

Flynn–Wall–Ozawa isoconversional methods were also applied to non-isothermal DSC data to investigate the dependence of E_a with monomer conversion (α). The results of all three methods were discussed and compared with isothermal and non-isothermal methods at 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$. The overall results demonstrate that DSC is a fast, convenient, and reliable method for studying the kinetics and thermodynamics of ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$.

Keywords Tributyltin *n*-butoxide · ϵ -Caprolactone · Ring-opening polymerization · Differential scanning calorimetry · Kinetics · Thermodynamics

Introduction

Poly(ϵ -caprolactone), PCL, is an attractive class of polyester due to its biocompatibility and biodegradability. PCL is one of the biodegradable polymers used in biomedical and pharmaceutical industries as a resorbable material and drug delivery systems [1]. PCL can be normally synthesized by ring-opening polymerization (ROP), in which high molecular mass can be obtained by a conventional coordination-insertion ROP of ϵ -caprolactone (ϵ -CL) monomer with metal alkoxide initiators or metal carboxylate [2, 3]. A large variety of metal alkoxide initiators with different oxidation states have been reported for ROP of cyclic ester monomers such as Al [4], Zn [5], Mg [6], Ti [7, 8], Sn [9–14]. Among these, organotin initiators have been widely used in industrial applications and academic research, especially for tin(IV) alkoxides. Tin(IV) alkoxides such as tributyltin alkoxides ($n\text{Bu}_3\text{SnOR}$), dibutyltin dialkoxides ($n\text{Bu}_2\text{Sn}(\text{OR})_2$) [9], and cycloctin(IV) alkoxides [10], which contain a reactive

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Sn–O bond, can effectively initiate the coordination-insertion ROP of ε -CL. Kricheldorf and co-workers [11] reported the efficiency of tributyltin derivatives such as tributyltin methoxide ($n\text{Bu}_3\text{SnOMe}$), tributyltin chloride ($n\text{Bu}_3\text{SnCl}$), tributyltin acetate ($n\text{Bu}_3\text{SnOAc}$), and tributyltin thioacetate ($n\text{Bu}_3\text{SnSAc}$) in the bulk polymerization of ε -CL. These $n\text{Bu}_3\text{SnOR}$ are an attractive class of initiators because they can be easily synthesized by the nucleophilic substitution of tributyltin chloride. Moreover, they are more stable to oxygen and soluble in common organic solvents [9, 11]. Also, the syndiotactic of desirable polyester can be effectively controlled using $n\text{Bu}_3\text{SnOMe}$ [15, 16]. However, there are a few reports on the kinetics of ROP of cyclic ester monomers initiated by $n\text{Bu}_3\text{SnOR}$ [9, 11], therefore their kinetic information is needed for more understanding on their catalytic behavior. In previous reports [9, 11], only $^1\text{H-NMR}$ as a time consuming technique was used to determine kinetic parameters such as % conversion ($\% \alpha$), rate constant of polymerization (k_p), and half-life of polymerization ($t_{1/2}$). But an activation energy (E_a) has not been reported before, due to the complicated processes of E_a determination from the $^1\text{H-NMR}$ technique. Thus, in this present work, an effective differential scanning calorimetry (DSC) technique is introduced to determine both kinetic and thermodynamic parameters of ROP of ε -CL.

Recently, DSC has been used to study the kinetics of ROP of cyclic ester monomers [17–20]. DSC provides a continuous history of the heat evolved during the polymerization which can be analyzed kinetically, either by the isothermal or non-isothermal methods. These two methods can be used to determine various useful kinetic and thermodynamic parameters. Isoconversional methods have been applied to non-isothermal kinetic data in order to investigate the dependence of E_a on monomer conversion (α) [7, 21–23]. To our best knowledge, the kinetics and thermodynamics information of ROP of ε -CL initiated by the synthesized $n\text{Bu}_3\text{SnOnBu}$ using DSC has not been reported before.

In this work, we are the first to report both the isothermal and non-isothermal DSC methods on investigation of the bulk ROP of ε -CL initiated by various concentrations of the synthesized $n\text{Bu}_3\text{SnOnBu}$. The kinetic parameters such as apparent rate constants (k_{app}), degree of aggregation (m), and E_a were determined. The dependence of E_a with monomer conversion as polymerization proceeds was observed by the Friedman [24], Kissinger–Akahira–Sunose (KAS) [25] and Flynn–Wall–Ozawa (FWO) [26–28] isoconversional methods. In addition, the thermodynamic parameters such as activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were determined by isothermal DSC technique.

Experimental

Materials

Commercial ε -CL monomer (Acros Organics) was purified by fractional distillation under reduced pressure over calcium hydride. Toluene (Carlo Erba) and *n*-butanol (Sigma-Aldrich) were purified by distillation over sodium metal. Tributyltin chloride (Acros Organics) was used as received without purification.

Synthesis of tributyltin *n*-butoxide

Tributyltin *n*-butoxide ($n\text{Bu}_3\text{SnOnBu}$) was synthesized by the nucleophilic substitution of tributyltin chloride ($n\text{Bu}_3\text{SnCl}$) by sodium *n*-butoxide (NaOnBu) in dry toluene. The reaction mixture was heated and then refluxed for 6 h as described in literature [29]. The obtained $n\text{Bu}_3\text{SnOnBu}$ was purified by vacuum distillation and its identification was confirmed by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) on a Bruker DPX-400 NMR spectrometer operating at 400 MHz in deuterated chloroform (CDCl_3).

DSC measurements

Non-isothermal method

Kinetic studies of the ROP of ε -CL initiated by 1.0, 1.5, and 2.0 mol% of synthesized $n\text{Bu}_3\text{SnOnBu}$ were carried out by means of DSC (Perkin–Elmer DSC-7). For each sample, about 6–10 mg was accurately weighed into an aluminum pan and then hermetically sealed. The samples were heated over temperature range of 20–300 °C at heating rates of 5, 10, 15, and 20 °C min^{-1} under a nitrogen atmosphere in order to observe the amount of heat liberated from the polymerization reaction. The E_a was determined by the methods of Kissinger and Ozawa. The dependence of E_a with monomer conversion was analyzed by the Friedman, KAS, and FWO isoconversional methods.

Isothermal method

For isothermal DSC polymerization, the sample was prepared similar to the non-isothermal method. The samples were held for 4 h to ensure the completion of polymerization at selected temperatures, which predicted from non-isothermal experiments (temperature prior to exotherm start). For thermodynamic studies, the k_{app} determined from the isothermal method was used to estimate the thermodynamic parameters for ROP of ε -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$. The m value was determined

from isothermal DSC polymerization of ϵ -CL initiated by 0.5–2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 165 °C.

Bulk polymerization of ϵ -caprolactone

ϵ -CL monomer with 0.125, 0.250, 0.500, and 1.000 mol% of $n\text{Bu}_3\text{SnOnBu}$ initiator were weighed into dry glass vials and capped in a controlled atmosphere glove box under dry nitrogen. The reaction vials were immersed in a pre-heated silicone oil bath at a constant temperature of 120 °C for 72 h. At the end of polymerization, the vials were immersed into the ice bath to stop the polymerization reaction. Then, the obtained crude PCLs were dissolved in chloroform and re-precipitated in cold methanol before drying in a vacuum oven at 45 °C until the constant mass. The molecular mass and polydispersity index (PDI) of the synthesized PCLs were determined by Water e2695 gel permeation chromatography (GPC) at 35 °C with refractive index and viscosity detectors. Tetrahydrofuran (THF) was used as an eluent with flow rate of 1.0 mL min⁻¹.

