

$\text{LnNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$ Alkoxide Clusters: Highly Active Single-Component Catalysts for the Homopolymerization and Copolymerization of ϵ -Caprolactone and Trimethylene Carbonate

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ABSTRACT: Heterometal alkoxide clusters of lanthanide and sodium, $\text{LnNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$ [where Ln = Nd (**1**) or Yb (**2**)], which were synthesized by the metathesis reaction of LnCl_3 with $\text{NaOC}(\text{CH}_3)_3$ and NaOH in a 1 : 10 : 1 molar ratio in high yields and fully characterized including X-ray analysis for **2**, were found to be highly active catalysts in the ring-opening polymerization of ϵ -caprolactone and trimethylene carbonate and their copolymerization. All of the polymers obtained showed a unimodal

molecular weight distribution, indicating that **1** and **2** could really be used as single-component catalysts. The dependence of catalytic activity on the lanthanide metals was observed: $\text{Yb} < \text{Nd}$. A coordination–insertion mechanism for the ring-opening polymerization is proposed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 454–460, 2009

Key words: catalysts; cooperative effects; copolymerization

INTRODUCTION

Polymers of lactones and cyclic carbonates are biomaterials with good biodegradability, biocompatibility, and low toxicity. Therefore, the development of simple, convenient, and efficient initiators for this ring-opening polymerization has attracted increasing attention.^{1–4} The application of lanthanide alkoxide (phenoxide) complexes as single-component initiators in the ring-opening polymerization of lactones and cyclic carbonates has attracted increasing attention because of their high activity and/or controllability and low toxicity.^{5–15} However, the study of the catalytic reactivity of heterometal alkoxides clusters of lanthanide and alkali metal has been quite limited,^{16–18} although these kinds of clusters are commonly known.^{19–25} Recently, we reported that the heterometal alkoxide clusters of lanthanide and sodium, $\text{Ln}_2\text{Na}_8(\text{OCH}_2\text{CH}_2\text{NMe}_2)_{12}(\text{OH})_2$ (where Ln = Nd, Pr, Sm, Y, or Ho)²⁶ and $\text{Ln}_2\text{Na}_8(\text{OCH}_2\text{CF}_3)_{14}(\text{THF})_6$ (where Ln = Sm, Yb, or Y and THF = tetrahydrofuran)²⁷ can be synthesized in high yields and used as single-component catalysts in the polymerization of ϵ -caprolactone (ϵ -CL) and trimethylene

carbonate (TMC). These two kinds of clusters displayed much higher reactivities than related monometallic lanthanide alkoxides and sodium alkoxides because of the cooperative effect between lanthanide and sodium metals.^{26,27} Encouraged by these results, we were prompted to study the rational synthesis of another heterometal alkoxide cluster in hope of understanding further the dependence of reactivity on the structure of the clusters and the potential application of heterometal alkoxide clusters in the ring-opening polymerization of cyclic esters.

In 1993, the heterometal *tert*-butyloxy cluster $\text{YNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$ was reported by Evans et al.²¹ as a byproduct of the reaction of YCl_3 with 3 equiv of $\text{NaOC}(\text{CH}_3)_3$ at a very low yield. The low yield prevents further study of its reactivity. We recently found that the addition of a definite amount of NaOH to a reaction solution of LnCl_3 and $\text{NaOCH}_2\text{CH}_2\text{NMe}_2$ resulted in the rational preparation of alkoxide clusters of lanthanide and sodium-containing hydroxide groups [$\text{Ln}_2\text{Na}_8(\text{OCH}_2\text{CH}_2\text{NMe}_2)_{12}(\text{OH})_2$] via self-assembly by hydroxide as a driving force. In addition, this approach proved to provide reproducible products in high yields and to be available to lanthanide metals from light to heavy.²⁶ Hence, this article is a preliminary report on the synthesis of the $\text{LnNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$ clusters by the same strategy. Indeed, the metathesis reaction of LnCl_3 with $\text{NaOC}(\text{CH}_3)_3$ in the presence of NaOH afforded the target clusters

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LnNa₈[OC(CH₃)₃]₁₀(OH) [where Ln = Nd (**1**) or Yb (**2**)] in reproducible high yields. Moreover, these clusters were found to be very high active catalysts in the ring-opening polymerization of ϵ -CL and TMC and their copolymerization.

EXPERIMENTAL

General procedures

All manipulations were performed under pure argon with the rigorous exclusion of air and moisture with standard Schlenk techniques. Metal analyses were carried out by complexometric titration. Carbon and hydrogen analyses were performed by direct combustion on a Carlo-Erba EA 1110 instrument (Germany). The melting points were determined on a Yanaco MP-500 melting point apparatus (England). The IR spectra were recorded on a Nicolet (USA) Magna IR 550 spectrometer. The ¹H-NMR spectra were recorded on a Unity Inova-400 spectrometer (USA). The number-average and weight-average molecular weights and molecular weight distributions (weight-average molecular weight/number-average molecular weight) were determined with gel permeation chromatography (GPC) with THF as an eluent and polystyrene as a standard on a Waters 1515 instrument equipped with three HR columns (HR-1, HR-2, and HR-4) and an ultraviolet visible detector.

