Anionic Polymerization of ε-Caprolactone Using Potassium *tert*-Butoxide/18-Crown-6 Initiating System

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ABSTRACT

The effect of 18-crown-6 ether (18C6) on the anionic polymerization of ε-caprolactone (ε -CL) using potassium tert-butoxide (t-BuOK) as the initiator was studied. The experimental results showed that 18C6 in combination with t-BuOK exhibited high selectivity for ring opening relative to trans-esterification and improved control toward the ROP of ε-CL, producing poly(ε-caprolactone) (PCL) with much higher molecular weight and relatively narrow distribution compared to those using t-BuOK alone as the initiator.The influences of reaction conditions, such as monomer concentration, monomer/initiator molar ratio, and [18C6]/[t-BuOK] molar ratio, as well as reaction temperature and time on the polymerization have been examined in detail. The resulting hopolymers were characterized by various analytical techniques, such as GPC, FTIR, ^{1}H NMR, DSC, TGA, and MALDI-ToF MS, to monitor the structures and property changes of PCLs.

Keywords: ε-Caprolactone, Potassium tert-Butoxide, 18-Crown-6, Anionic polymerization.

INTRODUCTION

Aliphatic polyesters are important biodegradable and biocompatible materials, which have received considerable attention due to their extensive applications[1-16]. Among these, the synthesis of poly(ε-caprolactone)(PCL) has attracted many focuses in the last decade, owing to its flexibility, crystallinity, glass transition temperature (T_g) of ca. -60 °C and a melting point (T_m) of ca. 61°C. Moreover, PCL can be biodegraded in compost, activated sludge, and natural water by the micro-

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organisms found in these environments. The hydrolytic or enzymatic degradation of PCL generates 6-hydeoxyhexanoic acid, a metabolite in the citric acid cycle, which is further metabolized to CO_2, CH_4, and H_2O.

Conventionally, PCLs are prepared by classical polycondensation of α, ω-hydroxy acids or diols and diacids, but for better control over the PCL's microstructure a catalytic ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) monomer is preferred approach. There is no doubt that metal initiators such as aluminum, tin, rare earth metals, and zinc compounds are dominant in this field considering nearly countless combinations of metal and ligands[17-18]. However, for most of medical applications, above metal initiators may lead to contamination of the polymers. In contrast, the use of alkali metals (sodium and potassium), which are innocuous, abundant elements in human body and are suitable for the catalytic synthesis of polyesters for use in medical-related fields, thus exploring sodium or potassium complexes as initiator for ring-opening polymerization of polyesters is very valuable.

Extensive studies have shown that alkali metal or alkali metal alkoxide can catalyze the ROP of ε-CL with high activity, but rarely highly selectivity[19]. As the ROP of ε-CL is a trans-esterification reaction, competitive trans-esterification of the resulting polymer can lead to broadening of the molecular weight distribution, depending on the relative rates of propagation (ring-opening) and chain transfer (trans-esterification, backbiting)[20]. For advanced practical applications, it is required that the molecular weight of PCL should be raised higher, and that molecular weight distribution be narrowed down. To improve the selectivity of alkali metal complex, here, we used a strategy of introducing a macrocyclic crown ether into an active alkali metal alkoxide, with suitable hindrance at the ring for increasing the interaction between the ε-CL and the active end of the PCL or ligand.

It is well known that crown ethers are interesting class of macrocyclic host compounds on account of their higher binding ability and selectivity with alkali-metal cations[21-24]. In particular, when the size of well-known 18-crown-6 (18C6) cavity matches that of the potassium (K^+) cation[25-30], crown ether can form complexes with K^+ ion. A steric barrier surrounding the K^+ ion can be formed. Most importantly, the addition of 18C6 can cause an increase in the solubility of K^+ alkoxide in the polymerization solvent, resulting in the efficient formation of initiating anion. Yokota et al.[31] reported "living" nature in anionic cyclopolymerization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol using the *t*-BuOK/18C6 initiating system in toluene. In 2014, sodium and potassium monophenoxides capped by 18-crown-6 reported by Wu et al.[32] can highly iso-selectively catalyze the ROP of *rac*-lactide in THF. In 2011, Wang et al.[33] reported various crown ether complexes that may accompany the active center with *t*-BuOK, in the anionic bulk polymerization of 2-furyloxirane. As such, as a continuous interest in *t*-BuOK/18C6 initiating system in the ROP of lactone, in this article, we examined the effect of 18C6 on the anionic polymerization of ε-CL using *t*-BuOK as initiator in THF. In this contribution, we

reported *t*-BuOK/18C6 complex, which is highly tunable and effective for the selective polymerization of ε-CL. As far as the polymerization of ε-CL initiated by *t*-BuOK is concerned, 18C6 may accompany the active center, enhancing the nucleophilicity of *t*-BuOK, producing anoutstanding activating effect, and reducing chain transfer and termination reactions to some extent[34-36], which may be beneficial for raising molecular weight of PCL. The polymerization provided PCL with controlled a high number average molecular weight of 7.55×10^4g mol^{-1} and a narrow distribution of 1.45 in 93.2% yield after polymerization at 25°C for 150 min. Moreover, the obtained PCL were detailedly characterized by ^{1}H NMR, FTIR, MALDI-ToF MS, DSC and TGA. The polymerization mechanism was proposed and analyzed.

