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A novel approach to RE–OR bond from *in situ* reaction of rare earth triflates and sodium alkoxides: A versatile catalyst for living ring-opening polymerization of ε-caprolactone

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ABSTRACT

A series of rare earth triflates ($RE(OTf)_3$, RE = Sc, Y and Lu) were used for the first time as moisture-stable precursors to generate rare earth alkoxide complexes through an *in situ* reaction with sodium alkoxides (NaOR) in tetrahydrofuran. ^1H NMR and ^{13}C NMR results confirmed the fast ligands exchange process and the formation of rare earth–oxygen (RE–OR) bond. The *in situ* formed catalysts displayed high reactivity toward living ring-opening polymerization (ROP) of ε-caprolactone (CL). For instance, $Lu(OTf)_3$/sodium isopropoxide (NaO^iPr)-catalyzed ROP of CL with the $[CL]_0/[NaO^iPr]_0/[Lu(OTf)_3]_0$ feeding ratio of 300/3/1 produced poly(ε-caprolactone) (PCL) with controlled molecular weight ($M_{n,exp}$ = 11.9 kDa *vs* $M_{n,theo}$ = 11.8 kDa) and narrow polydispersity (PDI) of 1.08 within 3 min at 25 °C. The kinetic studies and chain extension confirmed the controlled/living nature for the $Lu(OTf)_3/NaO^iPr$-catalyzed ROP of CL. In addition, end-functionalized PCLs bearing vinyl or alkynyl group with narrow PDIs were obtained by using functional sodium alkoxides in the presence of $Lu(OTf)_3$. ^1H NMR and MALDI-ToF MS analyses of the obtained PCLs clearly indicated the presence of the residue of OR groups at the chain ends. A coordination–insertion polymerization mechanism was proposed including a fast ligand exchange between $Lu(OTf)_3$ and NaOR giving the respective lutetium alkoxide complexes, and a CL insertion into RE–OR bond *via* acyl-oxygen cleavage.

1. Introduction

Over the past two decades, alkoxides or aryloxides of rare earth metals have been designed and successfully evaluated in controlled/living ring-opening polymerization (ROP) of lactones [1–5], lactides [6–10] and other cyclic monomers [11–14]. The synthesized polyester gained wide applications in the pharmaceutical, biomedical and industrial fields due to its excellent biocompatibility in body and miscibility with other polymers [15–17]. Compared with other metal alkoxide complexes, rare earth metal based initiators are much less toxic than aluminum alkoxides [18,19], and display higher polymerization activity in mild condition than tin(II) complexes [20–22]. Methods used in preparation of rare earth alkoxides fall into two main categories. The first one is so-called direct synthesis method, proceeding with the inhomogeneous and time-consuming salt-exchange reaction in solvent using the respective rare earth chlorides ($RECl_3$) and sodium alkoxides (NaOR) [23]. However, only few rare earth alkoxides can be prepared and they, $Y_5(\mu\text{–}O)(O^iPr)_{13}$ for example, have complicated structures and thus result in unpredictable initiation efficiencies [24]. The other includes ligands exchange reaction between alcohols and rare earth aryloxides [25,26], rare earth tris(hexamethyldisilyl)amide [27,28] and rare earth alkyl complexes [29–31]. The *in situ* formed rare earth alkoxides initiate the controlled ROP of ε-caprolactone (CL) and prevent the alkoxides from clustering. However, the rare earth complexes precursors themselves are very much moisture-sensitive and prepared in a tedious way similar to the first method. In addition, the exchange reactions produce proton-involved aromatic alcohol (ArOH) or 1,1,1,3,3,3-hexamethyldisilazane (HMDS), which may have some detrimental effects on polymerization rate and side reaction.

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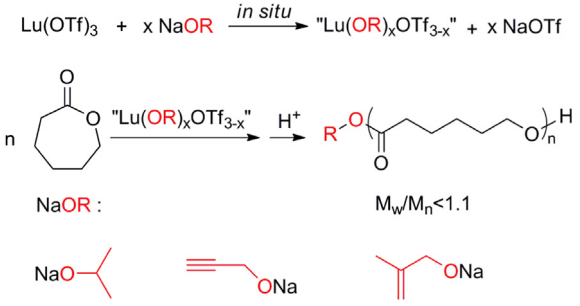


Scheme 1. ROP of CL using the *in situ* generated catalytic system of $Lu(OTf)_3$/sodium alkoxides where $x \leq 3$.

Nowadays rare earth metal triflates have received much attention toward organic synthesis in aqueous media thanks to their air and moisture stability compared with other conventional Lewis acids [32]. However, fewer attempts are promoted in polymer chemistry [33–35]. Okada et al. reported a cationic living ROP of lactones using scandium triflate ($Sc(OTf)_3$) as a catalyst and alcohols as initiators respectively *via* an activated monomer mechanism [36]. Nevertheless, long time and high temperature are indispensable to obtain proper monomer conversion due to the relatively low activity of this special catalytic system. For instance, it took 4 days to obtain poly(ε-caprolactone) (PCL) with molecular weight (MW) of 2200 and polydispersity index (PDI) of 1.30 when $Lu(OTf)_3$ and benzyl alcohol were used [37]. Moreover, pure end-functionalized polyesters were not accessible using $Sc(OTf)_3$/alcohol catalytic system since H_2O initiated contaminated polyesters could not be excluded [35,38]. Another example is a living/controlled cationic ROP of tetrahydrofuran (THF) using rare earth triflate catalyst in the presence of epoxide to produce well-defined polyethers [39].

