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Effect of tributyltin alkoxides chain length on the ring-opening polymerization of ε-caprolactone: Kinetics studies by non-isothermal DSC

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ABSTRACT

The kinetics of ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) initiated by 1.0 mol% of the tributyltin alkoxides (Bu_3SnOR; R = Me, Et, *n*Pr and *n*Bu) was investigated by non-isothermal DSC technique. The DSC curves showed the dependency of polymerization exotherms with the heating rate. The polymerization rate increased with increasing of heating rate for all initiating systems. The values of activation energy (E_a) obtained from the peak method of Kissinger for Bu_3SnOMe, Bu_3SnOEt, $Bu_3SnOnPr$ and $Bu_3SnOnBu$ initiated ROP of ε-CL were 52.4, 70.3, 75.9 and 78.0 kJ/mol, respectively. The values of E_a increased with increasing of alkoxy chain length but polymerization rate decreased. The variation of E_a with monomer conversion was investigated by Friedman and Starink isoconversional methods. The $Bu_3SnOnBu$ initiator produced the highest molecular weight and %yield of poly(ε-caprolactone) (PCL).

1. Introduction

Biodegradable poly(ε-caprolactone), PCL, have recently become an attractive class of aliphatic polyester for biomedical applications due to its biodegradability, biocompatibility, physical and chemical property [1–3]. PCL with high molecular weight is normally synthesized by ring opening polymerization (ROP) of ε-caprolactone (ε-CL) using various metal alkoxide and carboxylate initiators such as aluminum alkoxides [4,5], titanium alkoxides [6,7], tin alkoxides [8–10] and tin caboxylates [11–13]. Among them, tin(IV) alkoxides with different structures have been widely used as initiators for ROP of cyclic ester monomers [14–16]. Moreover, the tributyltin alkoxides (Bu_3SnOR) have been found to be the attractive class of initiators due to their easy synthesis procedure, high oxygen-moisture stability and high %yield [14]. Using this type of initiator, Kricheldorf et al. [14] reported the comparison for the reactivity of tributyltin derivatives consist of tributyltin chloride (Bu_3SnCl), tributyltin bromide (Bu_3SnBr), tributylin acetate (Bu_3SnOAc), tributyltin thioacetate (Bu_3SnSAc), tributyltin methoxide (Bu_3SnOMe) and tributyltin phenoxide (Bu_3SnOPh) in the ROP of ε-CL. From ^1H NMR investigation, they found that Bu_3SnOMe showed the highest reactivity than others tributyltin derivatives. Moreover, Kricheldorf and ThienBen [16] compared the reactivity of Bu_3SnOEt, $Bu_2Sn(OEt)_2$, and $BuSn(OEt)_3$ in ROP of ε-CL using ^1H NMR technique. The reactivity of initiators increased with increasing of alkoxy group. Our previous works focused on the theoretical investigation of the influence of alkoxy group of tributyltin alkoxide (Bu_3SnOR) in ROP of D-lactide (DL) using quantum calculations [17]. The effect of chain length of linear alkoxy group was not significant to the values of energy barrier. In contrast, the branch alkoxy group played an important role on the energy barrier of transition state. The energy barrier increased with increasing of steric hindrace of branch alkoxy group. Furthermore, we studied the steric effect of tin(II) alkoxide ($Sn(OR)_2$) initiator in ROP of ε-CL by using dilatometry technique [18]. From dilatometric results, it was found that the reactivity of synthesized tin(II) *t*-butoxide ($Sn(OtBu)_2$) catalyzed ROP of ε-CL slower than tin(II) *i*-butoxide ($Sn(OiBu)_2$) and tin(II) *n*-butoxide ($Sn(OnBu)_2$), respectively. The results from our previous studies clearly showed that the bulky alkoxy group decreased the reactivity of tin(II) alkoxide initiators. Moreover, we recently reported the computational investigation [19] on the catalytic behavior of $Sn(OnBu)_2$, tin(II) *n*-hexoxide ($Sn(OnHex)_2$) and tin(II) *n*-octoxide ($Sn(OnOct)_2$) in ROP of ε-CL. We found that the

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reactivity of Sn(O*n*Bu)$_2$ > Sn(O*n*Hex)$_2$ > Sn(O*n*Oct)$_2$. From literature review, the influence of alkoxy chain length on the reactivity of Bu_3SnOR has not been reported and discussed before. Moreover, there are a few papers reported on the kinetics of ROP of cyclic ester monomers initiated by Bu_3SnOR. So, the kinetic information is still needed to describe the structure-reactivity relationship of Bu_3SnOR initiators. In this study, we introduce the alternative, simple and convenient thermoanalytical technique, namely differential scanning calorimetry (DSC), which is a fast technique to study the kinetics of cyclic esters polymerization unlike the time consuming technique of ^{1}H NMR. DSC normally provides the profile of the heat released during the polymerization under the isothermal and/or non-isothermal conditions which various useful kinetic parameters can be obtained and analyzed. Moreover, it is an effective and reliable technique for the determination of some kinetic parameters such as rate constant (k), %conversion (%α) and activation energy (E_a) of polymerization process [20–22]. Generally, non-isothermal DSC gives an easy interpretation of kinetics profile by performing the experiment at different temperature programs [23,24]. We have used this technique to investigate the steric influence of titanium(IV) alkoxide ($Ti(OR)_4$) initiators on the ROP of ε-CL [7]. From the calorimetric results, the more steric Ti $(OR)_4$ showed the lower reactivity with higher values of E_a.