EXPERIMENTAL

Materials

ε-Caprolactone (Alfa Aesar, 99%) was dried and distilled over fresh calcium hydride (CaH_2) powder underreduced pressure and stored over activated 4Å molecular sieves at room temperature prior to use. Tetrahydrofuran (THF) was dried by refluxing over a benzophenone-sodium complex and distilled prior to use.*tert*-Butyl alcohol (*t*-BuOH) was refluxed over CaH_2 for 48h prior to its distillation. 18-Crown-6 ether (Aladdin, 99%) was dried over activated 4Å molecular sieves at room temperature in THF, filtered using a vacuum-laminar column and then evacuated THF under vacuum. Methanol was used as received without further purification.

Preparation of initiator

Potassium *tert*-butoxide (*t*-BuOK) was synthesized under vacuum by the reaction of *t*-BuOH with a potassium mirror. Excess alcohol was removed via distillation using a side tube. *t*-BuOK was purified by sublimation under vacuum before use.

Polymerization Procedures

Anionic polymerization was carried out in flame-dried and argon-purged glass ampoules. In a typical experiment, 6.55 mg (0.058 mmol) *t*-BuOK and 45.96 mg (0.174 mmol) of 18C6 were added the ampoule and dried connecting to the vacuum line. Once the moisture and air were thoroughly evacuated, the exact amount of ε-CL (1.0 g, 8.76 mmol) was micro-syringe into the ampoule and determined by weighting at each stage. Then dried THF (4.38 mL) was introduced into a 10 mL ampoule to maintain the initial concentration of ε-CL at 2.0 mol L^{-1}. The molar ratio of ε-CL to *t*-BuOK was controlled to 150. At the end, the ampoule was placed in a thermostat for the polymerization. The reaction mixture was quenched with a drop of methanol. The polymers were precipitated using cold methanol and then dried to constant weight under vacuum at 40°C.

Polymer characterization

Gel permeation chromatography (GPC) was performed using a PL-GPC220 chromatograph equipped with refractive index (RI) detector and a series of columns (PL gel 10 μm, MIXED-B 300 mm × 7.5 mm, PL gel 10 μm, Guard 50 mm × 7.5 mm) and calibrated using polystyrene standards. THF was used as the mobile phase at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight (M_n) and polydispersity index(PDI) of the synthesized PCL homopolymers were obtained from their molecular weight distribution curve and RI peak height from 40 to 60 mV.

The thermal properties of the purified polymers were evaluated by differential scanning calorimetry (DSC) calibrated with pure indium and sapphire standards. Samples (10 mg) were analyzed with a DSC (DSC 200 F3) at a heating rate of 10°C min^{-1} under nitrogen. Polymer samples were quenched to –60°C and then heated to 150°C at a rate of 10°C min^{-1}. The samples were then quenched once again to –60°C and subjected to a second run at a rate of 10°C min^{-1}. The midpoint of the heat capacity change was taken as the glass transition temperature (T_g) and melting temperature (T_m).The thermal behavior of PCL polymers was investigated using thermogravimetric analysis (TGA) on a TGA/DSC1 instrument. The test samples with weights of 5-10 mg were heated from room temperature to 600°C at a heating rate of 10°C min^{-1}.

The heat flow, sample temperature, residual sample weight were continuously recorded on the instrument. Within this temperature range, the polymers were completely degraded.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were carried out on a Bruker Ascend 600 spectrometer using a 5mm O.D. sample tube in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard.^{1}H NMR spectra were referenced using the residual solvent peak at 7.27 ppm for $CDCl_3$. All spectra were obtained at room temperature from 0.7 mL solutions in $CDCl_3$ containing 10 mg of sample.

FTIR spectra were obtained on a Varian 660 IR spectrometer with a smart orbit assessor in the range of 4000-400 cm^{-1}. Polymer solutions were obtained by dissolving 5 mg of polymers in 1mL of chloroform ($CHCl_3$). Then, the solution was crossed about 30 min, and then a small amount of solution was dropped onto a pre-pressed KBr pellet and dried for approximately five minutes.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) of the PCL was performed using a mass spectrometer (Autoflexspeed; Bruker) equipped with a Smartbeam/Smartbeam II modified Nd:YAG laser. Five hundred shots were used to obtain spectra at a 25 kV acceleration voltage in the positive linear mode. Polymer samples were dissolved in THF at a concentration of 10 mg mL^{-1}using a matrix of trans-2-[3-(4-tert-butylphenyl)-2-methyl- 2-propylidene] malononitrile (DCTB) dissolved in THF (20 mg mL^{-1}). MALDI-ToF MS samples were prepared by mixing the matrix solution, polymer solution, and sodium trifluoroacetate (2 mg mL^{-1} in THF) in a volume ratio of 10:1:1. Then,1.0 mL of this solution was spotted onto the MALDI-ToF sample plate before being air-dried.