Despite the many rare earth compounds reported for ROP of different cyclic esters, rare earth–oxygen (RE–OR) bond is actually the growing active site for monomer insertion [40–43]. However, only one lutetium alkoxide complex from alkyl lutetium and alcohol was reported as initiator for ROP of lactones [31]. Here we report novel lutetium alkoxide complexes *in situ* generated by a fast ligand exchange reaction of moisture-stable lutetium triflate ($Lu(OTf)_3$) with sodium alkoxides (NaOR) in THF within only 3 min excluding the formation of any other deleterious byproducts (Scheme 1). It exhibits high catalytic activity and excellent controllability towards ROP of CL in mild conditions, producing PCLs with predictable MWs and narrow PDIs below 1.10. Pure end-functionalized PCLs containing vinyl and alkynyl end-groups are also simply synthesized using $Lu(OTf)_3$ and corresponding sodium alkoxides.

2. Experimental

2.1. Materials

CL (Acros, 99%) was distilled under reduced pressure after being stirred over CaH_2 for 48 h. 2-Propanol (Sinopharm, AR), β-methallyl alcohol (Shanghai Jingchun, AR) and propargyl alcohol (Shanghai Jingchun, AR) were dried over 4Å molecular sieve for 48 h and then distilled under reduced pressure. THF was refluxed over potassium/benzophenone ketyl prior to use. NaOR were prepared from the respective alcohols and sodium metal in THF, and dried in vacuum to remove the residual alcohol and solvent. Sodium triflate (NaOTf) was prepared from the reaction of NaOH and triflic acid. $RE(OTf)_3$ (RE = Sc, Y, and Lu) were synthesized from corresponding RE_2O_3 and triflic acid according to the reported method [39]. Isolated $Lu(O^iPr)_3$ (**1**) compound, although its precise structure is still unknown, was prepared in a similar way to $Y_5(\mu\text{–}O)(O^iPr)_{13}$ according to the literature [44,1]. THF-d_8 (Acros, 99.5% deuterated) was dried over P_2O_5 and distilled into an NMR tube under reduced pressure.

2.2. Polymerization

CL polymerizations were carried out in THF in previously flamed and argon-purged 30 mL ampoules using Schlenk techniques. Solid NaOR was added and followed by predetermined amount of $RE(OTf)_3$ in THF solution. They were allowed to stir for 3 min at room temperature (20 °C) before CL was added. After predetermined time, a portion of the polymerization mixtures was taken out and added by a drop of trifluoroacetic acid to determine the monomer conversion in ^1H NMR measurements. Polymerization reaction was quenched by addition of an excess of 1 mol/L HCl solution. The polymer was isolated by reprecipitation from $CHCl_3$ in cold methanol and dried under vacuum to constant weight.

2.3. Kinetic study

NaO^iPr (37.4 mg, 0.456 mmol), THF (9.8 mL) and $Lu(OTf)_3$ (141.8 mg, 0.228 mmol) were mixed under argon in a 30 mL Schlenk tube. After stirring for 3 min at room temperature, the polymerization started upon addition of CL (5.2 g, 45.6 mmol). Samples were taken during the polymerization, and subjected to ^1H NMR and SEC analyses.

Table 1
Ring-opening polymerization of ε-caprolactone (CL) catalyzed by rare earth triflates ($RE(OTf)_3$) and sodium isopropoxide (NaO^iPr) in THF.[a]

Run	$RE(OTf)_3$	$[Lu]_0$:$[Na]_0$:$[CL]_0$ molar ratio	Time (min)	Conv[b] (%)	$M_{n(exp)}$[c] (kDa)	PDI[c]	$M_{n(theo.)}$[d] (kDa)
1	$Lu(OTf)_3$	1:1:100	50	90.0	9.7	1.09	10.2
2	$Lu(OTf)_3$	1:2:200	35	91.0	10.1	1.06	10.4
3	$Lu(OTf)_3$	1:3:300	3	99.0	11.9	1.08	11.8
4	$Lu(OTf)_3$	1:1:200	240	70.0	13.6	1.23	15.9
5	$Lu(OTf)_3$	1:2:400	110	50.6	11.0	1.05	11.5
6	$Lu(OTf)_3$	1:3:600	8	98.0	21.8	1.07	22.3
7	$Lu(OTf)_3$	1:4:800	3	97.0	24.1	1.28	22.1
8	$Lu(OTf)_3$	1:6:1200	2	95.3	21.7	1.53	21.7
9	$Y(OTf)_3$	1:3:600	0.5	90.2	23.3	1.27	20.5
10	$Sc(OTf)_3$	1:3:600	90	50.2	13.0	1.11	11.4
11	–[e]	0:1:100	2	92.2	9.8	2.01	10.5
12	$Lu(OTf)_3$	1:0:300	4 day	0	–	–	–

[a] $[CL]_0 = 3.0$ mol L^{-1}, 20 °C.
[b] Determined by ^1H NMR.
[c] Determined by SEC.
[d] Calculated from $([CL]_0/[NaO^iPr]_0) \times$ Conv × (MW of CL) + (MW of isopropanol).
[e] No $RE(OTf)_3$ was used.