So, the goal of this work is to compare the reactivity of the four synthesized Bu_3SnOR (R = Me, Et, *n*Pr and *n*Bu) in the ROP of ε-CL via non-isothermal DSC technique. The kinetic parameters such as half life of polymerization ($t_{1/2}$) and E_a are determined. The dependency of E_a with monomer conversion is investigated by the Friedman and Starink isoconversional methods. The results from non-isothermal DSC experiments will be discussed to evaluate the nucleophilicity of Bu_3SnOR on the ROP of ε-CL. Furthermore, the molecular weight of PCLs synthesized from Bu_3SnOR initiators will be compared and discussed.

2. Experimental

2.1. Materials preparation

Commercial ε-caprolactone (Acros Organics, 97.0%) was purified by vacuum distillation before used. Tributyltin chloride (Acros Organics, 95.0%) was used as received. Toluene (Carlo Erba, 99.8%), methanol (Sigma, 99.8%), ethanol (Sigma, 99.5%), *n*-propanol (Sigma, 99.5%), *n*-butanol (Sigma, 99.5%) were purified by distillation over sodium metal before used.

2.2. Synthesis of Bu$_3$SnOR initiators

Tributyltin alkoxides (Bu_3SnOR; R = Me, Et, *n*Pr and *n*Bu) were synthesized by the nucleophilic substitution of tributyltin chloride (Bu_3SnCl) by sodium alkoxides (NaOR; R = Me, Et, *n*Pr and *n*Bu) in anhydrous toluene at reflux conditions for 6 h as described in literature [14,25]. The synthesized Bu_3SnOR were purified by vacuum distillation and the chemical structure was identified by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) on a Bruker Avance 400 NMR Spectrometer operating at 400 MHz in chloroform-*d* ($CDCl_3$) and Fourier transform infrared spectroscopy (FT-IR) on a Bruker Tensor 27 FT-IR spectrometer.

2.3. Non-isothermal DSC polymerizations

Kinetic studies of the ROP of ε-CL initiated by 1.0 mol% of the synthesized Bu_3SnOR (R = Me, Et, *n*Pr and *n*Bu) were performed on a PerkinElmer DSC-7 under a flowing nitrogen atmosphere (20 ml/min). The ε-CL and Bu_3SnOR initiators were placed in dry vial and stirred vigorously for 10 min. For each experiment, 8–10 mg of the monomer-initiator mixture was weighed into an aluminum pan and hermetically sealed. The samples were heated from standby temperature of 20–300 °C at heating rate of 5, 10, 15 and 20 °C/min.

2.4. Synthesis of poly(ε-caprolactone)

ε-CL monomer and 0.25 mol% (molar ratio of monomer to initiator ([M]/[I]) = 400) of Bu_3SnOR (R = Me, Et, *n*Pr and *n*Bu) 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. The obtained crude PCLs were dissolved in chloroform and re-precipitated in cold methanol before drying in a vacuum oven at 45 °C until constant weight. The molecular weight and molecular weight distribution (MWD) 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}. The number average molecular weights ($\overline{M}_n$) of the synthesized PCLs were also determined by ^{1}H NMR technique.

3. Results and discussion

3.1. Synthesis and characterization of Bu$_3$SnOR initiators

The Bu_3SnOR can be synthesized by simple nucleophilic substitution of Bu_3SnCl by NaOR (R = Me, Et, *n*Pr and *n*Bu) in anhydrous toluene. The NaCl salt, the product from reaction, is separated from solution by filtration to obtain the crude Bu_3SnOR which was purified by vacuum distillation. The physical appearance of the Bu_3SnOR is the colorless liquid. The %yield of the synthesized Bu_3SnOMe, Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu are 80, 60, 62 and 76%, respectively. The chemical structures of the synthesized Bu_3SnOR are identified by FT-IR and ^{1}H NMR techniques. From FT-IR spectra shown in Fig. 1, the synthesized Bu_3SnOR initiators show the characteristic peaks of SnO stretching at 450 cm^{-1} and SnC stretching around 590 cm^{-1} which are close to the data reported in literature [26]. Moreover, the spectra of all initiators show CO stretching around 1070 cm^{-1}, CH_2,CH_3 bending and stretching at 1370 and 2900 cm^{-1}, respectively. For more details on the identification of Bu_3SnOR's structure, the ^{1}H NMR was used to support the results from FT-IR analysis.