RESULTS AND DISCUSSION

Homopolymerization of ε-CL Initiated by t-BuOK/18C6 System

Table 1 lists the characterization results of ε-CL polymerized by *t*-BuOK in THF without 18C6 and containing 18C6 as a co-initiator. In the conventional polymerization without 18C6, *t*-BuOK gradually dissolved into the polymerization solution.The polymerization of ε-CL initiated by only *t*-BuOK achieved a conversion of 87.7%, with a molecular weight of 3.55×10^4 g mol^{-1} and a PDI of 1.86 at a [ε-CL]/[*t*-BuOK] molar ratio of 300 (Table 1, entry 3). And it was found that the PDI of PCL was relatively broad from 1.86 to 1.99 when the molar ratio [ε-CL]/[*t*-BuOK] changed from 150 to 300 (Table 1, entries 1-3), indicating the presence of severe chain transfer and termination reactions.The addition of 18C6 increased in the solubility of *t*-BuOK in solvent, resulting in the efficient formation of an initiating anion. As can be seen from Table 1, entries 4-6, the addition of 18C6 notably increased the yield and molecular weight of the resulting polymers. The similar diameter between K^+ (0.266nm) and the 18C6 cavity (0.26–0.32nm) promoted the formation of a stable coordination compound, which exposed the terminal groups of active species and increased initiation and propagation. In a word, 18C6 in this study shows positive effect in reducing chain transfer and termination, which proved to be efficient for controlling M_n and PDI in the ROP of ε-CL.

The variation in conversion and M_n as function of various 18C6/*t*-BuOK ratios was depicted graphically in Fig. 1. At 18C6/*t*-BuOK molar ratio of 3:1, PCL yield is 93.2% and molecular weight is 7.55×10^4 g mol^{-1}. The molecular weight of the product increased with increasing 18C6/*t*-BuOK molar ratio from 1:1 to 2:1. However, at higher molar ratio (18C6/*t*-BuOK>3:1), both the monomer conversion and molecular weight of PCL decreased. This result can explain that 18C6/ K^+ complex of 3:1 was

TABLE 1. Effect of addition of 18C6 on the anionic polymerization of ε-CL using *t*-BuOK[a]

Entry	Co-initiator	[ε-CL](mol L^{-1}) (mol L^{-1})	[ε-CL]/[I] Molar ratio	Yield[b](%)	$Mn^c \times 10^4$ (g mol^{-1})	PDI[c]
1	none[a]	2	150	88.1	2.66	1.99
2	none[a]	2	200	85.1	3.46	1.89
3	none[a]	2	300	87.7	3.55	1.86
4	18C6[b]	2	150	92.9	7.52	1.46
5	18C6[b]	2	200	89.0	6.28	1.68
6	18C6[b]	2	300	83.3	5.36	1.67

[a]Polymerization reaction conditions: 25 °C, 120 min, in THF; [b]Yield; [c]M_n and PDI determined by GPC.

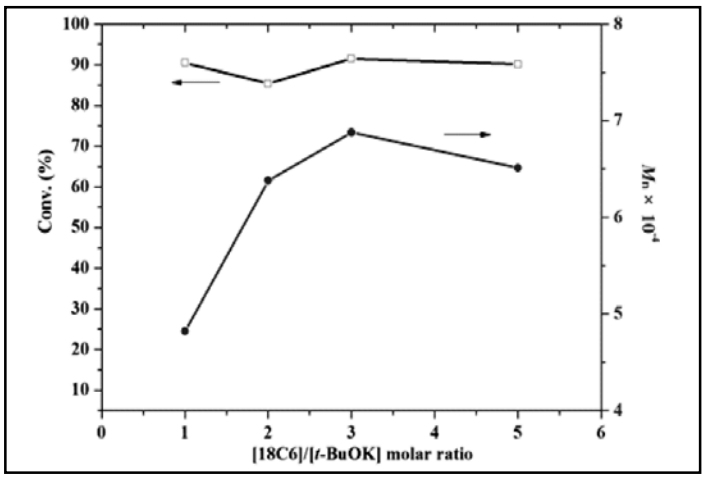


Fig. 1. Effects of molar ratio 18-crown-6/*t*-BuOK on ε-CL polymerization
Conditions: [ε-CL]=2.0 mol L^{-1}, 25°C, 150 min in THF

TABLE 2. Effects of monomer concentration and initiator concentration on the ε-CL polymerization at room temperature[a]

Entry	[ε-CL] (mol L^{-1}) (mol L^{-1})	[ε-CL]/[I] Molar ratio	Yield[b] (%)	$Mn^c \times 10^4$ (g mol^{-1})	PDI[c]
1	1.5	150	86.7	7.08	1.47
2	2.0	150	93.2	7.55	1.45
3	3.0	150	87.5	6.56	1.50
4	4.0	150	76.8	6.22	1.56
5	2.0	100	90.8	5.60	1.65
6	2.0	150	93.2	7.55	1.45
7	2.0	200	89.4	6.42	1.68
8	2.0	300	87.1	5.97	1.69

[a]Polymerization conditions: [18C6]/[*t*-BuOK] molar ratio = 3, 150 min, in THF; [b]Yield; [c]M_n and PDI determined by GPC.

stable enough to maintain stability through the exothermic reaction of rapid polymerization of ε-CL.

