

Synthesis and molecular structure of the cationic samarium phenoxide complex $[(\text{ArO})_2\text{Sm}(\text{DME})_2][\text{BPh}_4] \cdot \text{THF}$ and its catalytic activity for the polymerization of ϵ -caprolactone

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Abstract

The first cationic samarium phenoxide complex, $[(\text{ArO})_2\text{Sm}(\text{DME})_2][\text{BPh}_4] \cdot \text{THF}$ ($\text{ArO} = 2,6$ -di-*tert*-butyl-4-methyl-phenoxide) (**1**), has been synthesized by one-electron oxidation reaction of $(\text{ArO})_2\text{Sm}(\text{THF})_3$ with AgBPh_4 in high yield and structurally characterized. The complex **1** can be used as a single-component catalyst for the ring-opening polymerization of ϵ -caprolactone (ϵ -CL) with high activity. The activity of the complex **1** is much higher than that of the parent neutral complex $(\text{ArO})_3\text{Sm}(\text{THF})_2$, and is comparable to that of the divalent complex $(\text{ArO})_2\text{Sm}(\text{THF})_3$. A coordination-insertion polymerization mechanism was supposed according to the end-group analysis.

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Keywords: Cationic samarium phenoxide complex; ϵ -Caprolactone (ϵ -CL); Ring-opening polymerization

1. Introduction

The interest in the development of cationic complexes of the transition metals is steadily growing due to the high activity and selectivity of the cationic complexes in a variety of olefin polymerizations and transformations [1]. Until recently the chemistry of cationic lanthanide complexes has become one of the most attractive fields in lanthanide chemistry. Several families of cationic lanthanide alkyl complexes supported by cyclopentadienyl [2], monoanionic, non-cyclopentadienyl ligands [3], and neutral ligands [4,5] have been successfully synthesized. Moreover, the unprecedented catalytic behaviors of these cationic complexes in olefin polymerizations and transformations have also been explored very recently, including the polymeriza-

tions of ethylene, α -olefine [6,11] and styrene [6,10]; the copolymerizations of ethylene-styrene [6], ethylene-norbornene [8] and ethylene-dicyclopentadiene [9]; the terpolymerization of ethylene-styrene-dicyclopentadiene [9]; the stereospecific polymerization of diene [7]; intramolecular hydroamination cyclization [12], as well as alkyne dimerization [13]. However, the chemistry of cationic lanthanide alkoxide/phenoxide complexes has been quite limited. The first cationic yttrium alkoxide complexes: $[\text{Y}_3(\mu_3\text{-Cl})(\mu_3\text{-OR})_4(\mu\text{-OR})_4(\text{OR})_3(\text{THF})_2][\text{BPh}_4]$, $[\text{Y}_2(\mu_2\text{-Cl})(\mu_2\text{-OR})_2(\text{OR})_2(\text{THF})_4][\text{BPh}_4]$ and $[\text{Y}(\text{OR})(\text{Cl})(\text{THF})_5][\text{BPh}_4]$ ($\text{R} = \textit{t}Bu) were synthesized in 1990 by the metathesis reactions of yttrium alkoxide chloride with AgBPh_4 and NaBPh_4 , respectively [17]. Since then, no further report on their reactivity and the synthesis of lanthanide phenoxide complex has been found.$

The homoleptic lanthanide alkoxide/phenoxide complexes have been known to show high catalytic activity for the ring-opening polymerization of lactones [14–16]

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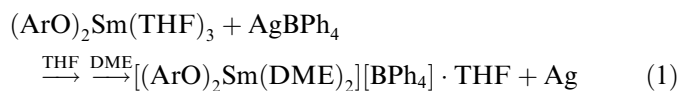
and the transformations of C–C and C–X (X = O, N, etc.) bond formation, so it's of interest to understand the catalytic behavior of the corresponding cationic species.

Here, we would like to report the synthesis and molecular structure of the first cationic samarium phenoxide complex $[(\text{ArO})_2\text{Sm}(\text{DME})_2][\text{BPh}_4] \cdot \text{THF}$ (**1**), as well as its catalytic activity for the ring-opening polymerization of ϵ -CL. Complex **1** can be used as a single-component initiator for the ring-opening polymerization of ϵ -CL with high activity. Its activity is much higher than that of the corresponding neutral trivalent complex $(\text{ArO})_3\text{Sm}(\text{THF})_2$ and comparable to that of the divalent complex $(\text{ArO})_2\text{Sm}(\text{THF})_3$.