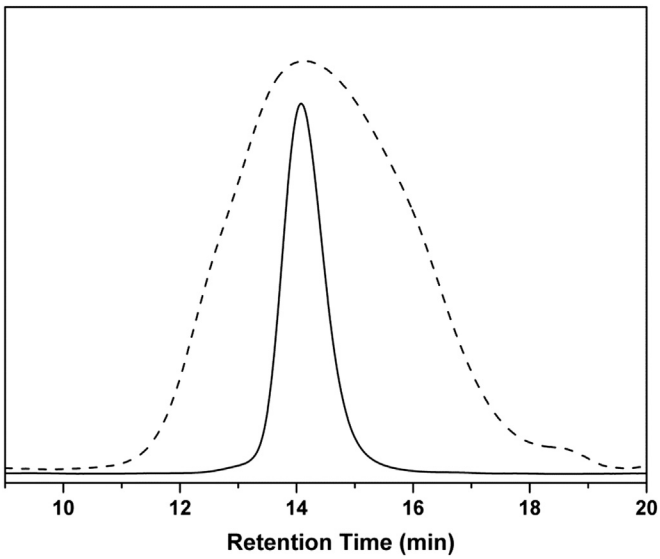


Fig. 1. SEC traces of the obtained PCLs catalyzed by $Lu(OTf)_3/NaO^iPr$ (solid line, Table 1, run 3) and by NaO^iPr alone (dashed line, Table 1, run 11).

2.4. Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DMX 500 MHz (^1H: 500 MHz and ^{13}C: 125 MHz) spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference or in THF-d_8. Size exclusion chromatography (SEC) was performed on a Waters-150C apparatus in THF with a flow rate of 1.0 mL/min at 40 °C using narrow PDI polystyrene (PS) standards for calibration. Number-average MW of PCL ($M_{n,PCL}$) was calculated according to the relationship $M_{n,CL} = 0.54 \times M_{n,PS}$ [45].

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectra were measured on an Applied Biosystems Voyager System 4350 equipped with a 337 nm nitrogen laser (3 ns pulse width). All polymer (3–5 mg/mL PCL) mass spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. 2,5-Dihydroxybenzoic acid (20 mg/mL in THF) was used as a matrix and NaI (10 mg/mL in THF) was used as the cationic agent.

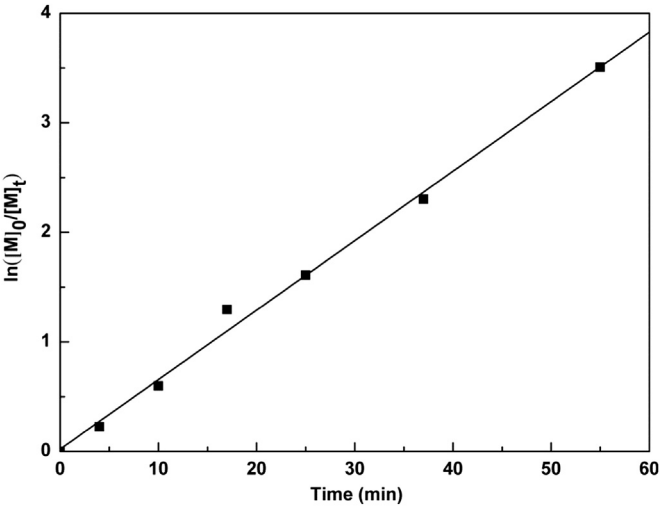


Fig. 2. First-ordered kinetic plot for the polymerization of CL catalyzed by $Lu(OTf)_3/NaO^iPr$ in THF at 20 °C, $[CL]_0 = 3.0$ mol L^{-1}, $[Lu(OTf)_3]_0 = 0.015$ mol L^{-1}, and $[NaO^iPr]_0 = 0.03$ mol L^{-1}.

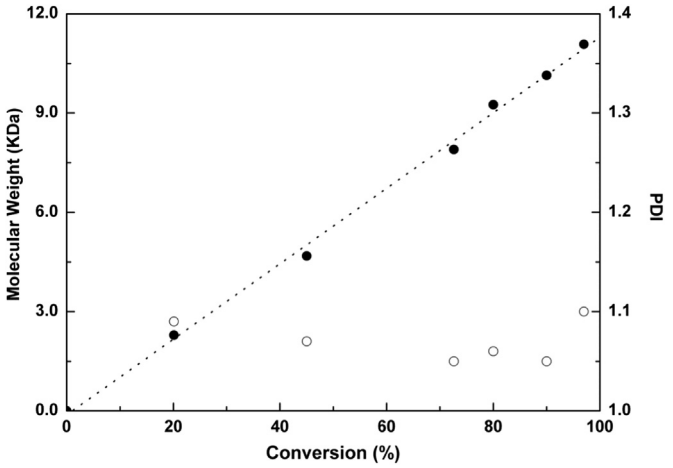


Fig. 3. Dependence of number-average molecular weight (M_n) and polydispersity (PDI) on monomer conversion for the CL ROP catalyzed by $Lu(OTf)_3/NaO^iPr$ in THF at 20 °C, $[CL]_0 = 3.0$ mol L^{-1}, $[Lu(OTf)_3]_0 = 0.015$ mol L^{-1}, and $[NaO^iPr]_0 = 0.03$ mol L^{-1}. Dotted line is the $M_{n,theo}$ values calculated as $([CL]_0/[NaO^iPr]_0) \times Conv \times (MW\ of\ CL)$.