All experiments were carried out at a molar ratio of crown ether to initiator of 3:1.The influence of the monomer concentration and [ε-CL]/[I] molar ratio on polymerization are shown in Table 2, where [ε-CL] represents the monomer concentration, and [I] expresses the initiator concentration. In order to control reaction, [ε-CL] of 2.0 mol L^{-1} in THF was selected both to minimize constraints related to monomer diffusion and to decrease the viscosity of the reaction mixture. Based on this, at a low monomer concentration ([ε-CL] =1.5 mol L^{-1}), a PCL yield of 86.7% was obtained in 150 min with a PDI of 1.47 (Table 1, entry 1). However, the yield and M_n of the polymers decreased when the ε-CL concentration was higher than 2.0 mol L^{-1} (Table 1, entries 3 and 4). Moreover, due to the increased viscosity of the reaction mixtures, interchain transfer occurred, which led to broadened PDIs. To evaluate the behavior of [I] in the ROP ε-CL, experiments with vary loading of initiator were conducted. It is noted that both the monomer conversion and the molecular weight of PCL increased from 5.60×10^4 to 7.55×10^4 g mol^{-1} in the range of [ε-CL]/[I] = 100 to 150 (Table 2, entries 5 and 6), but both dropped linearly afterward (Table 2, entries 7 and 8). It can be seen that the favorable [ε-CL]/[I] molar ratio is 150 in the studied range. On account of the less active center in polymerization system, the polymerization cannot happen when decreasing initiator content. Yet increasing initiator content can give rise to form more and shorter polymeric chains, thus decreasing the molecular weight and broadening PDI of PCL. As discussed above, the optimum ε-CL

TABLE 3. Effects of polymerization time and temperature on ε-CL polymerization at a molar ratio[18-crown-6]/[*t*-BuOK] =3[a]

Entry	Time[b](min)	Temp.[c](°C)	Yield[b] (%)	*Mn*[c]×10^4 (g mol^{-1})	PDI[c]
1	90	25	91.8	6.74	1.51
2	120	25	92.9	7.52	1.46
3	150	25	93.2	7.55	1.45
4	180	25	90.5	6.63	1.55
5	210	25	88.4	6.01	1.59
6	150	10	90.8	5.60	1.65
7	150	15	92.3	6.74	1.52
8	150	25	93.2	7.55	1.45
9	150	30	92.7	7.41	1.48
10	150	35	90.9	6.42	1.56

[a]Polymerization conditions: [ε-CL]=2.0 mol L^{-1}, [ε-CL]/[I]=150, in THF; [b]Polymerization time; [c]Polymerization temperature; [d]Yield; [e]M_n and PDI determined by GPC.

concentration and initiator amount on the polymerization are as follows: [ε-CL] = 2.0 mol L^{-1}, [ε-CL]/[I] = 150.

The influence of reaction time and temperature on the polymerization of ε-CL is summarized in Table 3.The data show that 150 min was the optimal polymerization time at 25°C, and ε-CL conversion was nearly complete under this tested condition. Further prolonging the reaction time, polymers are generated with a lower molecular weight and broader molecular weight distribution, which may be due to the trans-esterification reaction occurring. Obviously, the ε-CL conversion increased with increasing of the polymerization temperature. At 30°C, the conversion and M_n was decreased to from 93.2% to 92.7% with 150 min and the PDI became slight boarder from 1.45 to 1.48 (Table 3, entries 8 and 9). When the temperature was elevated to 35 °C (Table 3, entry 10), monomer conversion was further decreased to 90.9% with 150 min and a PCL sample with M_n of 6.42×10^4 g mol^{-1} and PDI of 1.56 was obtained. Thus, it was concluded that the optimum polymerization conditions for ε-CL monomer initiated by *t*-BuOK/18C6 are : [ε-CL]=2.0 mol L^{-1}, [ε-CL]/[I]= 150, 25°C, and 150 min, in THF.

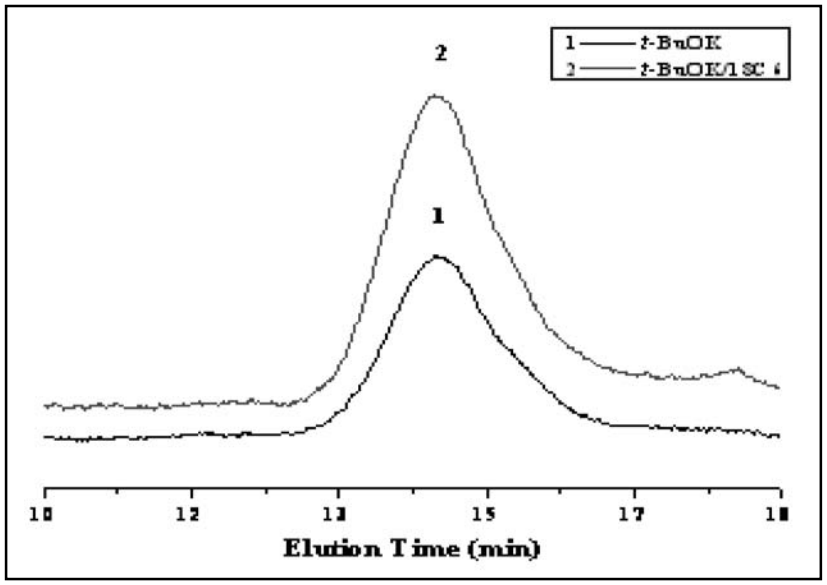


Fig. 2. Typical GPC curves of PCL (Table 1, entries 1 and 4).