Materials

ϵ -CL was purchased from Acros (USA), dried over CaH₂, and distilled under reduced pressure. TMC was prepared by the reaction of 1,3-propanediol with diethyl carbonate according to a published method,²⁸ dried further over CaH₂, and purified by recrystallization before use. Anhydrous LnCl₃ lanthanides were prepared according to a technique from the literature.²⁹ Toluene and THF were distilled from sodium/benzophenone ketyl.

Initiator synthesis

Preparation of NdNa₈[OC(CH₃)₃]₁₀(OH)

A Schlenk flask was charged with Na (0.55 g, 24 mmol), THF (25 mL), and a stirring bar. HOC(CH₃)₃ (1.88 mL, 20 mmol) was added with a syringe. After the mixture was stirred overnight, the pale gray slurry of NdCl₃ (0.50 g, 2 mmol) in 15 mL of THF was added. The resulting blue solution was stirred for 2 h, and then, NaOH (0.08 g, 2 mmol) was added. After it was stirred for another 48 h, the solvent was removed by vacuum, and the residue was extracted with toluene to remove NaCl by centrifugation. After the solution was concentrated, the product was obtained as violet crystals.

Yield: 1.40 g (65%). Decomposition point: 286–291°C. ANAL. Calcd for C₄₀H₉₁Na₈O₁₁Nd (1076.29): C, 44.64%; H, 8.52%; Nd, 13.40%. Found: C, 44.59%; H, 8.55%; Nd, 13.43%. IR (KBr pellet, cm⁻¹): 3401 (s), 1674 (m), 1453 (s), 1248 (w), 880 (s), 833 (w), 698 (m), 676 (m), 644 (w). ¹H-NMR (400 MHz, C₆D₆, 25°C, δ , ppm): 27.26 (s, 1.5H), 7.38 (s, 1.5H), 2.59 (s, 9H), -12.6 (s, 6H), -35.1 (s, 1H).

Preparation of YbNa₈[OC(CH₃)₃]₁₀(OH)

By the same procedure as that used for **1**, cluster **2** was prepared from the reaction of YbCl₃ (0.56 g, 2.0 mmol) with NaOC(CH₃)₃ and NaOH (0.08 g, 2.0 mmol) in THF as colorless crystals.

Yield: 1.72 g (78%). Decomposition point: 291–293°C. ANAL. Calcd for C₄₀H₉₁Na₈O₁₁Yb (1105.09): C, 43.47%; H, 8.30%; Yb, 15.66%. Found: C, 43.40%; H, 8.32%; Yb, 15.62%. IR (KBr pellet, cm⁻¹): 3326 (s), 1667 (m), 1436 (s), 1204 (w), 872 (s), 686 (m), 649 (w). ¹H-NMR (400 MHz, C₆D₆, 25°C, δ , ppm): 28.1 (s, 1.5H), 7.58 (s, 1.5H), 2.73 (s, 9H), -13.1 (s, 6H).

Homopolymerization of ϵ -CL and TMC

All homopolymerizations were carried out in a 50-mL Schlenk flask under a dry argon atmosphere with a similar procedure. A typical polymerization reaction is given as follows: a 50-mL Schlenk flask equipped with a magnetic stirring bar was charged with a solution of TMC (0.46 g, 4.51 mmol) in toluene (4.28 mL). A toluene solution of cluster **1** (0.23 mL, 1.0×10^{-2} mol/L) was added to this solution with a rubber septum and a syringe. The reaction solution was stirred vigorously for 1 min at 25°C. The polymerization was quenched by the addition of 1 mL of 5% HCl/ethanol (EtOH). The polymer was precipitated from EtOH and washed with EtOH three times and dried *in vacuo* at room temperature overnight. The polymer yield was determined gravimetrically.

Copolymerization of TMC with ϵ -CL

All copolymerizations were carried out in a 50-mL Schlenk flask under a dry argon atmosphere. A typical copolymerization reaction is given as follows: TMC (0.46 g, 4.51 mmol), ϵ -CL (0.50 mL, 4.51 mmol), and toluene (8.80 mL) were added to a dry flask at 25°C in turn. Then, the toluene solution of cluster **1** (0.23 mL, 1.0×10^{-2} mol/L) was introduced by syringe into the reaction solution. After 1 min, the copolymerization was quenched by the addition of 1 mL of 5% HCl/EtOH. The copolymer was precipitated from EtOH and dried *in vacuo*. The polymer yield was determined gravimetrically.