Poly(ϵ -caprolactone)s characterization

The obtained crude PCLs were characterized using a Bruker DPX-400 NMR spectrometer. Spectra were recorded using 5 mm o.d. tubes, deuterated chloroform as solvent and tetramethylsilane (TMS) as the internal standard at room temperature. The ¹H-NMR spectra were recorded at a resonance frequency with 32 scans, a 3.5 s acquisition time and a 6 μ s pulse width.

Non-isothermal and isothermal DSC data analysis

ROP of cyclic ester monomers is exothermic due to the covalent bond formation of monomers. The heat released from polymerization can be observed by exothermic curve of DSC. The kinetic of ROP can be investigated by both non-isothermal and isothermal methods. For non-isothermal DSC experiment, ROP occurred under different constant heating rates. The onset temperature of polymerization increases with increasing heating rate resulting in a shift of the exothermic peak to a higher temperature range. The fraction of monomer conversion (α) can be determined from the heat released at any time (ΔH_t) divided by total heat of polymerization (ΔH_{total}). The E_a can be determined by the methods of Kissinger and Ozawa [30–35]. The Kissinger method is based on the relationship between the heating rate (β) and the temperature at maximum rate of polymerization (T_m) which is shown in Eq. (1).

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

Therefore, the value of E_a can be obtained from the slope of a plot of $\ln(\beta/T_m^2)$ against $1/T_m$, where R is the gas constant. For Ozawa method, Doyle's approximation of $\log p(x) \cong -2.315 - 0.457E_a/RT$ for $x = E_a/RT > 20$ is used and the relationship of $\log \beta$ and $1/T_m$ yields the following Eq. (2).

$$\log \beta = \text{constant} - 0.457 \frac{E_a}{RT_m} \quad (2)$$

Nowadays, isoconversional methods have been applied to non-isothermal kinetics data to investigate the dependence of E_a with α . These methods allow multiple step processes to be detected via the dependence of E_a with α [21].

Friedman [24] showed the relationship of the natural logarithm of reaction rate, $\ln(d\alpha/dt)$, as a function of the reciprocal temperature, as shown in Eq. (3). This equation enables the E_a to be determined for each fraction of α , where A is the frequency factor and $f(\alpha)$ is the function of monomer conversion.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Af(\alpha)) - \frac{E_a}{RT} \quad (3)$$

This equation also implies that the reaction rate is only a function of temperature at a constant value of α . Therefore, E_a can be simply obtained from the slope of the plot of $\ln(d\alpha/dt)$ against $1/T$.

KAS method [25] is based on a linear relationship between $\ln(\beta/T^2)$ and the inverse of the temperature ($1/T$).

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{-RAf'(\alpha)}{E_a}\right) - \frac{E_a}{RT} \quad (4)$$

From Eq. (4), E_a can be determined from the slope of the plot of $\ln(\beta/T^2)$ against $1/T$. This method does not require knowledge of $f'(\alpha)$ and it only assumes that the process follows the same mechanism for a given conversion regardless of the polymerization temperature.

FWO method [26–28] using Doyle's approximation of the temperature integral is possible to obtain a complete evaluation of E_a throughout the whole conversion as shown in Eqs. (5) and (6).

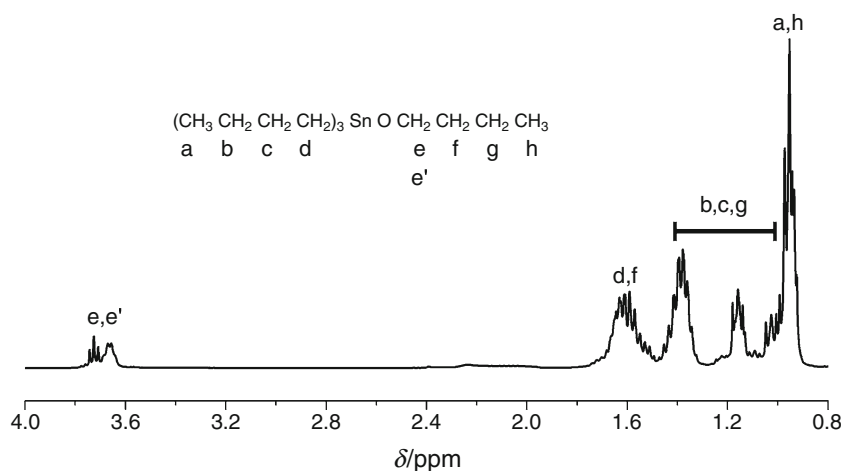
$$\ln \beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (5)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (6)$$

where $g(\alpha)$ is the integral conversion function. For a constant α , the E_a can be determined from the slope of the plot of $\ln \beta$ versus $1/T$.

To support the kinetic results from non-isothermal method, the isothermal method is used to determine the

Fig. 1 $^1\text{H-NMR}$ spectrum of the synthesized $n\text{Bu}_3\text{SnOnBu}$ initiator in CDCl_3



kinetic parameters for ROP of cyclic ester monomer as previously reported [17, 18]. The polymerization of lactones and lactides using metal alkoxides initiator is a first-order reaction with respect to monomer concentration as described in previous works [35–38]. So, the first-order reaction model was employed to determine the k_{app} as shown in Eq. (7) [17]. E_a can be derived from the Arrhenius equation (when $k_{\text{app}} = A_{\text{exp}}(-E_a/RT)$) in Eq. (8).

$$-\ln(1-\alpha) = k_{\text{app}}t \quad (7)$$

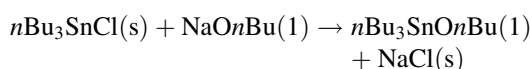
$$-\ln(1-\alpha) = A_{\text{exp}}\left(-\frac{E_a}{RT}\right)t \quad (8)$$

where α is the fraction of monomer conversion, A is the frequency factor, R is the gas constant, and t is the polymerization time.

Results and discussion

Synthesis and characterization of tributyltin *n*-butoxide initiator

The $n\text{Bu}_3\text{SnOnBu}$ initiator can be synthesized by the nucleophilic substitution of $n\text{Bu}_3\text{SnCl}$ with NaOnBu in dry toluene as shown in the reaction below.



The NaCl was precipitated out from the solution and the crude $n\text{Bu}_3\text{SnOnBu}$ was obtained and purified by vacuum distillation resulting in 76 % yield. The purified $n\text{Bu}_3\text{SnOnBu}$ is characterized by $^1\text{H-NMR}$ as shown in Fig. 1.