PCL Characterization

The GPC chromatograms of PCL samples synthesized using the *t*-BuOK/18C6 system and pure potassium *tert*-butoxide are displayed in Fig. 2.The PCL sample obtained with the *t*-BuOK/18C6 complex has a high molecular weight and narrow molecular weight distribution (PDI =1.46) with a 92.9% yield. It can be denoted in curve 2 of Fig. 1. Curve 1 represents the PCL sample obtained using pure potassium

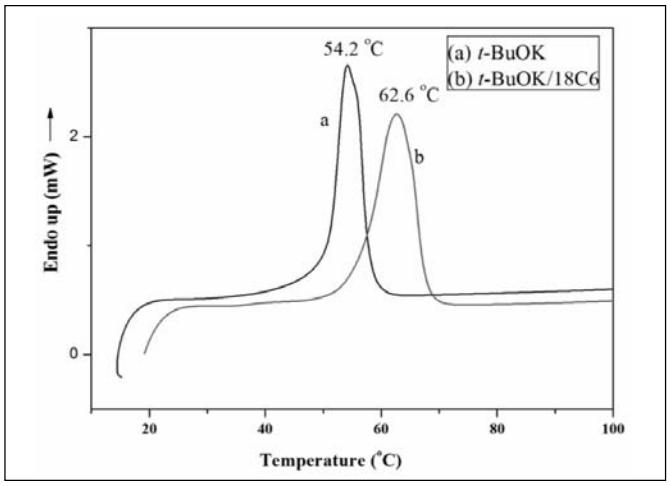


Fig. 3. DSC curves of PCL (Table 1, entries 1 and 4).

tert-butoxide, which has a relatively broader PDI. The unimodal peak profiles of both GPC curves were similar and confirmed the presence of only one type of active center.

The DSC traces of polymers are shown in Fig. 3. The PCL samples obtained by *t*-BuOK (a) and *t*-BuOK/18C6 (b) respectively displayed a single melting endothermic peak at 54.2°C and 62.6°C, in consistent with the thermal behavior of optically-pure PCL by other authors[37]. The prepared sample using the *t*-BuOK/18C6 system had a crystallinity of 52.9%; however, the crystallinity of PCL obtained using pure *t*-BuOK was only 43.7%

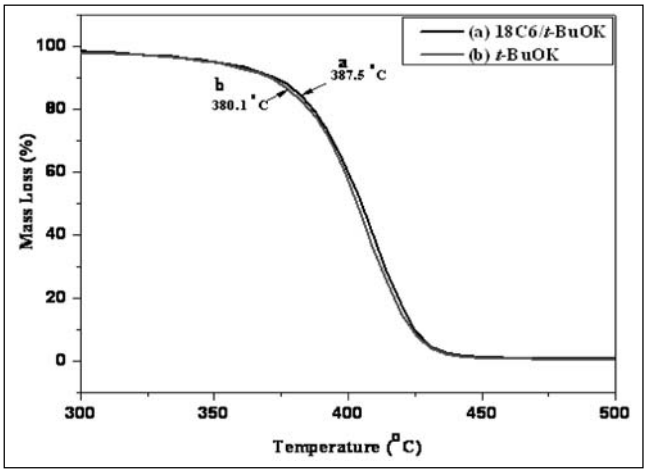


Fig. 4. TGA curves obtained at 10 °C min^{-1} under a nitrogen atmosphere: (a) PCL sample initiated by *t*-BuOK/18C6 (Table 1, entry 4); (b) PCL sample initiated by *t*-BuOK (Table 1, entry 1).

crystalline. The crystallinity increased with increasing of the molecular weight of the products. Moreover, the T_g was lower approximately -60 °C due to the presence of longer $–CH_2$ chains in the PCL sample.

The thermograms of pure PCL obtained by the two different catalysts are shown in Fig. 4 at a heating rate of 10 °C min^{-1} under an N_2 atmosphere. The weight loss was equal to the integral of the DTA curve against temperature. From the TG curves, PCL samples (a) and (b) showed the same degradation profile, with an initial mass loss occurring near 100°C.The thermal degradation of polycaprolactone proceeded in a single step and may have involved thermal degradation (Fig. 4). The thermal degradation temperature increased to 387.5°C from 380.1°C, which showed that the thermal stability of PCL increased with its molecular weight.

FTIR spectroscopy was utilized to examine the characteristic peak of the polymer functional groups. The two spectra in Fig. 5 are similar, and a weak peak attributed to the hydroxyl group was observed near 3400 cm^{-1}. A clear and sharp absorption peak near 1726 cm^{-1} showed the presence of an ester carbonyl.

In order to investigate the polymerization mechanism, the ^1H NMR spectrum of a PCL sample is presented in Fig. 6. The main signals in the spectrum were δ=2.30 ppm (H^a), δ=1.40 ppm (H^b), δ=4.04 ppm (H^c), and δ=1.64 ppm (H^d). Other signals in the spectrum included δ = 7.26 ppm ($CDCl_3$ solvent) and δ= 3.65 ppm (H^e).