TABLE I
Crystallographic Data for 2

| | | | |
|-----------------|--|--|--------------|
| Formula | C ₄₀ H ₉₁ Na ₈ O ₁₁ Yb | γ (°) | 90 |
| Formula weight | 1105.09 | V (Å ³) | 11,597.2(16) |
| Temperature (K) | 173(2) | Z | 8 |
| Wavelength (Å) | 0.71073 | D_{calc} (g/cm ³) | 1.266 |
| Size (mm) | 0.60 × 0.50 × 0.38 | Absorption coefficient (mm ⁻¹) | 1.718 |
| Crystal system | Orthorhombic | $F(000)$ | 4616 |
| Space group | $Pbca$ | θ range (°) | 3.02–25.35 |
| a (Å) | 21.1507(17) | Reflections collected | 106,004 |
| b (Å) | 20.0954(16) | R [$I > 3\sigma(I)$] | 0.0328 |
| c (Å) | 27.286(2) | R_w | 0.0704 |
| α (°) | 90 | Goodness of fit on F^2 | 1.127 |
| β (°) | 90 | | |

Oligomers for end-group analysis

The oligomerization of ϵ -CL was carried out with **1** in toluene at 25°C under the condition of $[\epsilon\text{-CL}]/[\mathbf{1}]$ (molar ratio) = 30. The reaction was terminated by the addition of 1 mL of 5% HCl/ⁱPrOH after 30 min. The oligomer was precipitated from EtOH. The product was dissolved in THF, followed by precipitation in EtOH. The procedure was repeated two times. The white product was dried *in vacuo*.

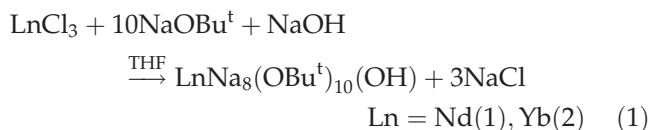
Structure solution and refinement for YbNa₈[OC(CH₃)₃]₁₀(OH)

A suitable single crystal of cluster **2** was sealed in a thin-walled glass capillary, and intensity data were collected on a Rigaku Mercury charged coupling device equipped with graphite-monochromated Mo $K\alpha$ (wavelength = 0.71073 Å) radiation. The structure was solved by direct methods, expanded with Fourier techniques, and refined on F^2 by the full-matrix least-squares method. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with the riding model. All the calculations were carried out with the Siemens SHELXTL PLUS program. The details of the intensity data collection and crystal data are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis and structural characterization

The treatment of LnCl₃ (Ln = Nd or Yb) with 10 equiv of NaOC(CH₃)₃ in the presence of 1 equiv of NaOH after workup gave violet crystals for Nd and colorless crystals for Yb, which were fully characterized to be LnNa₈[OC(CH₃)₃]₁₀(OH) [Ln = Nd (**1**) or Yb (**2**); eq. (1)]. Clusters **1** and **2** were reproduced at good yields (ca. 65% for **1** and 78% for **2**):



The ¹H-NMR spectra for the paramagnetic clusters **1** and **2** showed shifted signals. The elemental analysis was identical to the formula and indicated that molar ratio of Ln to Na was 1 : 8. Cluster **2** was further characterized by X-ray crystallography. Clusters

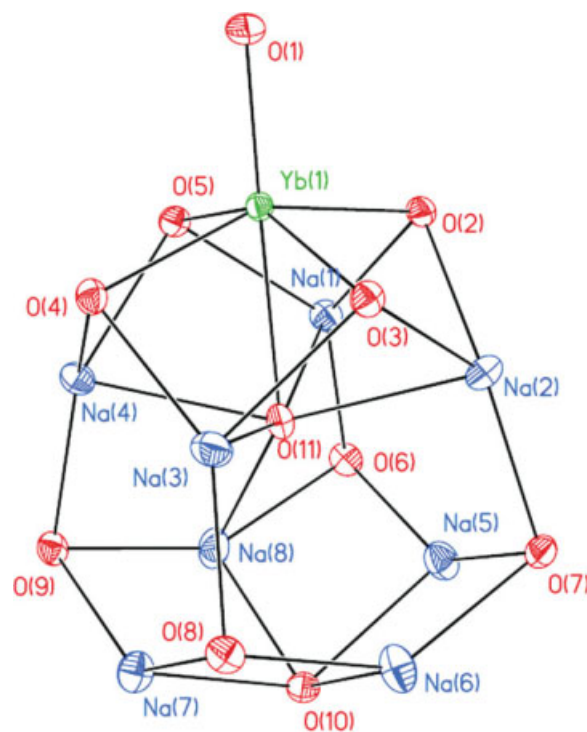


Figure 1 Molecular structures of YbNa₈[OC(CH₃)₃]₁₀(OH) (the *tert*-butyl groups are omitted for clarity). Selected bond lengths (Å) and bond angles (°) are as follows: Yb(1)—O(1) and 2.044(2), Yb(1)—O(2) and 2.238(2), Yb(1)—O(5) and 2.246(2), Yb(1)—O(3) and 2.251(2), Yb(1)—O(4) and 2.259(2), Yb(1)—O(11) and 2.632(2), Na(1)—O(6) and 2.244(3), Na(1)—O(2) and 2.336(2), Na(1)—O(5) and 2.345(2), Na(1)—O(11) and 2.400(2), O(2)—Yb(1)—O(5) and 85.86(8), O(2)—Yb(1)—O(3) and 86.76(8), O(5)—Yb(1)—O(4) and 85.94(8), O(3)—Yb(1)—O(4) and 86.50(8), O(1)—Yb(1)—O(11) and 178.74(8), O(2)—Yb(1)—O(11) and 75.41(7), O(5)—Yb(1)—O(11) and 73.31(7), O(3)—Yb(1)—O(11) and 75.54(7), and O(4)—Yb(1)—O(11) and 76.49(7). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Polymerization of ϵ -CL and TMC Initiated by **1** and **2**