From the ^{1}H NMR spectra of the synthesized Bu_3SnOR (R = Me, Et, *n*Pr and *n*Bu) shown in Fig. 2. The spectra showed the multiplet of methyl chain end and methylene proton at 0.90 (2′, 3′, 4, 4′) and 0.95–1.60 ppm (2, 3, 3′), respectively. For Bu_3SnOMe, the methoxy group showed singlet at 3.70 ppm (1′) and multiplet at 3.65 ppm (1″). For Bu_3SnOEt, the quartet of methylene proton of ethoxy group was found at 3.80 ppm (1″) and multiplet at 3.65 ppm (1″).

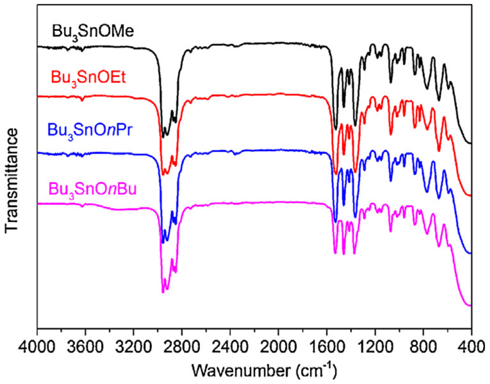


Fig. 1. FT-IR spectra of the synthesized Bu_3SnOMe, Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu.

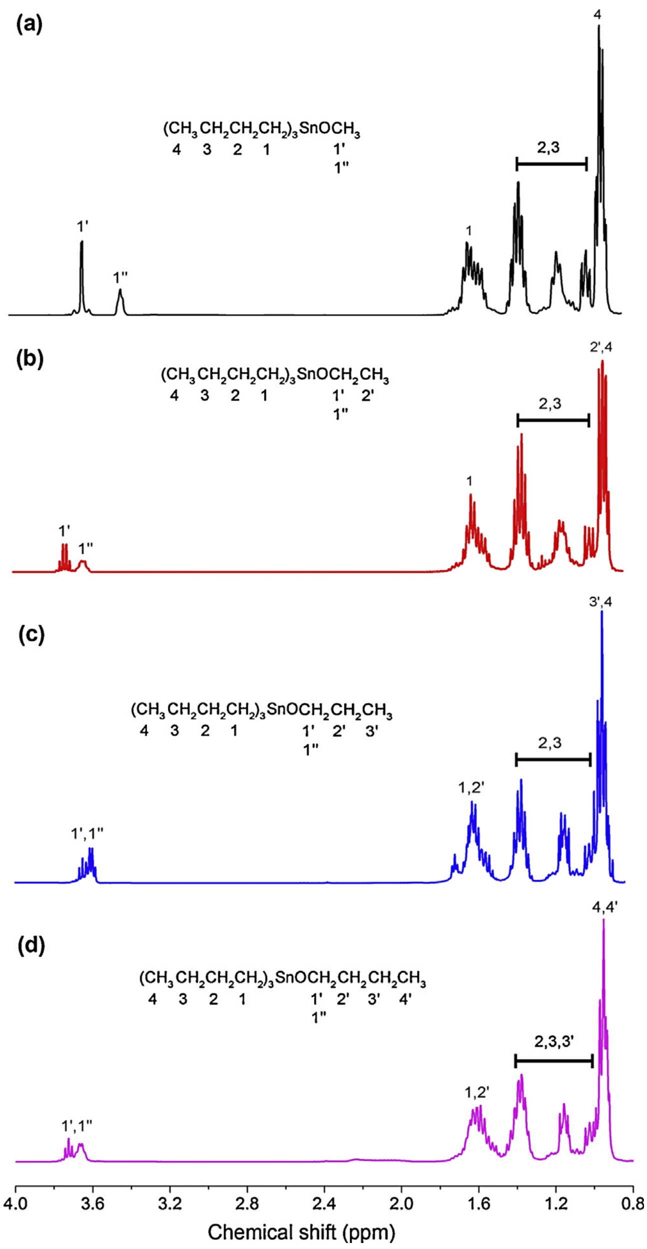


Fig. 2. ^{1}H NMR (400 MHz) spectra of the synthesized Bu_3SnOR in $CDCl_3$: (a) Bu_3SnOMe, (b) Bu_3SnOEt, (c) $Bu_3SnOnPr$ and (d) $Bu_3SnOnBu$.

For $Bu_3SnOnPr$ and $Bu_3SnOnBu$, the triplet of methylene proton connected to SnO was found at 3.60–3.65 ppm (1′, 1″). After structural characterization, the four synthesized Bu_3SnOR were used as initiator for ROP of ε-CL and the reactivity of them will be compared and discussed.