3. Results and discussion

3.1. ROP of CL using the in situ generated catalyst derived from rare earth triflates ($RE(OTf)_3$) and sodium isopropoxide (NaO^iPr)

Compared with the rare earth complex catalysts previously reported [27,46–48], the unique advantages of the present catalytic system include moisture-stable $RE(OTf)_3$, commercially available NaO^iPr, and simple *in situ* ligand exchange reaction without time-consuming isolation. Several polymerizations of CL were carried out in THF, using the *in situ* generated catalyst consisting of $RE(OTf)_3$ (RE = Sc, Y, Lu) and NaO^iPr as summarized in Table 1. When 1/3 molar ratio of $Lu(OTf)_3$ with respect to NaO^iPr was added, the conversion of CL was as high as 99% within 3 min (Table 1, run 3), maintaining a high propagation rate close to that observed in NaO^iPr and producing PCL with narrow PDI of 1.08. As illustrated in Fig. 1, SEC trace of PCL obtained by $Lu(OTf)_3/NaO^iPr$ (Table 1, run 3)

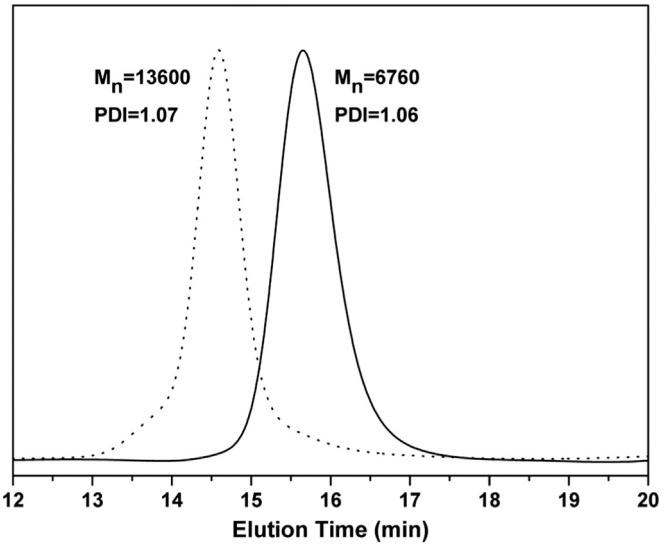


Fig. 4. SEC traces of PCL precursor (solid line, $[CL]_0 = 3.0$ mol L^{-1}, $[CL]_0/[NaO^iPr]_0/[Lu(OTf)_3]_0 = 120/2/1$, polymerization time = 3 min) and final product after the addition of a second batch of CL monomer (dotted line, polymerization time = 5 min).

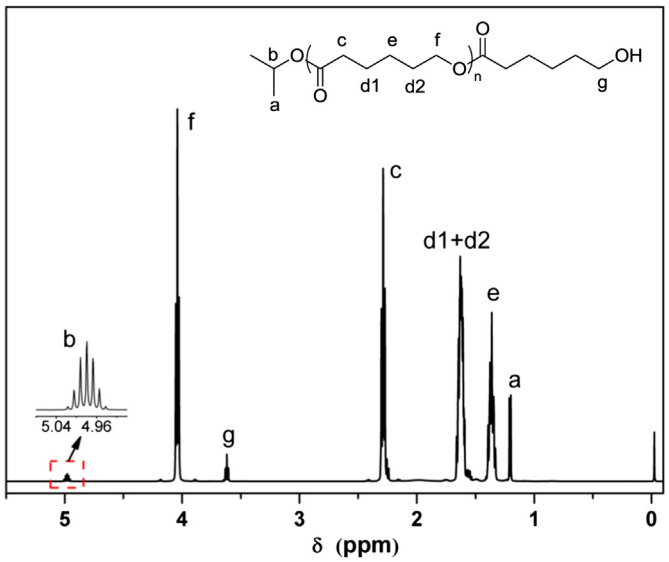


Fig. 5. ^{1}H NMR spectrum of the obtained PCL (Table 1, run 3) in $CDCl_3$.

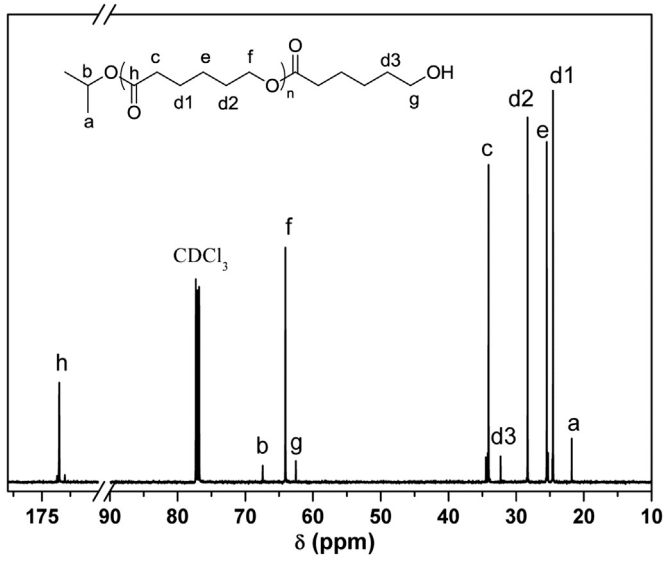


Fig. 6. ^{13}C NMR spectrum of the obtained PCL (Table 1, run 3) in $CDCl_3$.