| Entry | Monomer | Initiator | [M]/[I] | Time (min) | Conversion (%) ^a | M_n ($\times 10^4$) ^b | M_w/M_n ^b |
|-----------------|-------------------------------------|--|---------|------------|-----------------------------|--------------------------------------|------------------------|
| 1 | CL | 1 | 4,000 | 1 | 100 | 8.14 | 1.69 |
| 2 | | 1 | 8,000 | 1 | 98 | 11.1 | 2.04 |
| 3 | | 1 | 10,000 | 1 | 84 | 12.6 | 2.02 |
| 4 | | 2 | 4,000 | 1 | 100 | 12.0 | 2.29 |
| 5 | | 2 | 8,000 | 1 | 90 | 16.6 | 2.13 |
| 6 | | 2 | 10,000 | 1 | 72 | 18.4 | 1.93 |
| 7 ^c | | 2 | 4,000 | 1 | 79 | 6.17 | 1.54 |
| 8 | NaOC(CH ₃) ₃ | | 2,000 | 30 | 0 | — | — |
| 9 | | Nd ₂ Na ₈ (OCH ₂ CH ₂ NMe ₂) ₁₂ (OH) ₂ | 10,000 | 1 | 100 | 8.5 | 1.52 |
| 10 | | Yb ₂ Na ₈ (OCH ₂ CF ₃) ₁₄ (THF) ₆ | 4,000 | 30 | 12 | | |
| 11 | TMC | 1 | 2,000 | 1 | 100 | 3.93 | 1.89 |
| 12 | | 1 | 4,000 | 1 | 100 | 7.29 | 1.55 |
| 13 | | 2 | 2,000 | 1 | 100 | 4.33 | 1.95 |
| 14 | | 2 | 4,000 | 1 | 74 | 4.84 | 1.89 |
| 15 ^c | | 2 | 4,000 | 1 | 57 | 2.22 | 1.33 |
| 16 | | NaOC(CH ₃) ₃ | | 2,000 | 30 | 0 | — |

I = initiator; M = monomer; M_n = number-average molecular weight; M_w = weight-average molecular weight. Conditions: [catalyst] = 0.01 mol/L, toluene = solvent, solution volume/ ϵ -CL volume = 10 : 1, [TMC] = 1.0 mol/L, and temperature = 25°C.

^a Weight of the obtained polymer/weight of the used monomer.

^b Measured by GPC calibrated with standard polystyrene samples.

^c THF as the solvent.

1 and **2** were all soluble in THF and toluene but not in hexane. The crystal structure of **2**, which was a capped square antiprism with the Yb atom in the capping position, was the same as that for the Y cluster published previously.²¹ The skeleton diagram with all the C(CH₃)₃ groups omitted for clarity is shown in Figure 1. All the metals were connected together by two sets of four μ_3 -O groups, one μ_4 -O group, and a centralized hydroxide ligand. The coordination geometry around the lanthanide atom can be best described as a distorted octahedron geometry, in which O(1) and O(11) occupied axial positions.

Ring-opening polymerization of ϵ -CL with LnNa₈[OC(CH₃)₃]₁₀(OH)

The catalytic activity of **1** and **2** for the polymerization of ϵ -CL was first tested, and the preliminary results are summarized in Table II. The polymerization data published for the Ln₂Na₈(OCH₂CH₂NMe₂)₁₂(OH)₂ and Ln₂Na₈(OCH₂CF₃)₁₄(THF)₆ systems were also used for comparison. **1** and **2** exhibited very high activity under mild conditions, whereas NaOC(CH₃)₃ showed no activity under the same conditions (Table II, entry 8). The conversions were greater than 90% for 1 min in the case of a monomer/initiator molar ratio of 8000 (molar ratio) for both systems with **1** and **2** as catalysts. However, a difference in the reactivity between the two clusters was observed. For example, when the monomer/initiator molar ratio increased to 10,000, the conversion was as high as 84% for **1**,