3.2. Non-isothermal DSC kinetics analysis for ROP of ε-caprolactone initiated by Bu_3SnOR

The polymerizations under non-isothermal DSC condition provided useful kinetics and thermodynamics information which was extracted in a short period of time. The non-isothermal DSC curves for ROP of ε-CL initiated by 1.0 mol% of Bu_3SnOR are shown in Fig. 3. The results showed that the exothermic curves from polymerization reaction of ε-CL shift to higher temperature range as heating rate increases for all initiating systems [7,23,24]. At high heating rate, the curves showed wider and sharper exotherms which are related to the high polymerization rate. Moreover, the onset (T_0) and endset (T_f) temperatures of polymerization shift to lower temperature range as the alkoxy chain (OR) length and heating rate decreased indicating the structure of initiator affects the polymerization temperatures. The Bu_3SnOMe initiated ROP of ε-CL at lower temperature range than Bu_3SnOEt, $Bu_3SnOnPr$ and $Bu_3SnOnBu$, respectively.

It is important that the DSC exotherms of polymerization for all initiators are board related to the slow propagation of polymerization reaction which may be caused by two reasons. The first reason was the three butyl groups connected to tin atom reduced initiator's nucleophilicity by inductive effect of carbon atoms. The second was the steric interference of three butyl groups on the coordination of initiator with monomer that reduced the coordinating ability of initiator and monomer. From the obtained polymerization exotherms, the monomer conversion (α) can be determined by Eq. (1) [20,23].

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

where H_t is the heat generated during the polymerization process and H_p is the total heat released from polymerization reaction. From the obtained α, polymerization rate ($\mathrm{d}\alpha/\mathrm{d}t$) can also determined. Plots of α and $\mathrm{d}\alpha/\mathrm{d}t$ against polymerization time (t) at the identical conditions (initiator concentration 1.0 mol% and a heating rate of 10 °C/min) are shown in Fig. 4(a) and (b), respectively.

From the kinetic plots of conversion against temperature shown in Fig. 4(a), the polymerization of ε-CL occurred and completed faster as the alkoxy chain length of Bu_3SnOR decreased. The results showed that Bu_3SnOMe was reactive at lower temperature range than others initiators. Moreover, from the results shown in Fig. 4(b), it was found that the maximum rate of polymerization decreased with increasing of alkoxy chain length of Bu_3SnOR. For theoretical consideration for non-isothermal DSC kinetics analysis, the measured heat flow is related to the conversion of monomer (α) and polymerization rate ($\mathrm{d}\alpha/\mathrm{d}t$). So, the rate equation can be expressed as Eq. (2).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

In non-isothermal DSC, $\mathrm{d}\alpha/\mathrm{d}t = \beta(\mathrm{d}\alpha/\mathrm{d}T)$, where β is the heating rate (°C/min) and $k(T)$ is the rate constant expressed by the temperature-dependent Arrhenius equation, Eq. (2) can be written as [27]:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp(-\frac{E_a}{RT})f(\alpha) \tag{3}$$

where E_a is the activation energy, A is the frequency factor, T is the temperature, R is the universal gas constant. The Kissinger method [28,29] used the Murray and White approximation to determine the $p(y)$ value as shown in Eq. (4) [30]. When the constant monomer conversion at the stage of maximum rate of polymerization is reached, the Kissinger method based on the relationship between the heating rate (β) and the temperature at maximum rate of polymerization (T_m) as shown in Eq. (5).

$$p(y) = \frac{\exp(-y)}{y^2} \tag{4}$$

$$\ln\frac{\beta}{{T_m}^2} = -\frac{E_a}{RT_m} + C \tag{5}$$

Therefore, the value of E_a can be obtained from the slope of a plot of $\ln(\beta/{T_m}^2)$ against $1/T_m$, The plots of Kissinger method for all initiating systems are shown in Fig. 5.