From Fig. 1 the proton chemical shift of 0.90 ppm (a, h) is the triplet of methyl chain end ($-\text{CH}_3$), 0.95–1.60 ppm (b, c, d, f, g) is the multiplet of methylene proton ($-\text{CH}_2-$) of four *n*-butyl groups and 3.65–3.70 ppm (e, e') is the triplet of

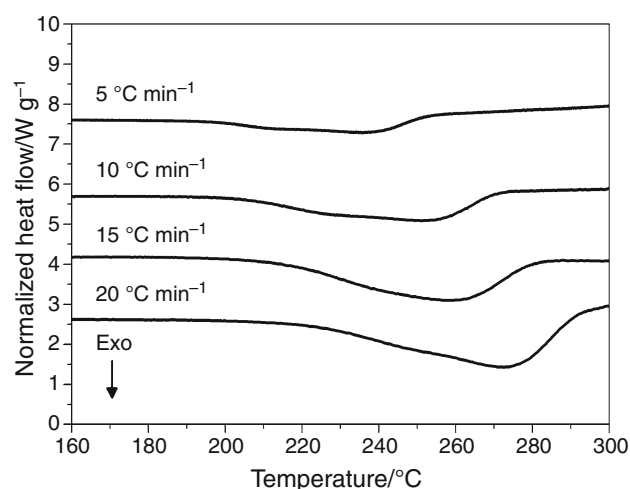


Fig. 2 Non-isothermal DSC curves for ROP of $\epsilon\text{-CL}$ at heating rates of 5, 10, 15, and 20 $^\circ\text{C min}^{-1}$ initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$

methylene proton connected to oxygen ($-\text{O}-\text{CH}_2-$). The chemical shift in the range from 3.60 to 3.70 ppm shows two complex peaks which may be caused by the aggregation of $n\text{Bu}_3\text{SnOnBu}$. However, in the polymerization process, the aggregation of $n\text{Bu}_3\text{SnOnBu}$ should be decreased by the solubilization of monomer which is described later in the determination of the degree of aggregation of $n\text{Bu}_3\text{SnOnBu}$ section.

Kinetic analysis for ROP of $\epsilon\text{-CL}$ initiated by tributyltin *n*-butoxide initiator

The polymerization measurement under dynamic condition provides a good alternative means of obtaining useful kinetic information over different temperature ranges. For non-isothermal DSC polymerization, each sample was heated from 20 to 300 $^\circ\text{C}$ at heating rates of 5, 10, 15, and

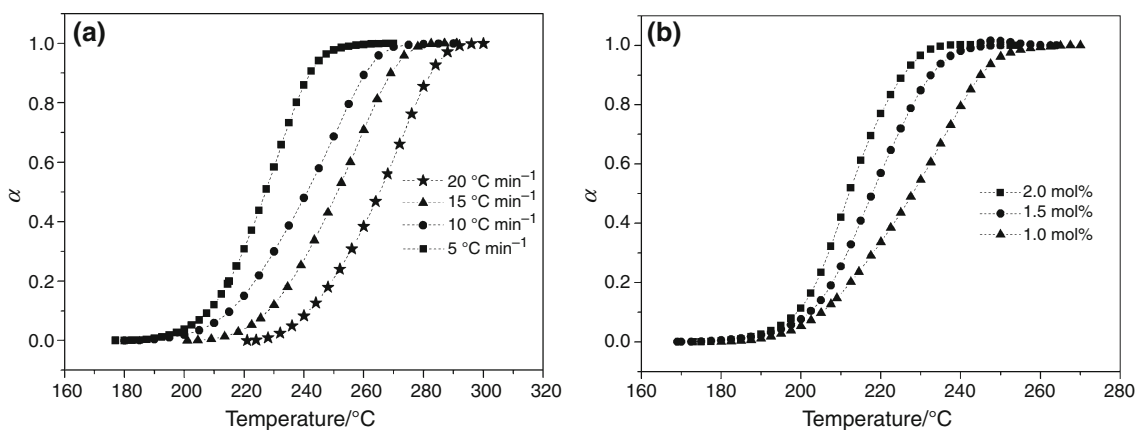


Fig. 3 Plots of monomer conversion as a function of polymerization temperature at different heating rates for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ (a) and plots of conversion as a function of

polymerization temperature of ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at heating rate of $5\text{ }^\circ\text{C min}^{-1}$ (b)

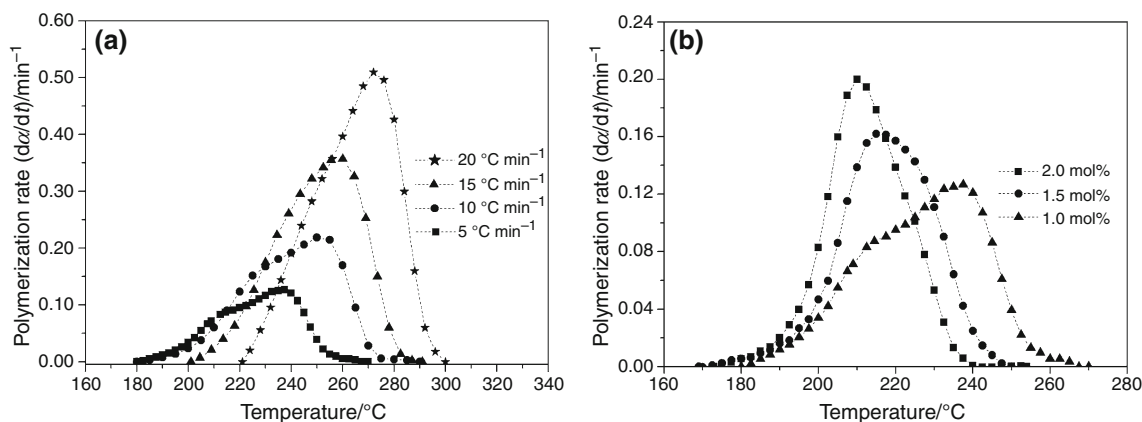


Fig. 4 Plots of reaction rate as a function of polymerization temperature at different heating rates for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ (a) and plots of reaction rate as a function

of polymerization temperature of ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at heating rate of $5\text{ }^\circ\text{C min}^{-1}$ (b)

$20\text{ }^\circ\text{C min}^{-1}$ and the obtained DSC curves are shown in Fig. 2. The average heats of ROP of ϵ -CL using 1.0, 1.5, and 2.0 mol% $n\text{Bu}_3\text{SnOnBu}$ initiator are 172.3, 176.1, 165.7 J g^{-1} , respectively.

From Fig. 2, under dynamic condition the temperatures at which the reaction starts and completes increase with increasing of heating rate as does the size of exothermic peak. As the initiator concentration increases, the polymerization exotherms shift to lower temperature range at all heating rates indicating the higher rate of polymerization. Moreover, each DSC curve shows broad exotherm which may be caused by the slow propagation (r_p) rate because this initiator contains only one active site (Sn-O) with three n -butyl groups which reduce the nucleophilic strength of initiator and cause the steric effect in the coordination of monomer. Although, the size of exothermic peak and the reaction rate increases with increasing heating rate, the time to complete polymerization decreases. At low

heating rates, the calorimetric signal is small, but the polymerization time is long. The opposite result occurs at higher heating rates when the liberation of heat accompanying polymerization reduces the time to complete reaction.

These are in good agreement with our previous work [7], which are clearly supported by the plots of monomer conversion as a function of polymerization temperature as shown in Fig. 3. The results showed that the polymerization completed faster at higher heating rate for all initiator concentrations. At the constant heating rate of $5\text{ }^\circ\text{C min}^{-1}$ as shown in Fig. 3(b), the polymerization was found to complete faster at higher $n\text{Bu}_3\text{SnOnBu}$ concentrations.