whereas the conversion was 72% for **2** (Table II, entries 3 and 6). The active sequence of Yb < Nd observed here was consistent with the increase in ionic radius, which was similar to those found in polymerization systems with lanthanide alkoxide.^{9,30} In comparison with the Ln₂Na₈(OCH₂CH₂NMe₂)₁₂(OH)₂ and Ln₂Na₈(OCH₂CF₃)₁₄(THF)₆ clusters, the reactivity followed the following trend: Ln₂Na₈(OCH₂CH₂NMe₂)₁₂(OH)₂ > LnNa₈[OC(CH₃)₃]₁₀(OH) > Ln₂Na₈(OCH₂CF₃)₁₄(THF)₆, in view of the conversions obtained on the basis of the same molar ratio of [ϵ -CL]/[Ln] (Table II, entries 3, 4, 9, and 10). The polymerization in toluene yielded a much higher conversion and polymers with higher molecular weights than that in THF (Table II, entries 4 and 7), which indicated that this polymerization might have occurred by a coordination–insertion mechanism. All polymers obtained by **1** or **2** showed a unimodal molecular weight distribution, which implied that both **1** and **2** were really used as single-component catalysts in the polymerization of ϵ -CL. The molecular weights of the resulting polymers were lower than those expected from the monomer-to-cluster ratio, which was similar to that found in the systems with the Ln₂Na₈(OCH₂CH₂NMe₂)₁₂(OH)₂ and Ln₂Na₈(OCH₂CF₃)₁₄(THF)₆ clusters. However, the system with LnNa₈[OC(CH₃)₃]₁₀(OH) afforded polymers with higher molecular weights and broader molecular weight distributions than those with the Ln₂Na₈(OCH₂CH₂NMe₂)₁₂(OH)₂ and Ln₂Na₈(OCH₂CF₃)₁₄(THF)₆ clusters (Table II, entries 3 and 9). No distinct difference in the catalytic behavior, such as the

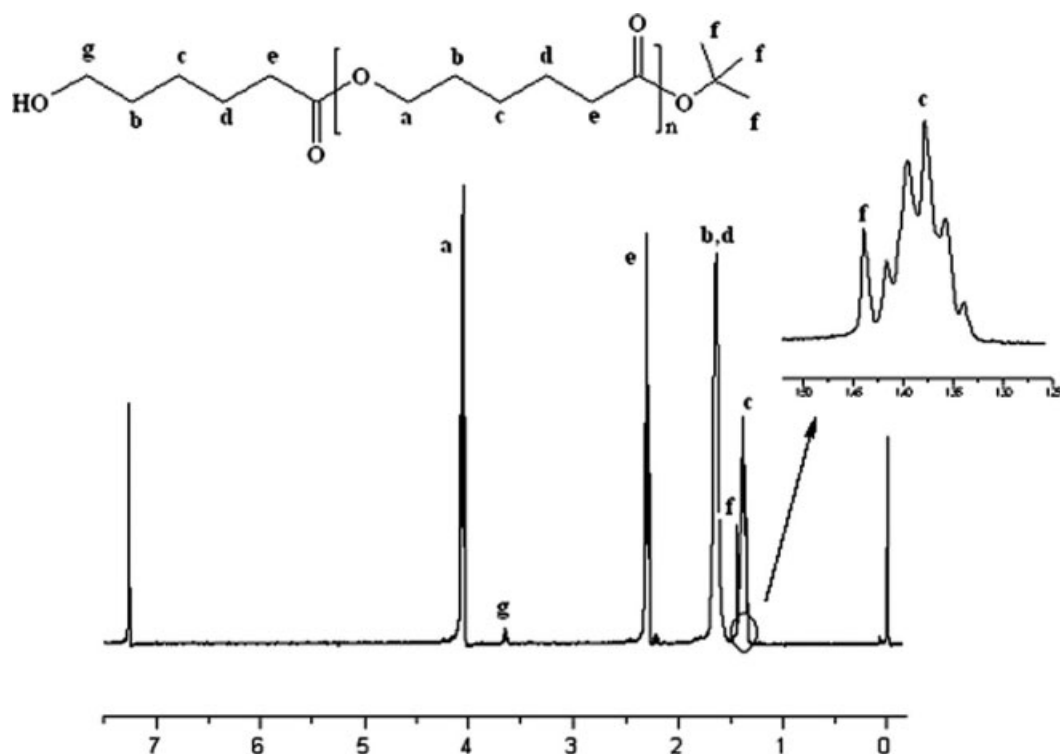


Figure 2 $^1\text{H-NMR}$ spectrum of the oligomer of $\epsilon\text{-CL}$ initiated by cluster **1** and terminated by isopropyl alcohol in CDCl_3 .

dependence of activity on the center metal and solvent, among the three kinds of clusters was observed, which indicated that the polymerizations with the three kinds of clusters as catalysts should have proceeded by the same mechanism.

The dependence of the activity on the lanthanide metal indicated that $\text{Ln-OC}(\text{CH}_3)_3$ bonds may have been the active species, and the lower activity shown in THF demonstrated that this polymerization system may belong to a coordination–insertion mechanism. To further elucidate the polymerization mechanism, an oligomer of $\epsilon\text{-CL}$ was produced from the oligomerization of $\epsilon\text{-CL}$ with a $[\epsilon\text{-CL}]/[\mathbf{1}]$ ratio of 30 and terminated by isopropyl alcohol. The $^1\text{H-NMR}$ spectroscopy of the oligomer revealed the presence of an end group of $\text{OC}(\text{CH}_3)_3$ at 1.46 ppm as a single peak (Fig. 2). The end-group analysis indicated the polymerization proceeded by acyl–oxygen bond cleavage, as shown in Scheme 1. An $\epsilon\text{-CL}$ could have coordinated to both Ln and Na metals concomitantly, and then, the activated $\epsilon\text{-CL}$ was inserted into one of $\text{Ln-OC}(\text{CH}_3)_3$ bonds. The process repeated to yield the polymer.