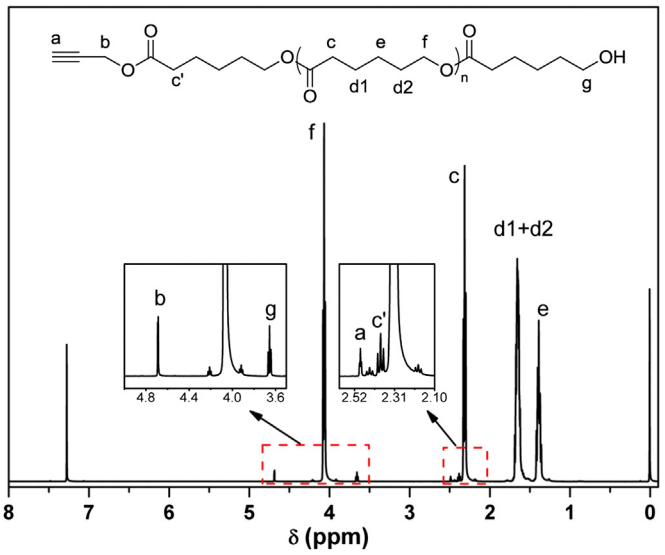
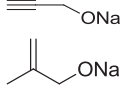
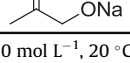
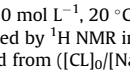


Fig. 7. ^{1}H NMR spectrum of the alkynyl-ended PCL (Table 2, run 1) in $CDCl_3$ from ROP of CL catalyzed by $Lu(OTf)_3$/sodium propargyloxide.

was symmetrical and narrow, in sharp contrast with that using NaO^{i}Pr alone (Table 1, run 11). As a typical anionic initiator, NaO^{i}Pr gave very fast polymerization of CL, but severe inter and intramolecular transesterification reactions occurred, leading to broad PDIs above 2.0 [49]. On the other hand, no PCL was obtained using $Lu(OTf)_3$ alone even after 4 days (Table 1, run 12).

With fixed $[CL]_0/[NaO^{i}Pr]_0$ ratio of 100 or 200 (Table 1, runs 1–3 or runs 4–6), propagation rate increased as $[NaO^{i}Pr]_0/[Lu(OTf)_3]_0$ molar ratios raised from 1 to 3. In addition, experimental MWs of the obtained PCLs were in agreement with those calculated from initial ratios of $[CL]_0/[NaO^{i}Pr]_0$ and monomer conversions, regardless of the various feeding ratios of $[NaO^{i}Pr]_0/[Lu(OTf)_3]_0$. Further increasing ratios of $[NaO^{i}Pr]_0/[Lu(OTf)_3]_0$ to 4 and 6 resulted in continuous rise of propagation rate, however, the controllability of the polymerization became poor as the PDIs of the obtained PCLs broadened to 1.5 (Table 1, runs 7 and 8). As a crucial component of the novel catalytic system, different $RE(OTf)_3$ exhibited distinctive activity towards ROP of CL (Table 1, runs 3, 9 and 10). For instance, $[NaO^{i}Pr]_0/[Y(OTf)_3]_0$ with ratio of 3 produced PCL with conversion of 90.2% in 30 s (Table 1, run 9), even faster than NaO^{i}Pr alone (Table 1, run 11). However, the broadened PDIs of PCLs up to 1.27 indicated the existence of adverse side reactions (Table 1, run 9). $Sc(OTf)_3$ exhibited the lowest catalytic activity among the three $RE(OTf)_3$, giving monomer conversion of 50.2% in 90 min under the same condition (Table 1, run 10), in contrast to its relatively high reactivity in the cationic cases [37]. The relatively low polymerization rate of scandium triflate may be contributed to the low activity of the corresponding scandium alkoxide as described in the scandium tris(2,6-di-*tert*-butyl-4-methylphenolate)-mediated ROP of CL [50].

Table 2
Synthesis of end-functionalized PCLs using different sodium alkoxides in the presence of $Lu(OTf)_3$ in THF.[a]

Run	NaOR	$[Lu]_0$:$[NaOR]_0$:$[CL]_0$ molar ratio	Conv[b] (%)	$M_{n(theo.)}$[c] (kDa)	$M_{n(NMR)}$[b] (kDa)	$M_{n(SEC)}$[d] (kDa)	PDI[d]
1		1:2:100	99.2	5.7	5.6	5.5	1.08
2		1:3:300	99.0	11.4	11.8	11.6	1.09
3		1:2:100	99.3	5.7	5.8	5.9	1.04

[a] $[CL]_0 = 3.0$ mol L^{-1}, 20 °C, 3 min.
[b] Determined by ^{1}H NMR in $CDCl_3$.
[c] Calculated from $([CL]_0/[NaO^{i}Pr]_0) \times Conv \times (MW\ of\ CL) + (MW\ of\ corresponding\ alcohol)$.
[d] Determined by SEC.