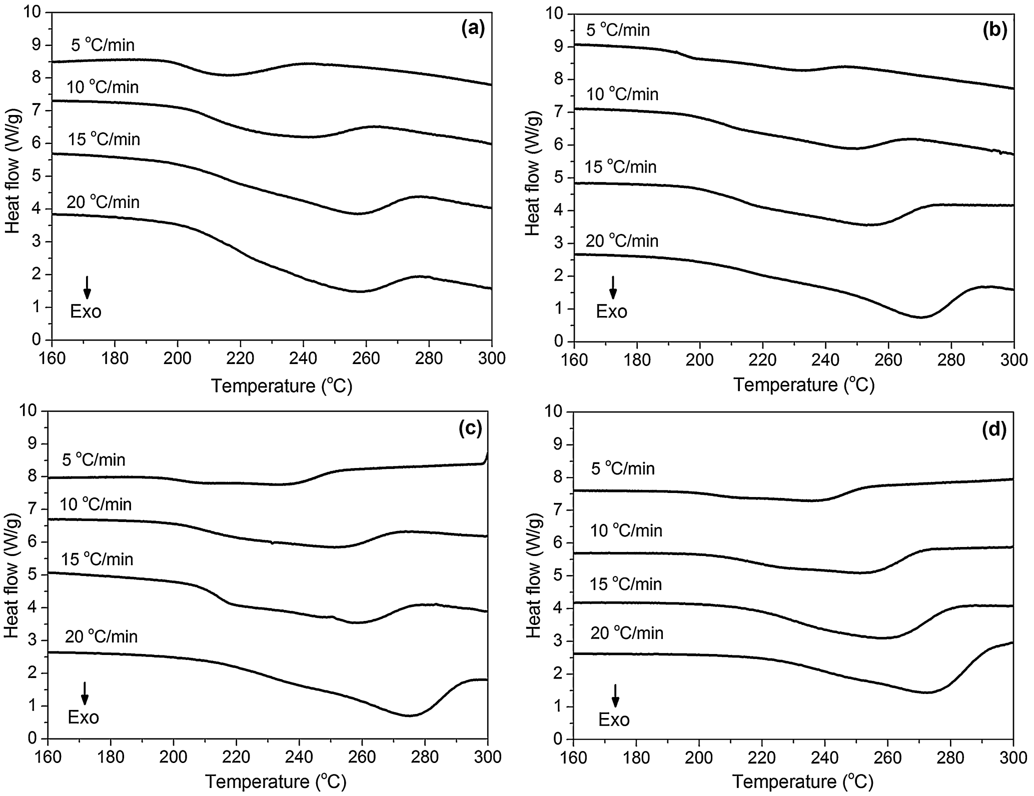


Fig. 3. Non-isothermal DSC curves for ROP of ε-CL initiated by 1.0 mol% of Bu_3SnOR at heating rates of 5, 10, 15 and 20 °C/min: (a) Bu_3SnOMe, (b) Bu_3SnOEt, (c) Bu_3SnO*n*Pr and (d) Bu_3SnO*n*Bu.

The obtained kinetic parameters from non-isothermal DSC polymerization of ε-CL initiated by the synthesized Bu_3SnOR are summarized in Table 1. The results from Table 1 showed that the values of T_m increased with increasing of heating rate and alkoxy chain length of initiator. The values of the half life ($t_{1/2}$) decreased with increasing of heating rate indicating the system required shorter time to reach the state of 50% monomer conversion. The values of $t_{1/2}$ for ROP of ε-CL initiated by $Bu_3SnOMe < Bu_3SnOEt < Bu_3SnO$*n*Pr $< Bu_3SnO$*n*Bu. These results indicated that the longer alkoxy group of initiator increased the time required for 50% of polymerization and decreased the reactivity of Bu_3SnOR. To support this relationship, the values of E_a obtained from Kissinger method was used to compare the reactivity of each initiating systems. The values of E_a obtained from Kissinger method for 1.0 mol% of Bu_3SnOMe, Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu initiated ROP of ε-CL are 52.4, 70.3, 75.9 and 78.0 kJ mol^{-1}, respectively. The results showed that the E_a of the four synthesized Bu_3SnOR initiators decreased with decreasing of alkoxy chain length or increasing of initiator's nucleophilic strength. These may be caused by the increasing of alkoxy chain length reduced the mobility of alkoxy group to attack the carbonyl carbon of ε-CL in the coordination insertion mechanism resulting in the lower reactivity and higher E_a. These results can be supported by the dependency of initiator's reactivity with alkoxy chain length of Sn$(OR)_2$ in ROP of ε-CL [19,31]. The results obtained from quantum calculations showed that the rate constant at 100 °C of Sn(O*n*Bu)$_2$ was higher than those of Sn(O*n*Hex)$_2$ and Sn(O*n*Oct)$_2$, respectively. Moreover, the energy barrier of Sn(O*n*Bu)$_2$ < Sn(O*n*Hex)$_2$ < Sn

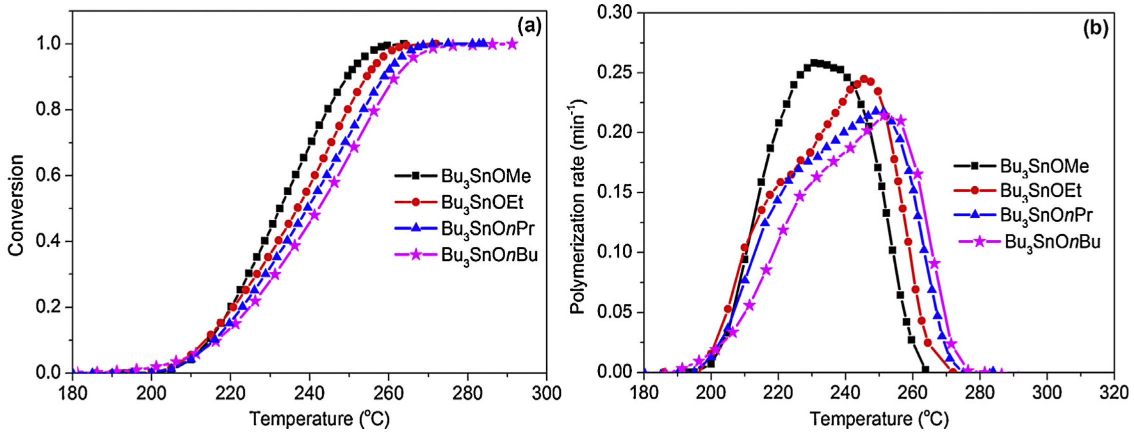


Fig. 4. Plots of monomer conversion (a) and polymerization rate (b) as a function of polymerization temperature at a heating rate of 10 °C/min for ROP of ε-CL initiated by 1.0 mol% of Bu_3SnOMe, Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu.