To support the effect of heating rate and initiator concentration, plots of polymerization rate as a function of polymerization temperature are shown in Fig. 4.

The results in Fig. 4(a) show that the rate of polymerization increased with increasing of the heating rate because

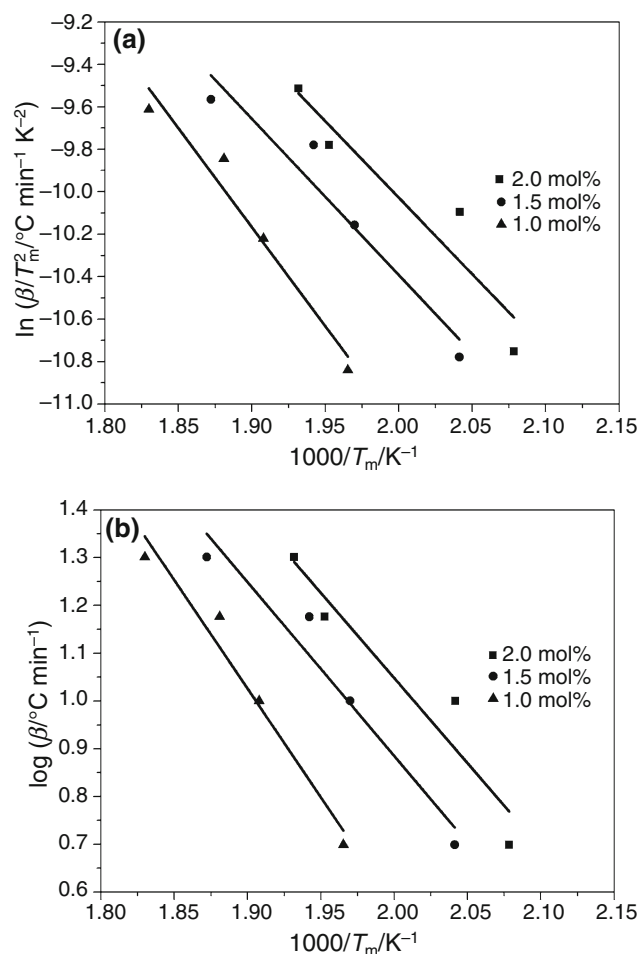


Fig. 5 Plots of $\ln(\beta/T_m^2)$ (a) and $\log(\beta)$ (b) against $1,000/T_m$ based on the methods of Kissinger and Ozawa for activation energy determination of ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$

the polymerization shifts to higher temperature range, related to the higher energy obtained in system. The dependency of the polymerization rate with the heating rate shown in Fig. 4(a) is similar to the polymerization of ϵ -CL with 1.5 and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$. In Fig. 4(b), as a concentration of $n\text{Bu}_3\text{SnOnBu}$ increased at heating rate of $5\text{ }^\circ\text{C min}^{-1}$, the reaction rate was found to increase due to the more active site (Sn–O) available to initiate ROP of ϵ -CL.

The values of E_a and ΔH_{total} are determined by the plots of Kissinger (Eq. (1)) and Ozawa (Eq. (2)) methods as shown in Fig. 5. The obtained values of E_a , summarized in Table 1, were used to compare and support the influence of initiator concentration on polymerization rate.

From Table 1, T_m increased with heating rate but decreased when the concentration of the initiator increased. In addition, the values of E_a determined from Kissinger method are lower than that of Ozawa method at all initiator concentrations. This is not clear for the difference in E_a values, but the small variation in E_a compared in each initiator concentration is probably caused by the difference in mathematic approximation which is used in each method. However, the obtained E_a from each method gave the same trend on the decrease in E_a as the increasing initiator concentration. So, the increase in concentration of $n\text{Bu}_3\text{SnOnBu}$ has a profound effect on the ROP of ϵ -CL by reducing the energy required to initiate the polymerization. Furthermore, in the non-isothermal condition, the values of collision frequency (A) of monomer with reactive center (Sn–O) increased with increasing of initiator concentration. This finding is similar to the non-isothermal DSC polymerization of glycolide with zinc octoate ($\text{Zn}(\text{Oct})_2$) reported by Mazzaro and co-workers [18].

Table 1 Kinetic parameters for ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ determined for non-isothermal DSC

[I] ₀ /mol%	$\beta/^\circ\text{C min}^{-1}$	$T_m/^\circ\text{C}$	$\Delta H_{\text{total}}/\text{J g}^{-1}$	$E_a/\text{kJ mol}^{-1}$				A^a/s^{-1}
				Kissinger	R^2	Ozawa	R^2	
1.0	5.0	235.7	160.7	78.3	0.975	82.8	0.980	2.2×10^8
	10.0	251.0	166.0					
	15.0	258.5	177.6					
	20.0	273.3	185.0					
1.5	5.0	216.8	165.5	61.1	0.962	66.2	0.970	1.3×10^9
	10.0	234.5	174.2					
	15.0	241.8	178.0					
	20.0	261.0	186.5					
2.0	5.0	210.4	160.6	59.9	0.950	64.9	0.963	8.3×10^9
	10.0	219.2	162.2					
	15.0	241.8	168.0					
	20.0	247.3	172.1					

^a The average values of A determined from Eqs. (3) and (4)

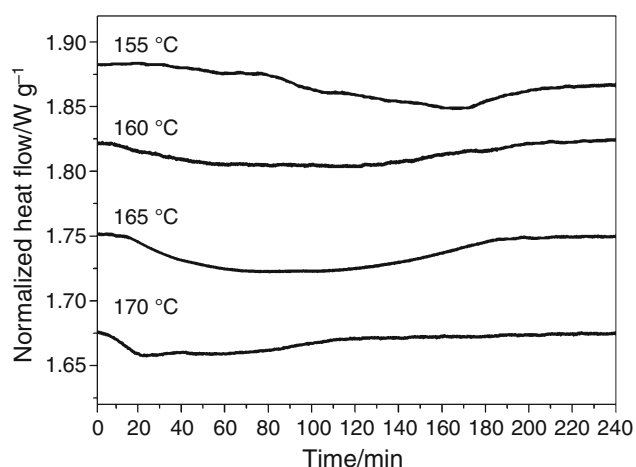


Fig. 6 Isothermal DSC curves for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 155, 160, 165, and 170 °C

To support the kinetic results from non-isothermal DSC data, the isothermal method was used to investigate the initiative behavior of $n\text{Bu}_3\text{SnOnBu}$ in ROP of ϵ -CL. The isothermal DSC curves for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ are shown in Fig. 6.

The same results as non-isothermal DSC method were observed with broad DSC curves showing the slow propagation step. It is worth noting that the polymerization occurred faster at higher temperature; however, polymerization still took longer time to complete due to the slow propagation step as described earlier. Moreover, from isothermal DSC curves shown in Fig. 6, the relationships between the monomer conversion and the polymerization time were plotted and illustrated in Fig. 7. The results from Fig. 7(a) showed that the monomer conversion is generally close to 1 (complete polymerization), faster at higher

temperature due to higher energy obtained in reaction mixture that increased the rate of polymerization. The obtained results from Fig. 7(a) are similar to the polymerization of ϵ -CL with 1.5 and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$. As the concentration of $n\text{Bu}_3\text{SnOnBu}$ increases at 165 °C (Fig. 7(b)), the complete conversion is faster which is similar to the results obtained from non-isothermal method.