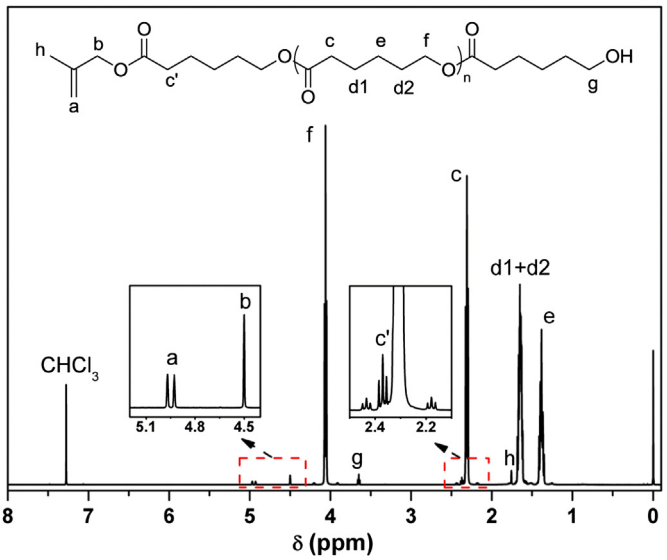


Fig. 8. ^{1}H NMR spectrum of the vinyl-ended PCL (Table 2, run 3) in $CDCl_3$ from ROP of CL catalyzed by $Lu(OTf)_3$/sodium β-methallyloxide.

3.2. Living ROP of CL catalyzed by $Lu(OTf)_3/NaO^iPr$

The kinetic and postpolymerization experiments were carried out to confirm the controlled/living nature of the $Lu(OTf)_3/NaO^iPr$-mediated ROP. Fig. 2 shows a distinct first-order relationship between reaction time and monomer consumption indicating a constant concentration of active species during the polymerization [51]. No induction period is observed according to the fact that the fitting line passes the origin, indicating that no substantial rearrangement of the catalytic species was required before the polymerization started [52,25]. MWs of the obtained PCLs linearly increase with the monomer conversions as high as 99% (Fig. 3). More importantly, the experimental $M_{n,(exp)}$ values of the obtained PCLs agree very well with the theoretical ones calculated by the feeding molar ratios of $[CL]_0/[NaO^iPr]_0$ and the monomer conversions. From the SEC results, the PDIs of the obtained PCLs show rather narrow values ranging from 1.05 to 1.09 throughout the polymerization. All of these evidences support the livingness of ROP.

As a further evidence of the controlled/living nature, a second batch of CL monomer with the same amount of the first one was added to a living PCL precursor with $M_{n,(exp)} = 6760$ g mol^{-1} and PDI = 1.06 after monomer conversion of 99.2% determined by ^{1}H NMR. The living chains kept growing and the MW of final PCL doubled at a total CL conversion of 98.9%. The narrow polydispersity (PDI = 1.07) in the SEC curves (Fig. 4) indicated the absence of chain termination and transfer reactions.

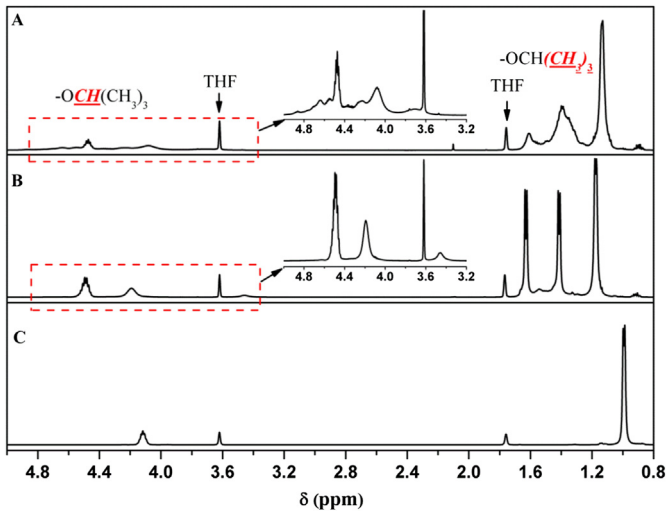


Fig. 10. ^{1}H NMR spectra of the *in situ* formed catalytic system by $Lu(OTf)_3$ and 3 equivalence of NaO^iPr (A), $Lu(O^iPr)_3$ (**1**) (B), NaO^iPr (C) in THF-d_8.

3.3. Synthesis of end-functionalized PCLs using different sodium alkoxides in the presence of $Lu(OTf)_3$

The results based on ^{1}H NMR and ^{13}C NMR analyses conclude that the obtained PCL possesses an isopropyl ester group at one

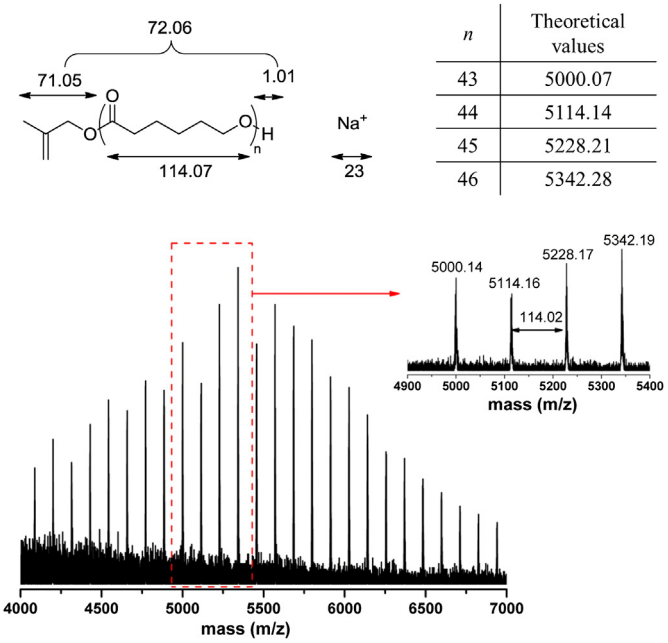


Fig. 9. MALDI-ToF MS spectrum of the vinyl-ended PCL (Table 2, run 3) from ROP of CL catalyzed by $Lu(OTf)_3$/sodium β-methallyloxide.