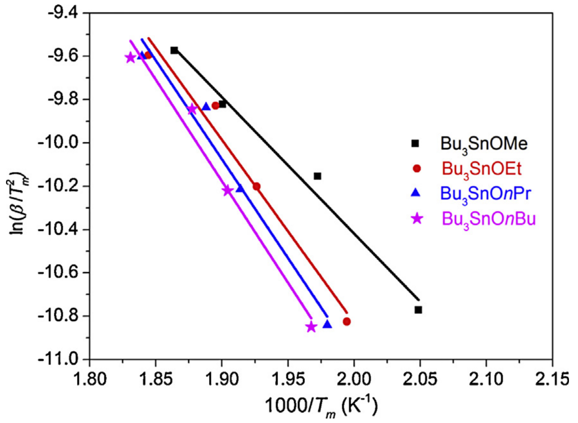


Fig. 5. Plots of $\ln(\beta/T_m{}^2)$ against $1000/T_m$ based on the peak method of Kissinger for ROP of ε-CL initiated by 1.0 mol% of Bu_3SnOMe, Bu_3SnOEt, $Bu_3SnO\textit{n}Pr$ and $Bu_3SnO\textit{n}Bu$.

$(O\textit{n}Oct)_2$. For more supportive information on the effect of alkoxy chain length, Kleawkla et al. [31] reported the kinetics data of $Sn(O\textit{n}Hex)_2$ and $Sn(O\textit{n}Oct)_2$ initiated ROP of ε-CL using the classical method of dilatometry. They found that the rate constant of polymerization obtained from $Sn(O\textit{n}Hex)_2$ is higher than $Sn(O\textit{n}Oct)_2$ at 140 °C indicating the higher reactivity of $Sn(O\textit{n}Hex)_2$ than $Sn(O\textit{n}Oct)_2$. From these results, the polymerization rate of ε-CL seems to depend on the size of alkoxy group of initiators. As reported by Kricheldorf et al. [14] that the polymerization rate of ε-CL with Bu_3SnOMe was higher than of Bu_3SnOPh ($[M]/[I] = 100$) as observed on the plots of conversion against time at 100 °C. The polymerization of ε-CL using Bu_3SnOMe as initiator completes faster than Bu_3SnOPh. The increasing of bulkiness of alkoxy group of initiator reduces the polymerization rate of ε-CL. Therefore, the results obtained from this work suggest that $Bu_3SnO\textit{n}Bu$ is the least reactive initiator due to the bulky alkoxy group as described earlier.

To support the results from Kissinger method, the dependency of E_a with monomer conversion was determined from Friedman and Starink isoconversional methods. These methods allow a single or a multiple step reaction process to be detected. For the single step reaction, the E_a is independent from monomer conversion (which is constant throughout polymerization). While in the multiple step reaction, the values of E_a generally vary with monomer conversion. In this work, the values of E_a were determined from the monomer conversion in a range of 0.2–0.8. The differential isoconversional method of Friedman [32–34] does not use any mathematics approximation for temperature integral. Thus, at a constant α, the values of E_a are directly determined by Eq. (6).

Table 1
The obtained kinetic parameters from non-isothermal DSC polymerization of ε-CL initiated by 1.0 mol% of Bu_3SnOR initiators.

Initiators	β(°C/min)	T_m[a](°C)	$t_{1/2}$[b](min)	E_a(kJ/mol)	
				Kissinger	r^2
Bu_3SnOMe	5	215.0	39.1	52.4 ± 0.75	0.99
	10	233.8	21.3		
	15	253.0	14.8		
	20	263.3	11.8		
Bu_3SnOEt	5	228.3	40.0	70.3 ± 1.06	0.98
	10	246.0	21.7		
	15	254.5	14.8		
	20	269.0	12.0		
$Bu_3SnO\textit{n}Pr$	5	232.0	40.9	75.9 ± 0.78	0.97
	10	249.3	22.0		
	15	256.5	14.9		
	20	270.5	12.2		
$Bu_3SnO\textit{n}Bu$	5	234.2	41.5	78.0 ± 1.24	0.98
	10	251.0	22.1		
	15	258.5	15.6		
	20	272.0	12.5		

[a] Temperature at maximum rate of polymerization is reached.
[b] Time require for 50% of monomer conversion.