2. Results and discussion

2.1. Synthesis and characterization of cationic samarium phenoxide complex **1**

Given the fact that cationic samarium metallocene complexes can be synthesized conveniently by the oxidation reaction of the corresponding divalent complex with AgBPh_4 , the oxidation route was used here for synthesis of the title complex. Thus, a THF solution of $(\text{ArO})_2\text{Sm}(\text{THF})_3$ [20] was added to the suspension of AgBPh_4 in THF in dark and then the color change of the mixture was observed immediately from brown to dark indicating the formation of Ag precipitate. After Ag was removed and the yellow solution obtained was concentrated, the expected orange–yellow cationic compound **1**, which was fully characterized by elemental analysis, ^1H NMR, and X-Ray crystal structural analysis, was isolated in 68% yield



Complex **1** is soluble in THF but not in toluene and hexane. The molecular structure of complex **1** is shown in Fig. 1. The selected bond distances and angles are given

in Table 2. As shown in Fig. 1, complex **1** is composed of a cation $[(\text{ArO})_2\text{Sm}(\text{DME})_2]^+$ and an anion $[\text{BPh}_4]^-$ with a free THF molecule in the unit cell. The cation is well separated from the anion. The overall structure of the cation $[(\text{ArO})_2\text{Sm}(\text{DME})_2]^+$ is similar to that of $(\text{Ar}'\text{O})_2\text{Sm}(\text{DME})_2$ [24]. Two phenoxide ligands and two DME molecules coordinate to the central metal forming a distorted octahedral geometry in which three oxygen atoms from two DME molecules (O(1), O(3), O(5)) and one oxygen atom from a phenoxide ligand (O(6)) can be considered to occupy equatorial positions and the other two oxygen atoms from a DME molecule (O(2)) and a phenolate ligand (O(4)), respectively, occupy axial positions.

The average distance of Sm–O (Ar) bond of complex **1** is 2.131 Å. The value is apparently shorter than those reported for samarium (II) phenoxide complexes, such as $(\text{ArO})_2\text{Sm}(\text{THF})_3$ (2.339(12) Å) [20], $[(\text{ArO})_2\text{Sm}(\text{THF})_3] \cdot \text{THF}$ (2.304(8) Å) [21], $[(\text{ArO})_2\text{Sm}(\text{THF})_3] \cdot \text{MePh}$ (2.335(7) Å) [22], $[(\text{ArO})_3\text{Sm}(\text{THF})\text{K}] \cdot \text{Ph}$ (2.339(9) Å) [23], and $(\text{Ar}'\text{O})_2\text{Sm}(\text{DME})_2$ (2.375(3) Å) [24], but comparable to those found for samarium (III) phenoxide complexes: $(\text{ArO})_3\text{Sm}(\text{THF}) \cdot \text{THF}$ (2.151(7) Å) [25] and $(2,6\text{-Pr}_2\text{-C}_6\text{H}_3\text{O})_3\text{Sm}(\text{THF})_3$ (2.158(2) Å) [26]. The difference observed in bond distances between Sm(II) and Sm(III) complexes can be explained by taking account of the difference of ionic radii of Sm(II) and Sm(III) (0.19–0.20 Å for Sm(II)/Sm(III)) [30]. The bond distance can also be compared with that for $[(\text{ArO})_3\text{Nd}(\text{THF})] \cdot \text{MePh}$ (2.176(7) Å) [27], when the difference in ionic radii between Sm and Nd is considered. The Sm–O (DME) distances range from 2.492(4) Å to 2.541(4) Å, with an average of 2.516(4) Å, which is well within the average value of coordination bonds.

The bond angle between two phenoxides O(1)–Sm–O(2) is 111.74(13)°, which is smaller than those in $(\text{ArO})_2\text{Sm}(\text{THF})_3$ (151.1(4)°) [20] and $[(\text{ArO})_2\text{Sm}(\text{THF})_3] \cdot \text{MePh}$ (148.3(2)°) [22]. This may be attributed to the more crowded coordinated environment around the Sm in complex **1** resulting from six coordinated groups. The Sm–