MALDI-ToF MS was also used to analyze the structure of PCL.The spectrum exhibited molecular ion peaks corresponding to linear PCL with BuO/H chain ends (Fig. 7; M_n = 114.14n+108.0+23.0 (Na^+) g mol^{-1}). A plot of

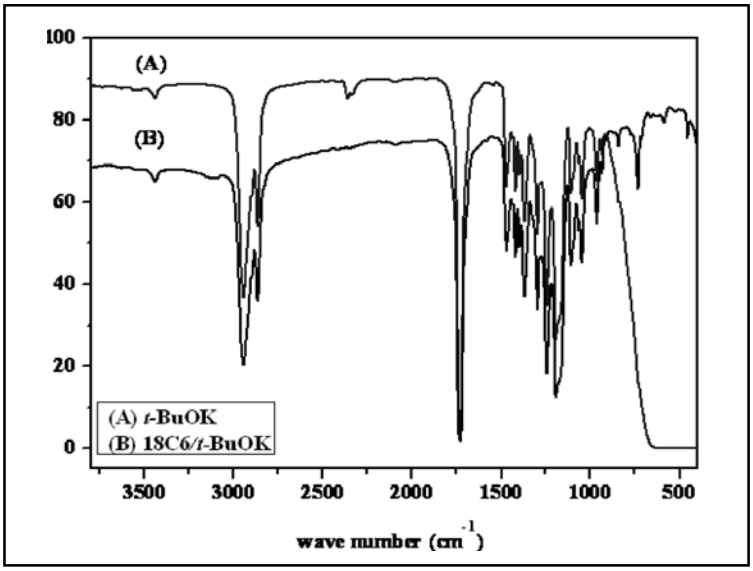


Fig. 5. FTIR spectra of PCL: (A) PCL obtained by *t*-BuOK/18C6 initiator system (Table 1, entry 4) and (B) PCL obtained by *t*-BuOK initiator system (Table 1, entry 1).

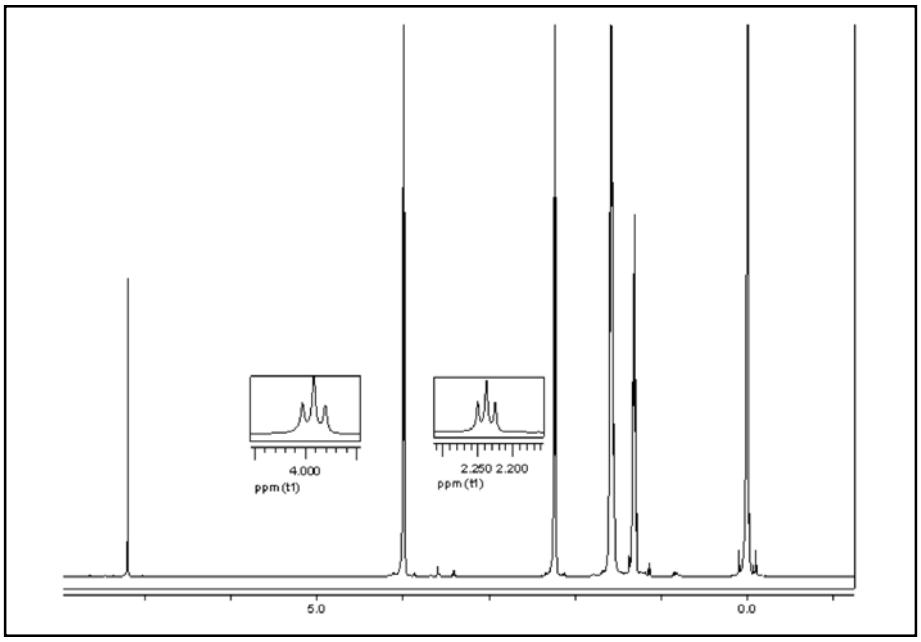
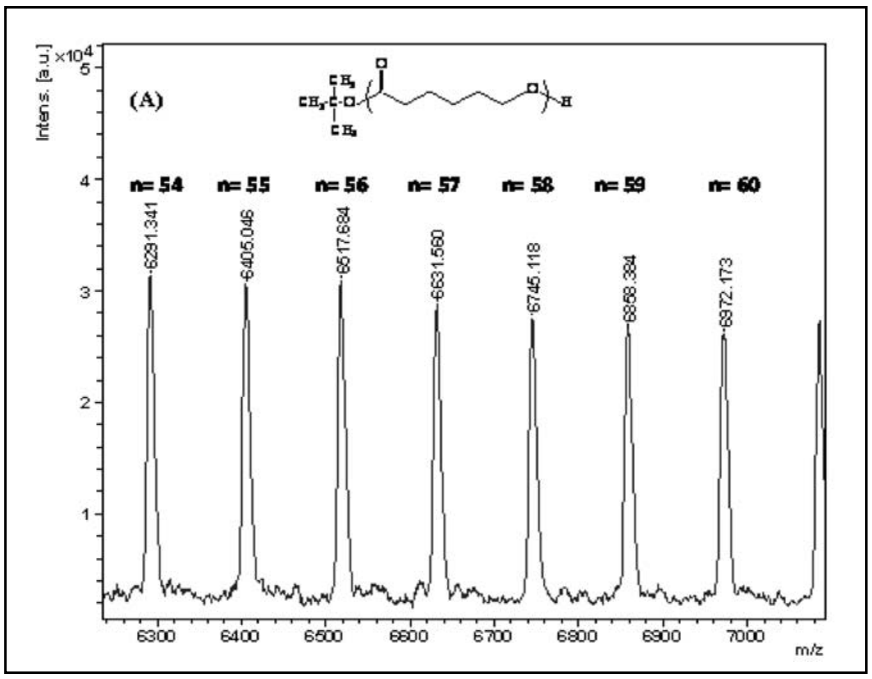