From the plots of $-\ln(1-\alpha)$ against polymerization time (Eq. (7)) shown in Fig. 8, the k_{app} was determined from the slope of these plots. This was considered as steady-state of polymerization reaction ($0.2 < \alpha < 0.6$) and diffusion control would not affect the rate of propagation. The first-order rate plots have a good linearity with $R^2 > 0.99$. From the obtained k_{app} , the E_a can be calculated from Arrhenius plots of $-\ln(k_{\text{app}})$ versus $1,000/T$ as shown in Fig. 9. The kinetic parameters determined from isothermal DSC are summarized in Table 2.

From Table 2, the values of k_{app} increased with increasing of temperature and initiator concentration because at higher temperature the initiators and monomers collide each other more frequently with accumulating energy surpassing the E_a resulting in higher k_{app} . At high initiator concentrations, more active sites for polymerization increase the rate of polymerization and reduce the energy required for driving the polymerization to occur. The values of A decreased with increasing of initiator concentration which are similar to the isothermal DSC polymerization of ϵ -CL initiated by Ti(IV) alkoxide reported by Li et al. [17]. The decreasing of E_a as a function of $n\text{Bu}_3\text{SnOnBu}$ concentration from isothermal DSC has the same trend as the results from non-isothermal DSC. The determined E_a values from isothermal method are close to those of non-isothermal method suggesting that the

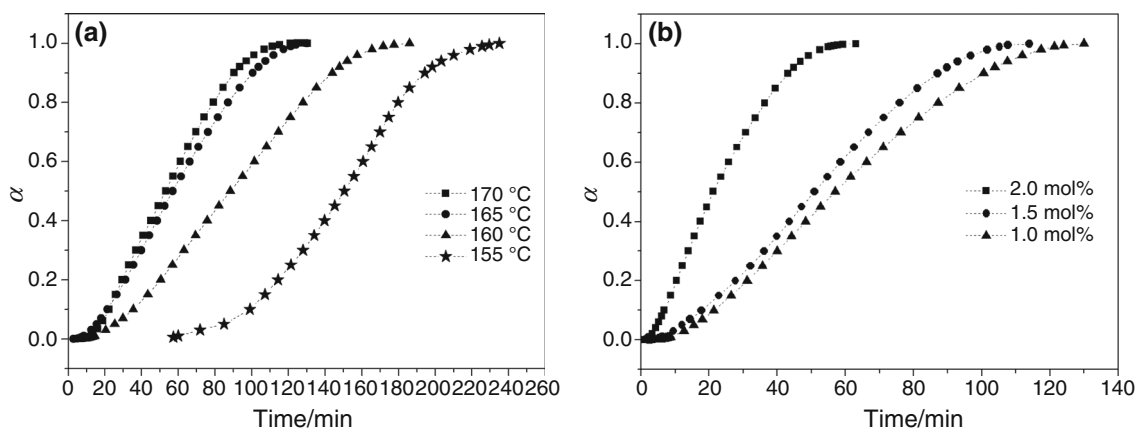


Fig. 7 Plots of monomer conversion as a function of polymerization time for ROP of ϵ -CL at different temperatures initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ (a) and plots of monomer conversion as a function of

polymerization time for ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 165 °C (b)

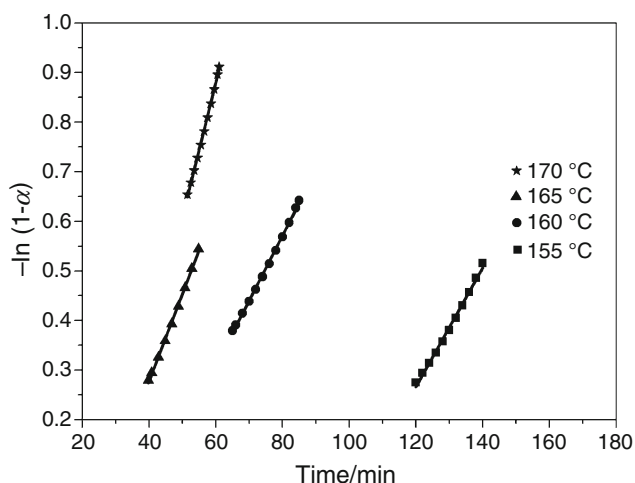


Fig. 8 First-order rate plots for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$: **a** 155, **b** 160, **c** 165, and **d** 170 °C

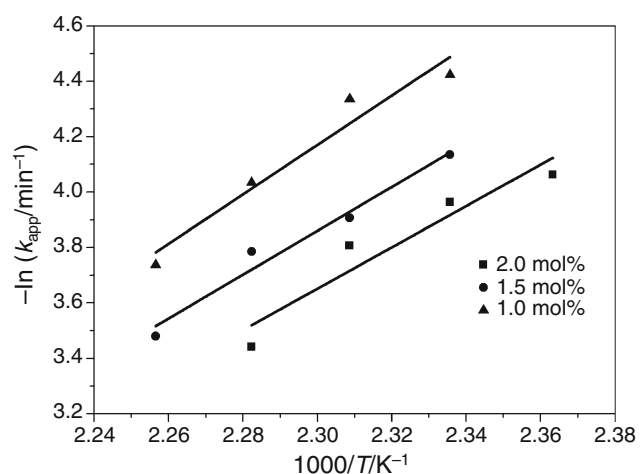


Fig. 9 Arrhenius plots of $-\ln(k_{\text{app}})$ as a function of reciprocal temperature ($1,000/T$) for ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$

DSC method is convenient and reliable to obtain the kinetic parameters especially E_a values of the ROP of ϵ -CL.

Bulk ring-opening polymerization and mechanistic aspect

The ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$ occurs via the conventional coordination-insertion mechanism as shown in Scheme 1. The coordination-insertion mechanism comprises two steps. The first step is the coordination of monomer and initiator molecule by the interaction of carbonyl oxygen of ϵ -CL and the second step is the acyl-oxygen cleavage of ϵ -CL by the attack of $-\text{OnC}_4\text{H}_9$ group, then the new ϵ -CL will insert into the propagating species

Table 2 Kinetic parameters for ROP of ϵ -CL initiated by 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ determined from isothermal DSC

$[I]_0/$ mol%	$T/^\circ\text{C}$	$1,000/T/$ K^{-1}	$k_{\text{app}}/$ min^{-1}	R^2	A/s^{-1a}	$E_a/$ kJ mol^{-1}
1.0	155.0	2.34	0.012	0.996	1.3×10^7	74.2
	160.0	2.31	0.013	0.999		
	165.0	2.28	0.018	0.999		
	170.0	2.26	0.024	0.999		
1.5	155.0	2.34	0.016	0.999	1.7×10^6	65.8
	160.0	2.31	0.020	0.997		
	165.0	2.28	0.023	0.999		
	170.0	2.26	0.031	0.998		
2.0	150.0	2.36	0.017	0.998	7.3×10^5	62.0
	155.0	2.34	0.019	0.998		
	160.0	2.31	0.022	0.999		
	165.0	2.28	0.032	0.999		