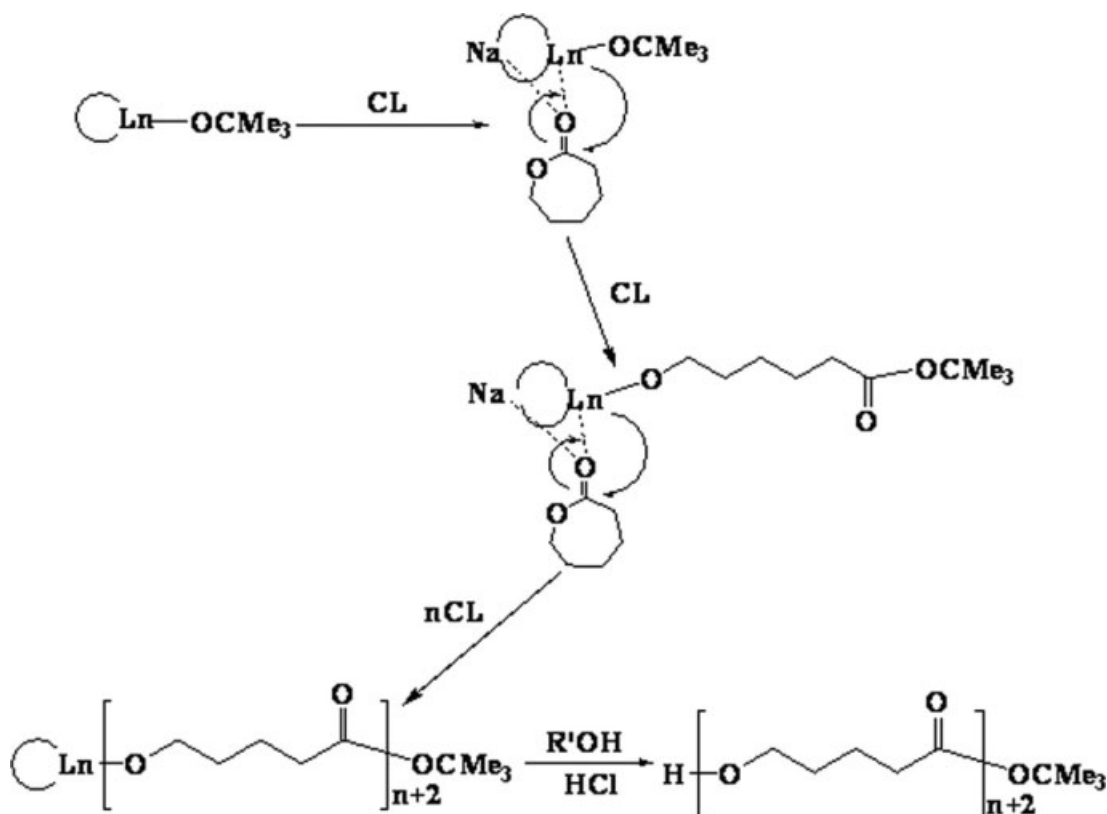
Ring-opening polymerization of TMC with $\text{LnNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$

The catalytic reactivity of clusters **1** and **2** for the polymerization of TMC was then measured. They were also extremely active catalysts for the polymerization

of TMC. For example, complete conversions of the monomer into poly(trimethylene carbonate) (PTMC) were achieved within 1 min for monomer-to-cluster ratios of up to 2000 (Table II, entries 11 and 13), whereas $\text{NaOC}(\text{CH}_3)_3$ showed no activity under the same conditions (Table II, entry 16). The catalytic behavior of **1** and **2** for the polymerization of $\epsilon\text{-CL}$, including the same dependence of reactivity on lanthanide metal and on solvent. For example, the conversion was as high as 100% for **1** and 74% for **2** when the TMC/initiator molar ratio was increased to 4000 (Table II, entries 12 and 14). The active sequence of $\text{Yb} < \text{Nd}$ was observed. The polymerization in toluene gave higher conversion and polymers with higher molecular weights in comparison with that in THF (Table II, entries 14 and 15). All of the GPC curves of the resulting polymers were unimodal molecular weight distributions, which suggested **1** and **2** really worked as single-component catalysts for the polymerization of TMC.

Copolymerization of TMC/ $\epsilon\text{-CL}$ with $\text{NdNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$

It is well known that the copolymers of aliphatic carbonates with lactones can provide new materials with new thermal behaviors, new crystallization properties, and new degradabilities that are rather different from those resulting from the homopolymers.^{31–35}



Scheme 1 Postulated mechanism for the ring-opening polymerization of $\epsilon\text{-CL}$.