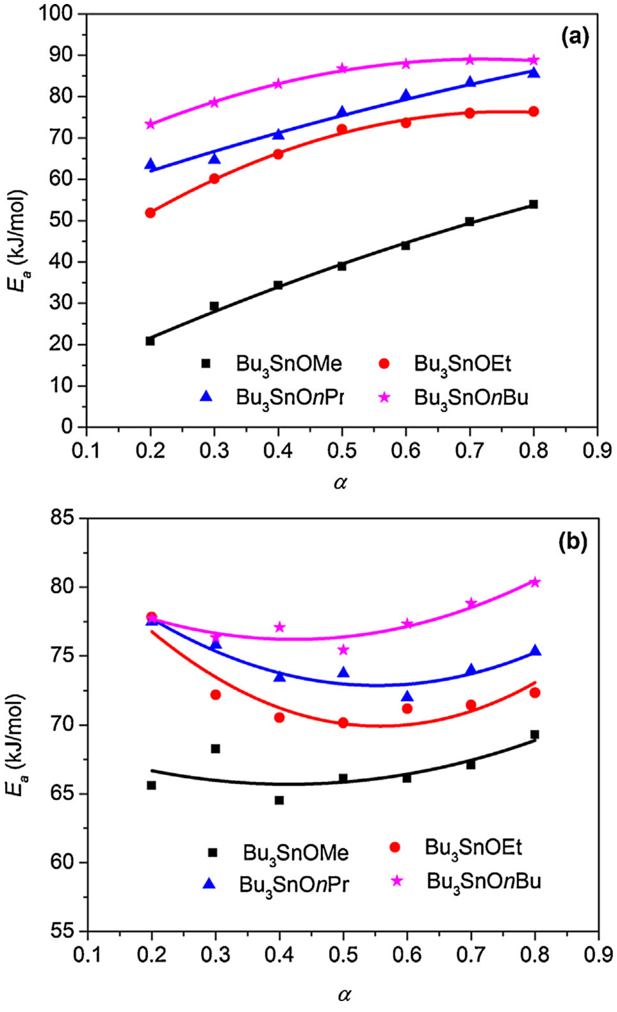


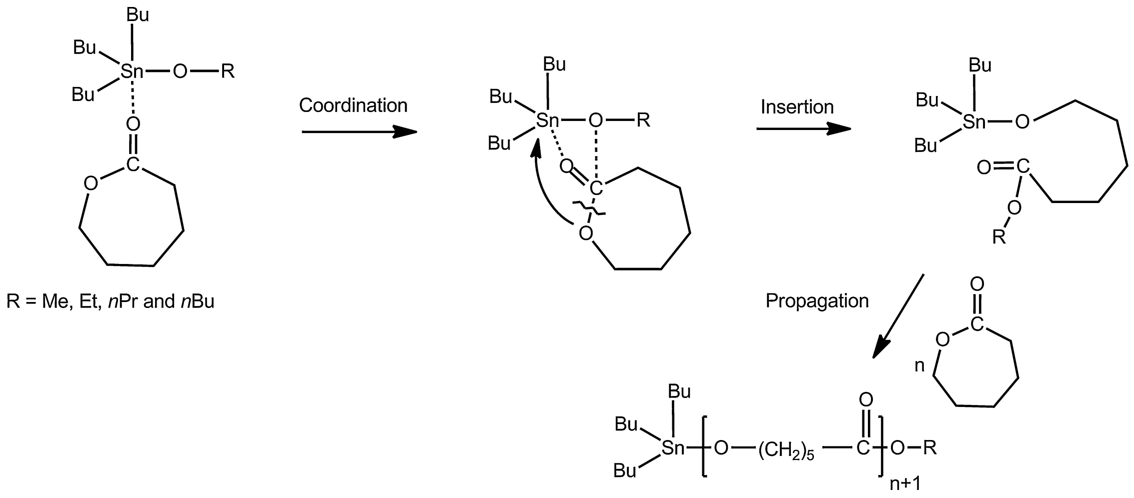
Fig. 6. Plots of E_a against monomer conversion (α) obtained from different isocnversional methods for the ROP of ε-CL initiated by 1.0 mol% of Bu_3SnOMe, Bu_3SnOEt, $Bu_3SnO\textit{n}Pr$ and $Bu_3SnO\textit{n}Bu$: (a) Friedman and (b) Starink isoconversional methods.

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln(A_\alpha f(\alpha)) - \frac{E_{a,\alpha}}{RT_{\alpha,i}} \tag{6}$$

where the subscript α refers to the value at a particular conversion and i refers to data for a given heating rate. Moreover, more accurate method in estimation of E_a was reported by Starink [27,30] which is based on the relationship of $\ln(\beta/T^{1.92})$ and $1/T$ as shown in Eq. (7).

$$\ln\left(\frac{\beta}{T_{\alpha,i}^{1.92}}\right) = \text{Constant} - 1.0008\left(\frac{E_{a,\alpha}}{RT_\alpha}\right) \tag{7}$$

From the obtained values of E_a from both methods, the dependency of E_a with monomer conversion is illustrated in Fig. 6. The results reveal that the values of E_a obtained from the Friedman and Starink isoconversional methods for the ROP of ε-CL



Scheme 1. The coordination insertion mechanism of Bu_3SnOR initiated ROP of ε-CL.