^a Determined from Eq. (8)

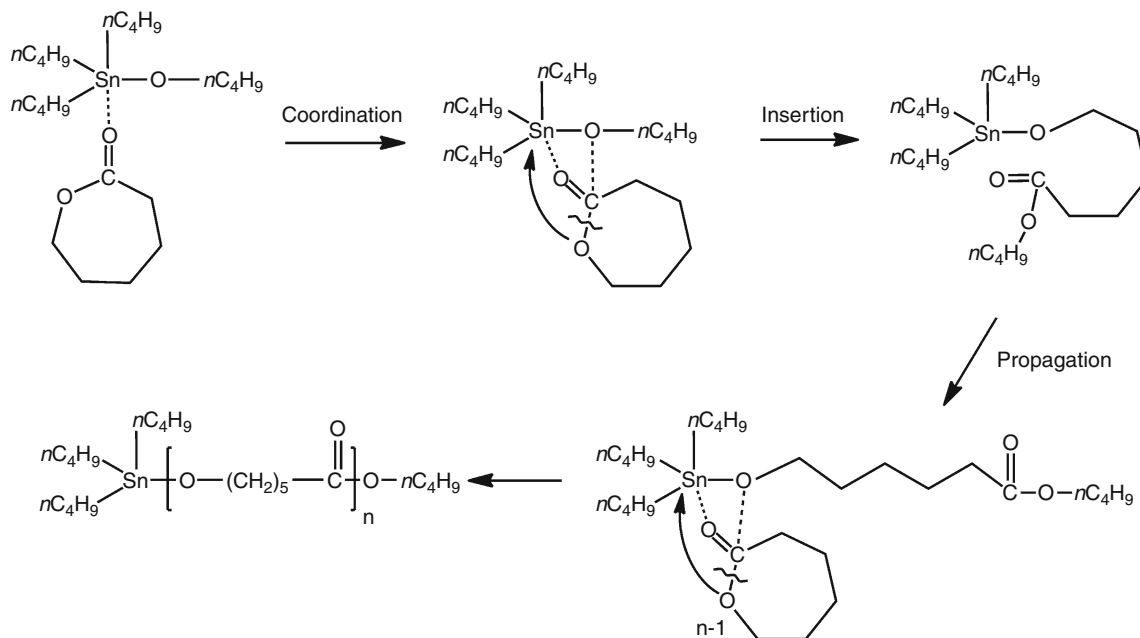
($n\text{Bu}_3\text{SnOnBu}$ -opened ϵ -CL). As the propagation step proceeds, the PCL will be formed.

This well-known mechanism was confirmed by the ^1H -NMR spectrum of crude PCL synthesized from isothermal DSC polymerization of ϵ -CL at 170 °C as shown in Fig. 10. As shown, the methyl proton of four n -butyl groups was found at 0.90 ppm (a, s) and the small peak at 3.65 ppm (e) was assigned as $-\text{Sn}-\text{O}-\text{CH}_2-$ of living polymer chain [10, 39]. The spectrum reveals that the polymerization is nearly complete with 98 % of monomer conversion which is determined from the intensity of PCL peak divided by the summation of intensity of PCL and ϵ -CL peaks [39]. However, there is still a small amount of monomers left in the crude PCL indicating by the monomer peaks at 2.65 (a') and 4.22 (e') ppm which are attributed to $-\text{CH}_2-\text{CO}-$ and $-\text{CH}_2-\text{O}-$ of the ϵ -CL monomer ring, respectively. So, this observation can be used to confirm that ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$ proceeds via the coordination-insertion mechanism.

From the bulk ROP of ϵ -CL at 120 °C, the molecular mass of PCL increased with increasing of monomer to initiator concentration ($[M]/[I]$) ratio and it was successfully controlled by adjusting the $[M]/[I]$ ratio as listed in Table 3. In addition, this synthesis condition gave the % yield of PCL higher than 85 %. At high initiator concentration or low $[M]/[I]$ ratio, the $n\text{Bu}_3\text{SnOnBu}$ initiated polymerization faster resulting in the low molecular mass PCL as shown in Table 3. Moreover, the synthesized PCL show PDI values close to 2 due to the occurrence of transesterification reaction.

Determination of the thermodynamic parameters

The thermodynamic parameters such as enthalpy (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were used to describe the



Scheme 1 Coordination insertion mechanism for ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$

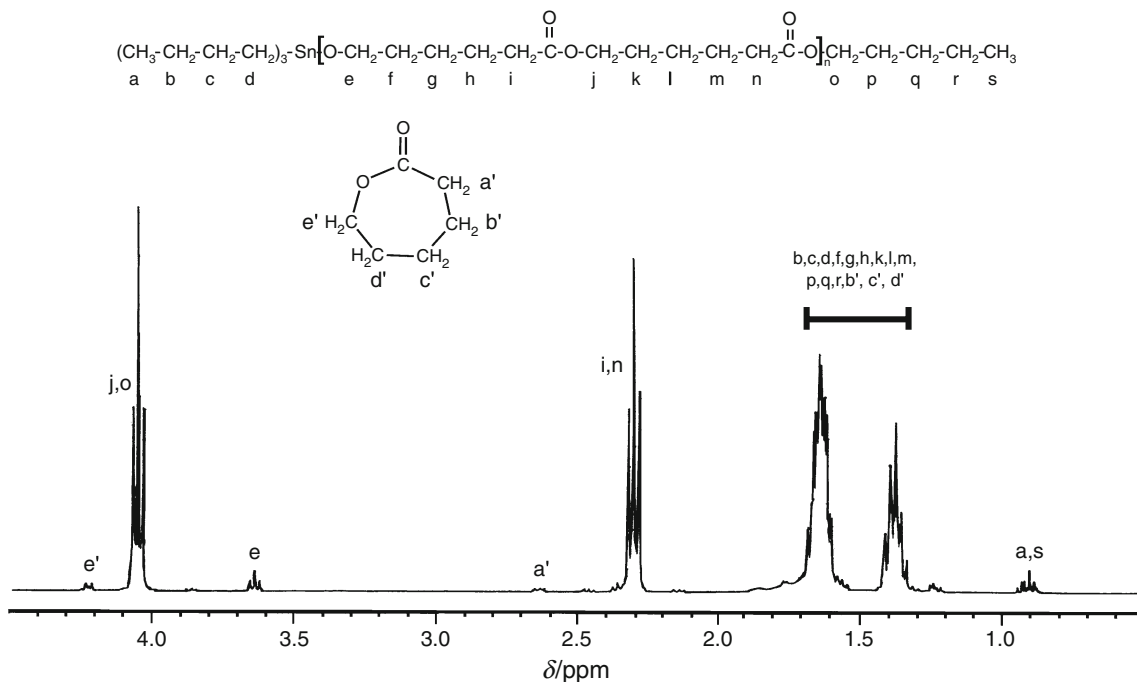


Fig. 10 $^1\text{H-NMR}$ spectrum of crude PCL in CDCl_3 synthesized by isothermal DSC polymerization of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 170°C

order of transition state (TS) of activated complex of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$ as similar to the estimation of the thermodynamic parameters for ROP of L-lactide with tin(IV) alkoxides reported by Chrisholm and co-workers [40]. The thermodynamic parameters of transition state can be simply determined by the Eyring equation [41]. In this work, the Eyring equation was modified using the k_{app}

values obtained from isothermal DSC (see Table 2) and the new expression is shown in Eq. (9).