Therefore, the catalytic activity of **1** for the copolymerization of $\epsilon\text{-CL}$ with TMC was further investigated. The experimental results are listed in Table III. Cluster **1** was also an efficient catalyst for the copolymerization of $\epsilon\text{-CL}$ with TMC. The copolymerization gave the copolymer in about a quantitative yield with moderate molecular weight distributions in the case of $([\text{TMC}] + [\epsilon\text{-CL}])/[\mathbf{1}] = 4000$ (molar ratio). All of the copolymers obtained with various feeding molar ratios of the monomers to catalyst had unimodal molecular weight distributions, which indicated

that the polymers obtained were pure copolymers without both homopolymers of $\epsilon\text{-CL}$ and TMC. The molar ratio of the TMC units and $\epsilon\text{-CL}$ units in the copolymer were determined according to the two characteristic resonances in their $^1\text{H-NMR}$ spectra at about 2.05 ppm (TMC unit) and about 2.3 ppm ($\epsilon\text{-CL}$ unit), respectively.³⁶ The molar composition of the copolymer showed a close matching to the variation of the comonomer feed (Fig. 3). Differential scanning calorimetry (DSC) was another good method for confirming the structure of the copolymers. In our case,

TABLE III
Copolymerization of $\epsilon\text{-CL}$ with TMC Initiated by **1**

| Entry | Feeding molar ratio (TMC/ $\epsilon\text{-CL}$) | Conversion (%) ^a | M_n ($\times 10^4$) ^b | M_w/M_n ^b | T_m ($^\circ\text{C}$) | TMC/ $\epsilon\text{-CL}$ in the polymer ^c |
|-------|--|-----------------------------|--------------------------------------|------------------------|----------------------------|---|
| 1 | 100 : 0 | 100 | 7.29 | 1.55 | 38.5 | — |
| 2 | 60 : 40 | 98 | 13.2 | 1.67 | 43.8 | 59.8 : 40.2 |
| 3 | 50 : 50 | 96 | 14.4 | 1.65 | 42.2 | 49.5 : 50.5 |
| 4 | 40 : 60 | 98 | 14.6 | 1.64 | 48.5 | 39.4 : 60.6 |
| 5 | 20 : 80 | 95 | 10.7 | 1.61 | 53.9 | 18.7 : 81.3 |
| 6 | 0 : 100 | 100 | 8.14 | 1.69 | 64.5 | — |

M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature. Conditions: [catalyst] = 0.01 mol/L, [TMC + $\epsilon\text{-CL}$] = 1.0 mol/L, [TMC + $\epsilon\text{-CL}$]/[**1**] = 4000, time = 1 min, temperature = 25 $^\circ\text{C}$, and solvent = toluene.

^a Weight of the obtained polymer/weight of the used monomer.

^b Measured by GPC calibrated with standard polystyrene samples.

^c Calculated from the $^1\text{H-NMR}$ spectrum (PTMC signal at 2.05 ppm and PCL signal at 2.30 ppm).

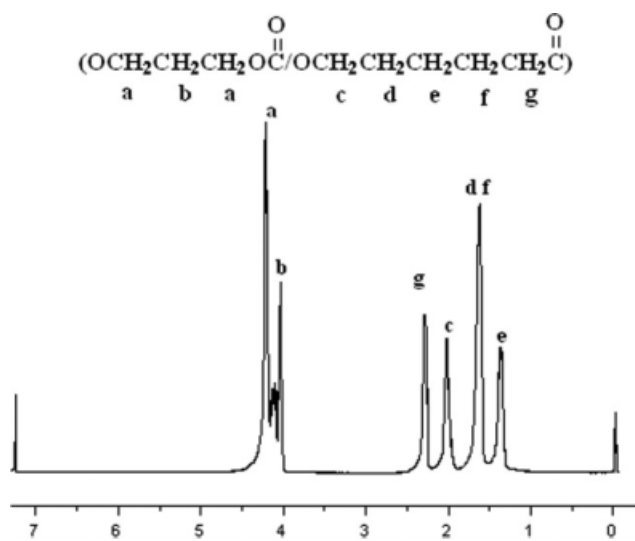


Figure 3 $^1\text{H-NMR}$ spectrum of a typical poly(trimethylene carbonate-*co*- ϵ -caprolactone) (conditions: [catalyst] = 0.01 mol/L, [TMC + ϵ -CL] = 1.0 mol/L, [TMC + ϵ -CL]/[1] = 4000, [TMC]/[ϵ -CL] = 50 : 50, time = 1 min, temperature = 25°C, and solvent = toluene).

melting temperatures of 64.5°C for the PCL homopolymer and 38.5°C for the PTMC homopolymer were detected, whereas new melting temperature peaks appeared and no melting temperature for either homopolymer was found in the DSC spectra of poly(trimethylene carbonate-*co*- ϵ -caprolactone). One melting temperature peak observed in the DSC spectrum of one copolymer indicated that the copolymers had a random structure. The melting temperatures were dependent on the composition of the copolymers. Therefore, it is expected that a quite distinct thermal behavior of the copolymers could be obtained by the modification of the feeding molar ratio of the two monomers in the copolymerization.