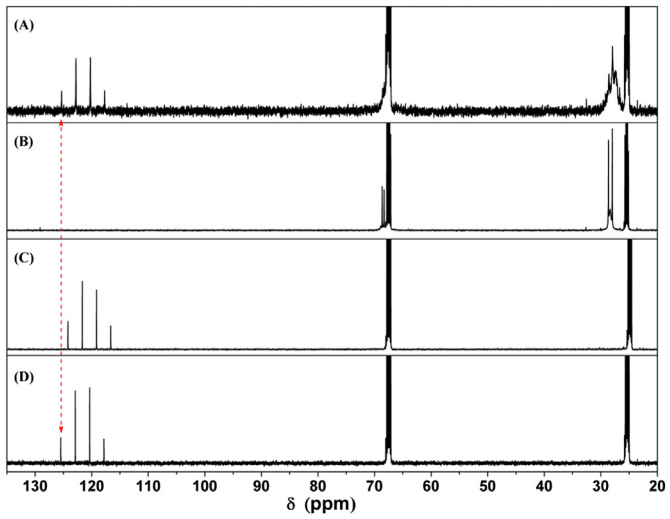


Fig. 11. ^{13}C NMR spectra of *in situ* formed catalytic system by $Lu(OTf)_3$ and 3 equivalence of NaO^iPr (A), $Lu(O^iPr)_3$ (**1**) (B), $Lu(OTf)_3$ (C) and NaOTf (D) in THF-d_8.

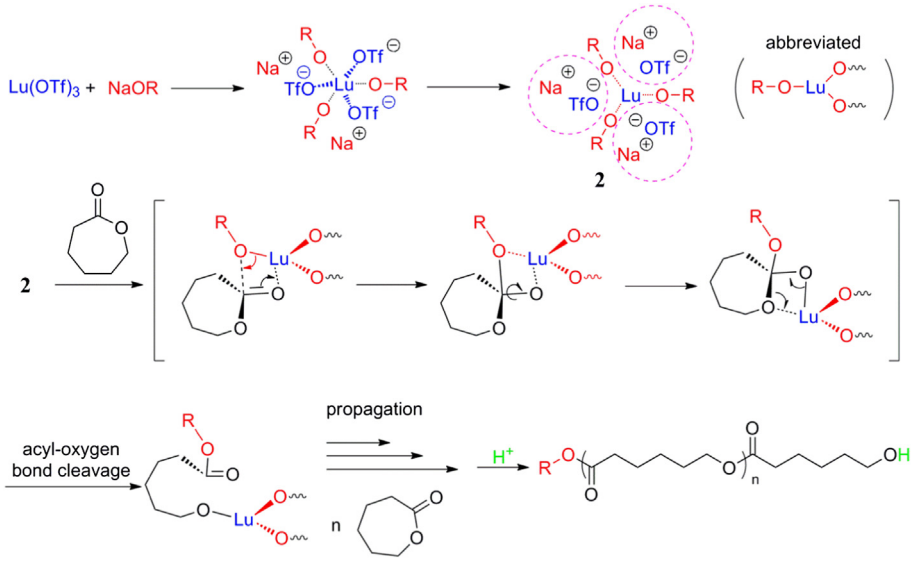
chain end and a hydroxyl group at the other, as illustrated in Figs. 5 and 6 [53]. The characteristic signals of the isopropyl ester end group are observed at 1.21 ppm (H^a) and 4.98 ppm (H^b) [53,45], and the methylene protons of the other chain end (H^g) is found at 3.62 ppm (Fig. 5). In addition, the corresponding ^{13}C signals are found at 21.8 ppm (C^a) and 67.4 ppm (C^b).

Because PCLs produced by the $Lu(OTf)_3/NaO^iPr$ are capped by an isopropyl ester end group from the residue of the sodium alkoxide used, it is a straightforward way to change the alcohol so as to tailor the PCL end group and to contribute to the macromolecular engineering of PCL. Table 2 summarizes the PCLs end capped by vinyl and alkynyl groups prepared by the corresponding sodium alkoxides in the presence of $Lu(OTf)_3$. All the $Lu(OTf)_3$/NaOR catalytic systems initiate ROP of CL proceeded in a well-controlled manner to yield PCLs with predictable MWs and narrow PDIs below 1.10 (Fig. S1 in Supporting Information). These functional end groups are confirmed by ^1H NMR analysis (Figs. 7 and 8). A characteristic triplet peak of 2.50 ppm ascribed to alkynyl proton (H^a) and a doublet of 4.71 ppm to methylene protons (H^b) confirm the successful introduction of the alkynyl group at PCL chain end. With respect to the β-methallyl ester group, methyl protons (H^h), vinyl protons (H^a) and methylene protons adjacent to the ester linkage (H^b) appear at 1.76, 4.95 and 4.50 ppm, respectively. In addition, the MALDI-ToF mass spectrum of PCL catalyzed by $Lu(OTf)_3$/sodium β-methallyloxide reveals only one population of polymers possessing a β-methallyl residue and a hydroxyl chain end (Fig. 9). Thus we reach the conclusion that $Lu(OTf)_3$/NaOR is an efficient catalyst for the ROP of CL to generate well-defined PCLs applicable for future modification by Click reactions.