$$\ln\left(\frac{k_{\text{app}}}{T}\right) = \ln\left(\frac{k_{\text{B}}}{h}\right) + \frac{\Delta S^\ddagger}{R} + \ln[I]_0 - \frac{\Delta H^\ddagger}{RT} \quad (9)$$

where k_{app} is the apparent rate constant of polymerization, k_{B} is the Boltzmann constant, h is the Planck's constant,

Table 3 Number average molecular mass (\bar{M}_n), mass average molecular mass (\bar{M}_w), polydispersity index (PDI) and %yields of PCLs from bulk polymerization of ϵ -CL at 120 °C for 72 h using different $n\text{Bu}_3\text{SnOnBu}$ concentrations

$[I]_0/\text{mol}\%$	$[M]/[I]^a$	\bar{M}_n^b	\bar{M}_w^b	PDI ^b	%Yield ^c
0.125	800	2.2×10^4	3.9×10^4	1.8	86
0.250	400	2.0×10^4	3.7×10^4	1.9	87
0.500	200	1.8×10^4	3.3×10^4	1.9	85
1.000	100	1.1×10^4	2.0×10^4	1.8	86

^a Molar ratio of monomer to initiator

^b GPC measurements in THF at 35 °C calibrated with polystyrene standard

^c Amount of polymer formed after precipitation in methanol

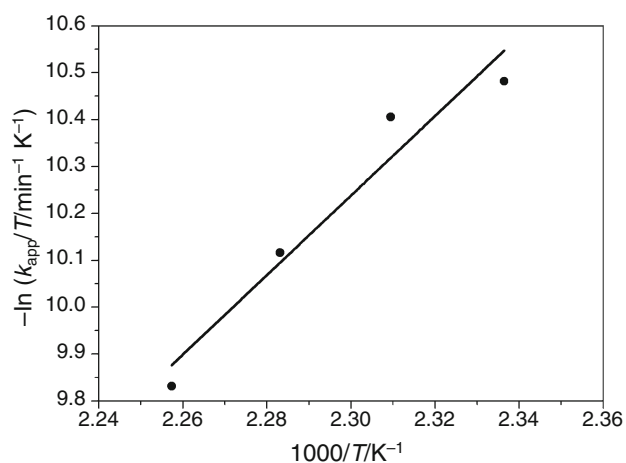


Fig. 11 Plot of $-\ln(k_{\text{app}}/T)$ against $1000/T$ for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$

ΔH^\ddagger is the activation enthalpy, ΔS^\ddagger is the activation entropy, and $[I]_0$ is the initial concentration of $n\text{Bu}_3\text{SnOnBu}$. From the Eq. (9), the values of ΔH^\ddagger and ΔS^\ddagger can be calculated from the slope and extrapolated intercept of the linear plot of $-\ln(k_{\text{app}}/T)$ versus $1000/T$ (as shown in Fig. 11), respectively.

From Fig. 11, the plot has a good linearity with $R^2 = 0.946$. The obtained values of ΔH^\ddagger and ΔS^\ddagger are 70.5 kJ mol^{-1} and $-100.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The result shows that DSC is also a convenient method to estimate the thermodynamic parameters for ROP of ϵ -CL. The negative value of ΔS^\ddagger indicates that the transition state (TS) has a restricted (highly ordered) orientation, resulting in the ensured formation of PCL.

Determination of the degree of aggregation (m) of $n\text{Bu}_3\text{SnOnBu}$

Metal alkoxide initiators generally exist as molecular aggregates in equilibrium with monomeric species. They

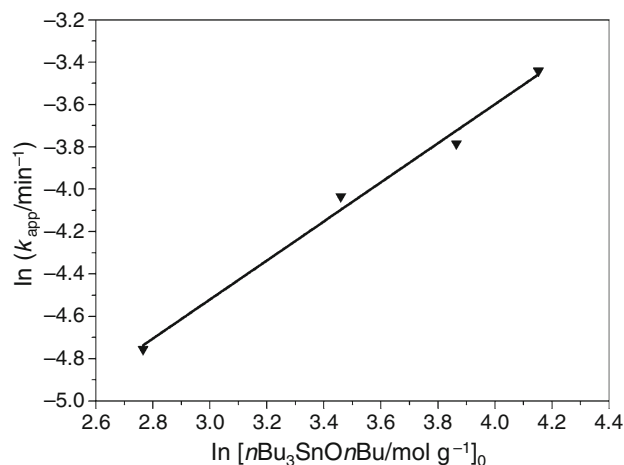


Fig. 12 Plot of $\ln(k_{\text{app}})$ against $\ln[n\text{Bu}_3\text{SnOnBu}]_0$ for the ROP of ϵ -CL initiated by 0.5, 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 165 °C

Table 4 The values of apparent rate constant (k_{app}), degree of aggregation (m), and reaction order to initiator (n) for ROP of ϵ -CL initiated by 0.5, 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ at 165 °C

$[n\text{Bu}_3\text{SnOnBu}]_0/\text{mol}\%$	$k_{\text{app}}/\text{min}^{-1}$	m	n
0.5	0.009	1.08	0.92
1.0	0.018		
1.5	0.023		
2.0	0.032		

normally have significantly different reactivities depending on the degree of aggregation (m). The m value of metal alkoxides can be determined from the method of Penczek and co-workers [42, 43] from a kinetic plot of $\ln(k_{\text{app}})$ versus $\ln[I]_0$ as shown in Eq. (10).

$$\ln(k_{\text{app}}) = 1/m \ln[I]_0 + C \quad (10)$$

where k_{app} is the apparent rate constant, $[I]_0$ is the initial concentration of initiator, m is the degree of initiator aggregation, and C is a constant. The plot of $\ln(k_{\text{app}})$ versus $\ln[n\text{Bu}_3\text{SnOnBu}]_0$ is shown in Fig. 12, and the m value is calculated from the slope of this plot. In addition, the order of the reaction (n) with respect to initiator concentration can also be determined by $1/m$. The kinetic parameters that used to determine the values of m and n are summarized in Table 4.

In according to Fig. 12, the slope of the plot of $\ln(k_{\text{app}})$ versus $\ln[I]_0$ is 0.92 ($= 1/m$) which, therefore, gives a degree of aggregation (m) of 1.08. This m value (closed to 1) suggests that, within the initiator concentration ($[n\text{Bu}_3\text{SnOnBu}]_0 \leq 2.0 \text{ mol}\%$) used in this study, the initiator is in non-aggregated form (high solubility in monomer).