Fig. 6. ^{1}H NMR spectrum of PCL samples with *t*-BuOK/18C6 system (Table 2, entry 6).



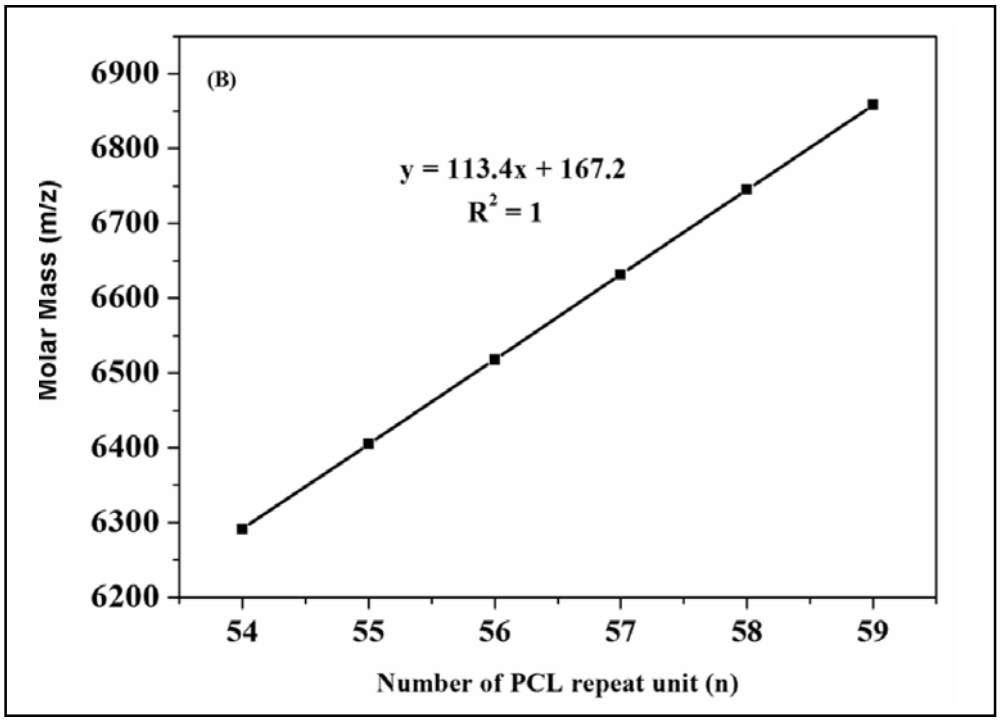


Fig. 7. MALDI-ToF MS spectrum of the obtained PCL sample (Table 2, entry 6) in the positive linear mode (A). Detail including experimentally observed mass; (B) the plot of the molar mass (m/z) versus the number of monomer repeat units (n).

m/z values of this series versus the number of monomer repeat units (n) yielded a straight line ($R^2 = 1$). In addition, another signals present, predominately as an oligomer, was assigned to sodium complexed with cyclic PCL, which was formed by intramolecular trans-esterification reaction. Based on this analysis, the *t*-BuOK/18C6 system catalyzed the anionic ring-opening polymerization of ε-CL. First, a nucleophilic ethoxide anion attached the carbonyl carbon atom of ε-CL, and the ε-CL monomer ring was opened into a negative oxygen ion adduct. In the second step, monomer was successively initiated by the negative oxygen ion to form PCL propagation chains. The α-chain end of PCL bears the ester from *t*-BuOK, and the ω-chain end is a primary alcohol that serves as the nucleophile in subsequent propagation steps.

CONCLUSIONS

In this study, 18C6 showed suitable complexing ability with K^+, which provided a high-activity system for the ring-opening polymerization of ε-CL. The complexation of *t*-BuOK with 18C6 showed higher initiator efficiency toward the ROP of ε-CL and produced PCL with higher molecular weight and relatively narrow distribution. The effects of addition of 18C6 and reaction conditions on anionic

polymerization were systematically investigated. A PCL homopolymer with a high molecular weight up to 7.55×10^4 g mol^{-1} was synthesized using *t*-BuOK/18C6 system after 150 min at [ε-CL]=2.0 mol L^{-1}, [ε-CL]/[I] = 150, and 25°C in THF.The thermal properties and crystallization of PCL were characterized by TGA and DSC methods.The molecular structure of the polymer was studied by ^{1}H NMR and MALDI-ToF MS. A mechanism for the polymerization of ε-CL was proposed using *t*-BuOK/18C6 complex.