CONCLUSIONS

Alkoxide clusters of lanthanide and sodium, $\text{LnNa}_8[\text{OC}(\text{CH}_3)_3]_{10}(\text{OH})$ (where Ln = Nd or Yb), were synthesized in high yields. The clusters were highly active single-component catalysts for the homopolymerization and copolymerization of ϵ -CL and TMC. The reactivity depended on the lanthanide metal with the sequence of Yb < Nd. The end-group analysis showed that the polymerization proceeded via a coordination/insertion mechanism by the acyl-oxygen bond cleavage. The results presented here indicated that the heterometal alkoxide clusters might have great potential in the ring-opening polymerization of cyclic esters as single-component catalysts because of the cooperative effect between the two metals. Further work in this area is proceeding in our laboratory.

References

- Xue, M. Q.; Sun, H. M.; Zhou, H.; Yao, Y. M.; Shen, Q.; Zhang, Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 1147.
- Qi, C. Y.; Wang, Z. X. *J Polym Sci Part A: Polym Chem* 2006, 44, 4621.
- Zhou, L. Y.; Sun, H. M.; Chen, J. L.; Yao, Y. M.; Shen, Q. *J Polym Sci Part A: Polym Chem* 2005, 43, 1778.
- Sheng, H. T.; Zhou, L. Y.; Zhang, Y.; Yao, Y. M.; Shen, Q. *J Polym Sci Part A: Polym Chem* 2007, 45, 1210.
- Stevens, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* 1996, 29, 8296.
- Stevens, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Polym Prepr* 1996, 37, 190.
- Schappacher, M.; Fabre, T.; Mingotaud, A. F.; Soum, A. *Biomaterials* 2001, 22, 2849.
- Nishiura, M.; Hou, Z. M.; Koizumi, T. A.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* 1999, 32, 8245.
- Yao, Y. M.; Xu, X. P.; Liu, B.; Shen, Q. *Inorg Chem* 2005, 44, 5133.
- Xu, X. P.; Yao, Y. M.; Shen, Q. *J Polym Sci Part A: Polym Chem* 2006, 44, 4409.
- Ling, J. Z.; Shen, Q.; Huang, Q. H. *Macromolecules* 2001, 34, 7613.
- Yu, C. P.; Zhang, L. F.; Shen, Z. Q. *J Mol Catal A* 2004, 212, 365.
- Ling, J.; Shen, Z. Q. *Macromol Chem Phys* 2002, 203, 735.
- Martin, E.; Dubois, P.; Robert, J. *Macromolecules* 2000, 33, 1530.
- Ling, J.; Chen, W.; Shen, Z. Q. *J Polym Sci Part A: Polym Chem* 2005, 43, 1787.
- Habaue, S.; Yoshikawa, M.; Okamoto, Y. *Polym J* 1995, 27, 986.
- Chai, J.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H. G.; Nottmeyer, M.; Hosmane, N. S. *J Am Chem Soc* 2005, 127, 7521.
- Peng, H. M.; Yao, Y. M.; Deng, M. Y.; Zhang, Y.; Shen, Q. *J Rare Earths* 2006, 24, 509.
- Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J Am Chem Soc* 1988, 110, 1841.
- Evans, W. J.; Sollberger, M. S. *Inorg Chem* 1988, 27, 4417.
- Evans, W. J.; Sollberger, M. S.; Ziller, J. W. *J Am Chem Soc* 1993, 115, 4120.
- Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W. *Inorg Chem* 1989, 28, 4027.
- Gromada, J.; Mortreux, A.; Chenal, T.; Ziller, J. W.; Leising, F.; Carpentier, J. F. *Chem—Eur J* 2002, 8, 3773.
- Schumann, H.; Kociok-Köhn, G.; Loebel, J. *Z Anorg Allg Chem* 1990, 581, 69.
- Kuhn, N.; Schumann, H.; Wolmershauser, G. Z.; *Naturforsch, B. Chem Sci* 1991, 46, 896.
- Sheng, H. T.; Xu, F.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Inorg Chem* 2007, 46, 7722.
- Sheng, H. T.; Li, J. M.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Polyhedron* 2008, 27, 1665.
- Sarel, S.; Pohoryles, L. A. *J Am Chem Soc* 1958, 80, 4596.
- Taylor, M. D.; Carter, C. P. *J Inorg Nucl Chem* 1962, 24, 387.
- Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* 1996, 29, 1798.
- Shen, Y. Q.; Shen, Z. Q.; Zhang, Y. F.; Hang, Q. H. *J Polym Sci Part A: Polym Chem* 1997, 35, 1339.
- Pego, A. P.; Zhong, Z. Y.; Dijkstra, P. J.; Grijsma, D. W.; Jan, F. J. *Macromol Chem Phys* 2003, 204, 747.
- Ling, J.; Zhu, W.; Shen, Z. Q. *Macromolecules* 2004, 37, 758.
- Li, C.; Wang, Y. R.; Zhou, L. Y.; Sun, H. M.; Shen, Q. *J Appl Polym Sci* 2006, 102, 22.
- Zhao, B.; Lu, C. R.; Shen, Q. *J Appl Polym Sci* 2007, 106, 1383.
- Schappacher, M.; Fabre, T.; Mingotaud, A. F.; Soum, A. *Biomaterials* 2001, 22, 2849.