Table 2
Number average molecular weight ($\overline{M}_n$), weight average molecular ($\overline{M}_w$), molecular weight distribution (MWD) and %yield of PCLs from bulk polymerization of ε-CL initiated by 0.25 mol% of Bu_3SnOR initiators at 120 °C for 72 h.

Initiators	[I] (mol%)	[M]/[I][a]	$\overline{M}_{n,\mathrm{NMR}}$[b]	$\overline{M}_n$[c]	$\overline{M}_w$[c]	MWD[c]	%Yield[d] (%)
Bu_3SnOMe	0.25	400	5.7×10^3	1.1×10^4	2.0×10^4	1.8	85
Bu_3SnOEt			6.1×10^3	1.4×10^4	2.0×10^4	1.4	86
Bu_3SnO*n*Pr			8.3×10^3	1.7×10^4	3.2×10^4	1.9	88
Bu_3SnO*n*Bu			1.4×10^4	2.0×10^4	3.7×10^4	1.9	89

[a] Molar ratio of monomer to initiator.

[b] Determined from the end group analysis using ^{1}H NMR technique, $\overline{M}_{n,\mathrm{NMR}} = [(1 + 1(I_{CH_2OCO}/I_{CH_2OH})) \times M_{wCL}] + M_{wOR}$

[c] GPC measurements in THF at 35 °C calibrated with polystyrene standard.

[d] Amount of polymer formed after precipitation in methanol.

initiated by Bu_3SnOMe are lower than those of Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu, respectively. The E_a values obtained from isoconversional kinetics analysis are similar to the peak method of Kissinger. Furthermore, the E_a values obtained from Starink isoconversional method are constant throughout polymerization implying that the polymerization reaction proceeds through a single coordination insertion mechanism. However, the values of E_a determined from Friedman isoconversional method are different from Starink method. This may be caused by the uncertainty in determination of $d\alpha/dt$ which is sensitive to baseline quality [27]. In addition, for the least active Bu_3SnO*n*Bu, the E_a increases with monomer conversion due to the increasing viscosity of reaction mixture which reduces the coordination ability of monomer and active center.

3.3. Bulk polymerization of ε-caprolactone and mechanistic consideration

From the kinetics results, it is found that the reactivity of Bu_3SnOR depends on the size of alkoxy group. In this part, the efficiency of Bu_3SnOR in the synthesis of PCL is discussed. The ROP of ε-CL initiated by Bu_3SnOR occurs through the conventional coordination insertion mechanism as depicted in Scheme 1. The polymerization starts with the coordination of ε-CL and Bu_3SnOR by the interaction of carbonyl oxygen of ε-CL with tin atom. The second step is the acyl-oxygen cleavage of ε-CL by the nucleophilic attack of —OR group to carbonyl carbon of ε-CL, then the propagating species (—Sn—O—) is formed. The propagation step then proceeds by the insertion of ε-CL into reactive Sn—O bond.

To investigate the efficiency of Bu_3SnOR initiators in the synthesis of PCL, the bulk polymerization of ε-CL was conducted at 120 °C for 72 h. From GPC and ^{1}H NMR analyses listed in Table 2, it is found that the molecular weight of PCL increases with increasing of alkoxy chain length of Bu_3SnOR. The Bu_3SnO*n*Bu produces the highest molecular weight of PCL among initiators used in this work. However, the synthesized PCLs show MWD values close to 2 indicating the occurrence of transesterification reaction. Moreover, the %yields of PCLs synthesized from Bu_3SnOR initiators are higher than 85%. The results demonstrate that Bu_3SnOR (R = Me, Et, *n*Pr and *n*Bu) are the efficient initiator in the ROP of ε-CL.

4. Conclusions

Non-isothermal DSC technique is a convenient method to study kinetics of ROP of ε-CL initiated by the synthesized Bu_3SnOR with different alkoxy (OR) chain length (R = Me, Et, *n*Pr and *n*Bu). The synthesized Bu_3SnOR can effectively initiate ROP of ε-CL at the condition used in non-isothermal DSC experiments. The values of E_a obtained from Kissinger method for Bu_3SnOMe are lower than those of Bu_3SnOEt, Bu_3SnO*n*Pr and Bu_3SnO*n*Bu, respectively. From the Friedman and Starink isoconversional kinetics analysis, the reactivity of Bu_3SnOMe is found to be highest compared to other initiators. The results from non-isothermal DSC show the decreasing of E_a with decreasing of alkoxy chain length and increasing of the nucleophilicity of Bu_3SnOR. The molecular weight of PCL synthesized from Bu_3SnO*n*Bu initiator was higher than Bu_3SnO*n*Pr, Bu_3SnOEt, Bu_3SnOMe, respectively. Moreover, the results from this work may be applied to describe the catalytic behavior of other initiating systems in ROP of ε-CL.

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