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REFERENCES

1. S. de Valence, J. Tille, D. Mugnai, W. Mrowczynski, R. Gurny, M. Moller and B. H. Walpoth. *Biomaterials* 33 (2012) 38.
2. R. R. Duling, R. B. Dupaix, N. Katsube and J. Lannutti. *J. Biomech. Eng.* 130 (2008) 011006.
3. W. Amass, A. Amass and B. Tighe. *Polym. Int.* 47 (1998) 89.
4. H. Shirahama, M. Shiomi, M. Sakane and H. Yasuda. *Macromolecules* 29 (1996) 4821.
5. K. Phomphrai, C. Pongchan-o, W. Thumrongpatanaraks, P. Sangtrirutnugul, P. Kongsaeree and M. Pohmarkotr. *Daton Trans.* 40 (2011) 2157.
6. K. Makiguchi, T. Satoh and T. Kakuchi. *Maromolecules* 44 (2011) 1999.
7. L. You, Z. Shen, J. Kong and J. Ling. *Polymer* 55 (2014) 2404.
8. C. Wei, X. Kou, S. Liu and Z. Li. *Polym. Chem.* 10 (2019) 5909.
9. Y. Wang, Y. Han and L. Zhang. *RSC Adv.* 10 (2020) 25979.
10. C. Jerome and P. Lecomte. Adv. *Drug Delivery Rev.* 60 (2008) 1056.
11. S. Penczek, M. Cypryk, A. Duda, P. Kubisa and S. Slomkowski. *Prog. Polym. Sci.* 32 (2007) 247.
12. L. You, Z. Shen, J. Kong and J. Ling. *Polymer* 55 (2014) 2404.
13. H. Li, N. Zhao, C. Ren, S. Liu and Z. Li. *Polym. Chem.* 8 (2017) 7369.
14. C. Jerome and P. Lecomte. *Adv.Drug Delivery Rev.* 60 (2008) 1056.
15. Y. Li, N. Zhao, C. Wei, A. Sun, S. Liu and Z. Li. *Eur. Polym. J.* 111 (2019) 11.
16. J. Xu, H. Wang, S. Xu, T. Guo, K. Yang and K. Guo. *Eur. Polym. J.* 113 (2019) 197.
17. C.A. Wheaton, P. G. Hayes and B. J. Ireland. *Dalton Trans.* 25 (2009) 4832.
18. N. Ajellal, J. F. Carpentier, C. Guillaume, M.S. Guillaume, M. Helou, V. Poirier, Y. Sarazin and A. Trifonov. *Dalton Trans.*39 (2010) 8363.
19. H. Amri, M. N. Belgacem and A. Gandini. *Polymer* 37 (1996) 4815.
20. S. Penczek, T. Biela and A. Duda. *Macromol. Rapid Commun.* 21 (2000) 941.
21. C. J. Pedersen. *Angew. Chem. Int. Ed.* 27 (1988) 1021.
22. J. Orvik. *J. Am. Chem. Soc.* 98 (1976) 3322.
23. S. Boileau, A. Deffieux, D. Lassale, F. Menezes and B. Vidal. *Tetrahedron Lett.* 20 (1978) 1767.
24. H. Koinuma, H. Naito and H. Hirai. *Makromol. Chem.* 183 (1982) 1383.
25. Y. Inokuchi, T. Ebata, T. R. Rizzo and O. V. Boyarkin. *J. Am. Chem. Soc.* 136 (2014) 1815.
26. R. Dorati, C. Colonna, I. Genta and B. *Conti. Berlin, Heidelberg: Springer.* 8 (2011) 259.
27. J. Igwe, A. Amini, P. Mikael, C. Laurencin and S. Nukavarapu. *Berlin, Heidelberg: Springer.* 22 (2011) 169.

28. A. Gurarslan, J. L. Shen and A. E. Tonelli. *Polymer* 54 (2013) 5747.

29. A. Deffieux and S. Boileau. *Macromolecules* 9 (1976) 369.

30. J. F. Ding, D. Attwood, C. Price and C. Booth. *Eur. Polym. J.* 27 (1991) 901.

31. T. Hatakeyama, M. Kamada, T. Satoh and K. Yokota. *Macromolecules* 31 (1998) 2889.

32. J. Zhang, J. Xiong, Y. Sun, N. Tang and J. Wu. *Macromolecules* 47 (2014) 7789.

33. R. Su, Y. Qin, L Qiao, J. Li, X. Zhao , P. Wang, X. Wang and F. Wang. *J. Polym. Sci.: Part A: Polym. Chem.* 49 (2011) 1295.

34. A. Stolarzewicz and Z. Grobelny. *Makromol. Chem.* 193 (1992) 531.

35. A. Stolarzewicz, D. Neugebauer and Z. Grobelny. *Macromol. Chem. Phys.* 196 (1995) 1301.

36. T. Hatakeyama, M. Kamada, T. Satoh and K. Yokota. *Macromolecules* 31 (1998) 2889.

37. R. F. Storey, K. R. Herring and D.C. Hoffman. *J. Polym. Sci. Part A: Polym. Chem.* 29 (1991) 914.

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