3.4. Mechanisms

Based on chain end analysis of PCL, the alkyloxy residue group supports that the real active site is RE–OR bond derived from ligand exchange reaction of $Ln(OTf)_3$ and NaOR. A reaction of $Lu(OTf)_3$ with 3 equivalent NaO^iPr in THF-d_8 was carried out for the analyses of ^1H NMR and ^{13}C NMR spectroscopy. Fig. 10 compares the signals of the *in situ* mixture of $Lu(OTf)_3$ and NaO^iPr, $Lu(O^iPr)_3$ (**1**) and NaO^iPr. The broad methine signal covering 3.7–4.7 ppm and multiple peaks of methyl group at 1.1–1.6 ppm move downfield from those of NaO^iPr at 4.12 and 0.99 ppm, respectively. The peaks are in good agreement with three doublets at 1.63, 1.41 and 1.18 ppm found in **1**. Additional evidence is found in ^{13}C NMR (Fig. 11). The peak at far left of the quadruple carbon signal of OSO_2CF_3 in the mixture of $Lu(OTf)_3/NaO^iPr$ is found at 125.36 ppm which is the same as that in NaOTf rather than that in $Lu(OTf)_3$ at 124.20 ppm (Fig. 11). All the above suggests a fast ligand exchange reaction between $Lu(OTf)_3$ and NaO^iPr generating lutetium complex **2** containing Lu–O^iPr bond similar to that in metal alkoxide. According to hard–soft acid–base (HSAB) theory [54,55], Na^+ is considered as harder acid than Lu^{3+} and OTf^- is a harder base than O^iPr^-. Na^+ prefers to ionically bind with harder Lewis bases of OTf^- and Lu^{3+} with O^iPr. By comparison, ROP of CL using $Lu(O^iPr)_3$ (**1**) and NaOTf as initiators were carried out in THF and toluene (Table S1). All the polymerizations initiated by **1** show good reactivity but low initiation efficiency. The $M_{n(exp)}$s are higher than the theoretical values, indicating a slow equilibrium between aggregated and monomeric Lu complex similar to the reported $Y_5(\mu\text{–}O)(O^iPr)_{13}$ catalyst [19,45]. In contrast, NaOTf alone cannot initiate ROP of CL, indicating that the NaOTf is not an active site. Together with the living manner in the previous kinetic study, it supports that the real active site of **2** is Lu–OR bond analogous to **1**.

A coordination–insertion mechanism of CL ROP is illustrated in Scheme 2. A fast ligand exchange reaction of $Lu(OTf)_3$ and NaOR leads to the *in situ* formed lutetium alkoxide complex **2**, where Na^+ and OTf^- combine into tight ion pairs surrounding and stabilizing the lutetium metal centers to prevent their aggregation. The reason for the ligand exchanged reaction is faster than that of $RECl_3$ and NaOR is the good solubility of $Lu(OTf)_3$ in THF leading to a homogenous mixture and the higher affinity between Na^+ and OTf^- than Cl^- [39]. Because one $Lu(OTf)_3$ can only exchange with at most three Na^iOPr, excessive Na^iOPr initiates anionic ROP of CL leading to broad PDIs (Table 1, runs 6–8). The coordination of the lutetium complex onto the carbonyl group of CL activates the selective acyl-oxygen cleavage of the CL followed by its insertion into the lutetium–oxygen bond in a way that maintains the growing chain bound to the lutetium through an active alkoxide bond [42,43]. Therefore, an ester group with R residue is generated at the PCL chain end during the initiation. When quenched by acid, a hydroxyl group caps the other end. This structural feature agrees with the "coordination–insertion" mechanism reported in the case of aluminum alkoxide initiators and rare-earth alkoxides as well [19,52].



Scheme 2. Mechanism of ring-opening polymerization of CL catalyzed by the *in situ* generated catalytic system of $Lu(OTf)_3$ and NaOR.

4. Conclusions

A novel lutetium alkoxide complex **2** containing active RE–OR bond was formed by simply mixing $Lu(OTf)_3$ with NaOR in THF for 3 min at room temperature without any tedious intermediate purification. Both of the two precursors were commercially available, quite stable and easy to handle compared with those used in other synthetic routes of rare earth alkoxides. The *in situ* generated complex **2** was excellent initiator for living ROP of CL affording PCLs with predictable MWs and narrow PDIs below 1.10. In addition, sodium β-methallyloxide and propargyloxide were used to synthesize pure end-functionalized PCL with vinyl and alkynyl end-groups ready for further modifications including Click reactions. These novel rare earth alkoxide complexes are also expected as effective initiators for ROP of lactide and other cyclic esters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.03.032.

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