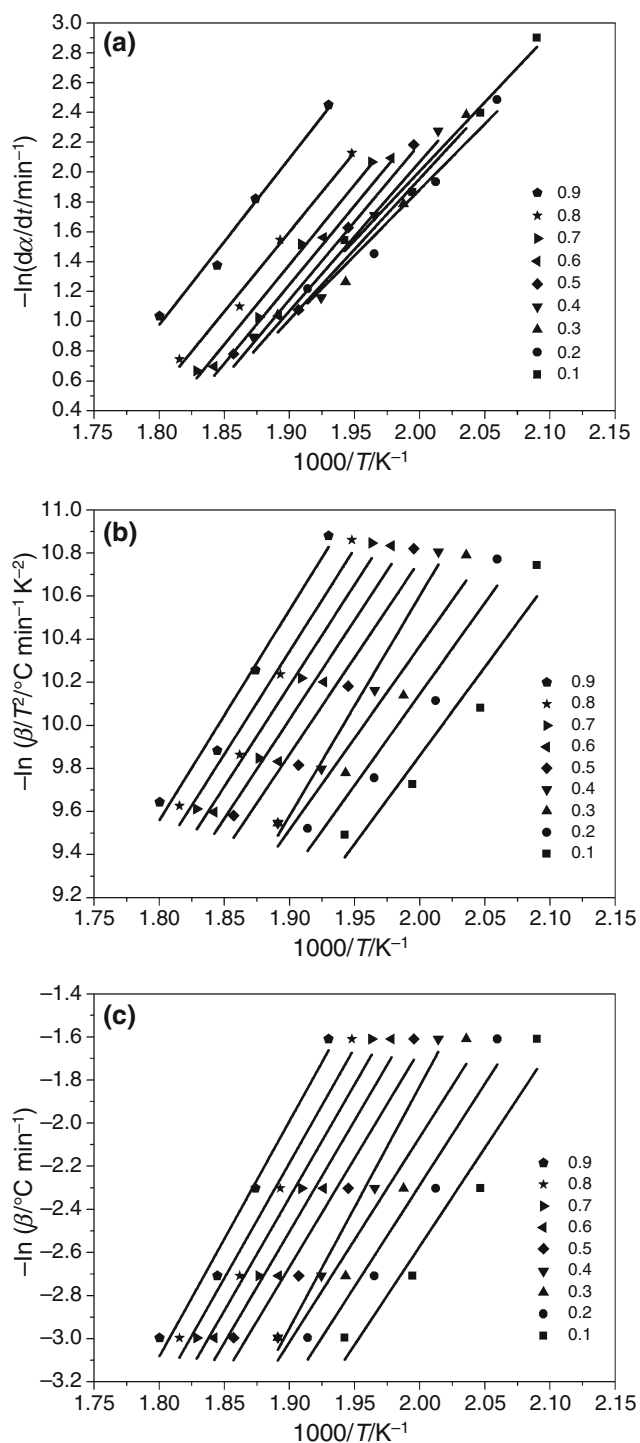


Fig. 13 Plots of **a** $-\ln(dx/dt)$, **b** $-\ln(\beta/T^2)$ and **c** $-\ln(\beta)$ against $1000/T$ based on the methods of Friedman, KAS, and FWO, respectively for ROP of ϵ -CL initiated by 1.0 mol% of $n\text{Bu}_3\text{SnOnBu}$

Isoconversional kinetic analysis

The dependence of E_a with α can also be investigated by isoconversional methods. In general, for a single step polymerization, the E_a is constant for all α which is

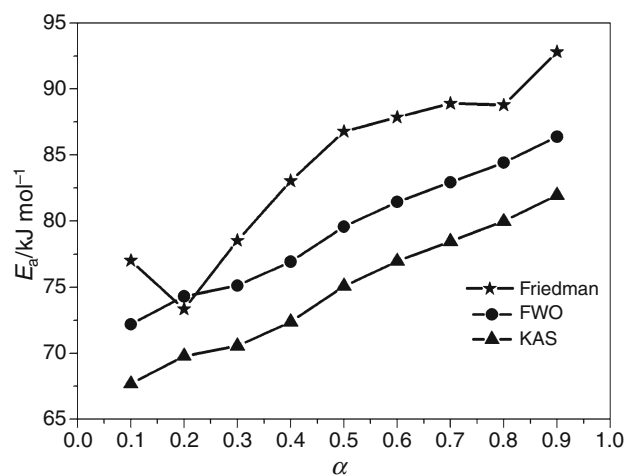


Fig. 14 Plots of E_a as a function of monomer conversion obtained from Friedman, KAS, and FWO isoconversional methods

different from a multi-step polymerization [20, 21]. The differential method (Friedman) and the integrated methods ((KAS) and (FWO)) were used in this work to investigate the dependence of E_a with α [44, 45]. These three methods were applied to non-isothermal kinetic data to determine E_a from the ROP of ϵ -CL initiated by a selected initiator concentration (1.0 mol%). The results from kinetic plots of each method (Fig. 13) show that the Friedman method has the less uniform of the plots, caused by the uncertainty in the determination of polymerization rate (dx/dt). Moreover, this method has no mathematic approximation that makes the obtained values of E_a higher than KAS and FWO methods [7, 46]. The dependence of E_a with α shown in Fig. 14 indicates that the E_a is not constant for the whole range of α which is different from Ti(IV) alkoxides initiating system as reported by Meelua et al. [7]. This might be caused by the difference in the rate of initiation (r_i) and the rate of propagation (r_p) of this initiating system. This finding agrees with the report of Kricheldorf and co-workers [11] that the r_i is faster than r_p in ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOMe}$. The E_a determined from Friedman, KAS, and FWO methods for ROP of ϵ -CL using 1.0 mol% $n\text{Bu}_3\text{SnOnBu}$ as initiator are 73–92, 67–81, and 72–86 kJ mol^{-1} , respectively. The values of E_a determined from isoconversional method are close to those of isothermal and non-isothermal methods.

Conclusions

The DSC, proven as a fast and convenient technique with non-isothermal and isothermal methods, has been used to investigate the kinetics and thermodynamics of ROP of ϵ -CL initiated by the synthesized $n\text{Bu}_3\text{SnOnBu}$. For the

kinetic parameters, the activation energies (E_a) of the reaction at 1.0, 1.5, and 2.0 mol% of $n\text{Bu}_3\text{SnOnBu}$ were found to be 78–83, 61–66, and 60–65 kJ mol^{-1} for non-isothermal method, and 74.2, 65.8, and 62.0 kJ mol^{-1} for isothermal method, respectively. The obtained E_a values from both methods show the same trend as a function of initiator concentration, indicating that the DSC method is reliable to study the kinetics of ROP of ϵ -CL initiated by $n\text{Bu}_3\text{SnOnBu}$. Moreover, the non-aggregation of the synthesized $n\text{Bu}_3\text{SnOnBu}$ initiator in monomers was confirmed by the isothermal method. For the thermodynamic parameters, the ΔH^\ddagger and ΔS^\ddagger of the reaction using the isothermal DSC were observed to be 70.5 kJ mol^{-1} and $-100.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of ΔS^\ddagger implies that the highly ordered transition state of $n\text{Bu}_3\text{SnOnBu}$ and ϵ -CL is observed. The dependence of E_a with monomer conversion was further investigated by isoconversional method and the determined E_a is close to the non-isothermal and isothermal methods. Finally, the molecular mass of PCL was effectively controlled by the $[M]/[I]$ ratio. Our present investigation for kinetic and thermodynamic parameters on the ROP of ϵ -CL with synthesized $n\text{Bu}_3\text{SnOnBu}$ initiator using DSC technique both non-isothermal and isothermal method has proven to be rapid and effective, which could be practical to the most ROP of cyclic esters with other initiators.

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