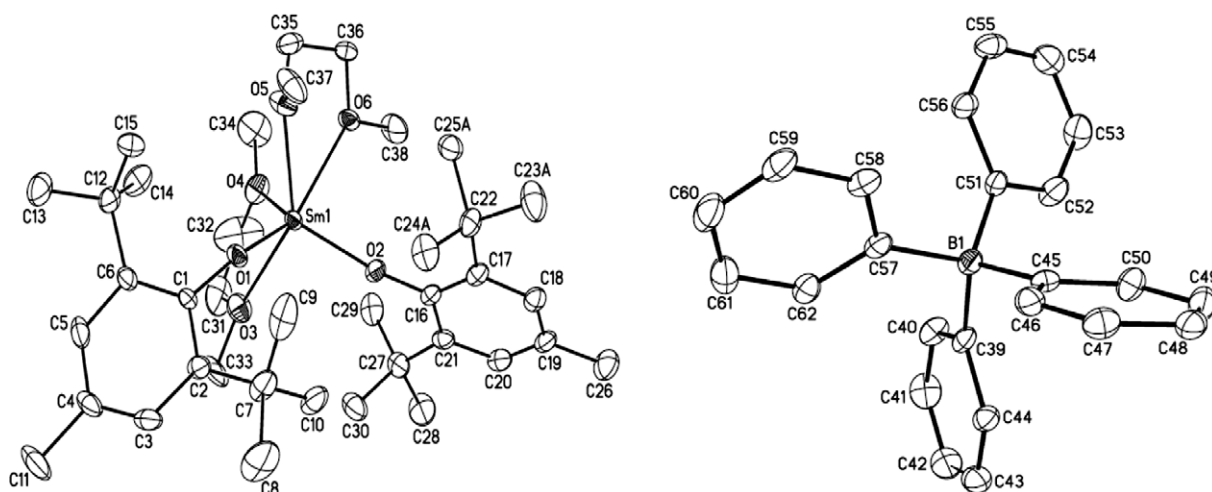


Fig. 1. ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Details of the crystallographic data of **1** and **2**

	1	2
Empirical formula	C ₆₆ H ₉₄ O ₇ BSm	C ₇₂ H ₁₁₈ O ₁₀ Sm ₂
Formula weight	1160.57	1444.36
Temperature (K)	193(2)	193(2)
Wavelength (Å)	0.7107	0.7107
Size (mm)	0.50 × 0.30 × 0.10	0.50 × 0.30 × 0.25
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>p</i> 21/ <i>n</i>
<i>a</i> (Å)	11.7787(6)	14.3031(8)
<i>b</i> (Å)	13.6127(5)	16.6091(8)
<i>c</i> (Å)	21.4498(15)	15.7354(9)
α (°)	78.519(6)	90
β (°)	85.751(6)	105.5150(10)
γ (°)	65.415(4)	90
<i>V</i> (Å ³)	3064.7(3)	3601.9(3)
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.258	1.332
Absorption coefficient (mm ⁻¹)	1.008	1.667
<i>F</i> (000)	1226	1508
θ Range for collection (°)	3.06–25.35	3.20–27.48
Reflection collected	30662	39647
Independent reflections	11175	8232
	[<i>R</i> (int) = 0.0564]	[<i>R</i> (int) = 0.0271]
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0572	0.0301
<i>R</i> _w	0.1126	0.0705
Goodness-of-fit on <i>F</i> ²	1.138	1.118

O(1)–C(1) bond angle is 172.5(3)°, while the Sm–O(2)–C(16) is 149.4(3)°. The anion [BPh₄][−] has normal bond distances and angles.

We tried several times to synthesize the analogous cationic complex with Ar'O ligand (Ar'O = 2,6-di-tert-butylphenoxide), but failed. The reaction of (Ar'O)₂Sm(THF)₃ with the same AgBPh₄ used in the above reaction afforded no definite complex but a small amount of by-product [(Ar'O)₂Sm(μ-OH)(THF)₂ · 2THF (**2**), which was confirmed by X-ray diffraction. It seems that the formation of **2** should result from the presence of a trace of water.

Table 2
Selected bond distances (Å) and angles (°) for **1**

Bond distance			
Sm(1)–O(1)	2.147(3)	Sm(1)–O(2)	2.114(3)
Sm(1)–O(3)	2.492(4)	Sm(1)–O(4)	2.541(4)
Sm(1)–O(5)	2.492(4)	Sm(1)–O(6)	2.536(3)
O(1)–C(1)	1.375(6)	O(2)–C(16)	1.360(6)
C(39)–B(1)	1.643(7)	C(45)–B(1)	1.661(7)
C(51)–B(1)	1.653(8)	C(57)–B(1)	1.643(7)
Bond angles			
O(2)–Sm(1)–O(1)	111.74(13)	O(2)–Sm(1)–O(5)	118.83(14)
O(1)–Sm(1)–O(5)	81.02(13)	O(2)–Sm(1)–O(3)	97.61(14)
O(1)–Sm(1)–O(3)	82.45(15)	O(5)–Sm(1)–O(3)	143.39(15)
O(2)–Sm(1)–O(6)	84.45(12)	O(1)–Sm(1)–O(6)	143.11(13)
O(5)–Sm(1)–O(6)	62.34(12)	O(3)–Sm(1)–O(6)	129.73(14)
O(2)–Sm(1)–O(4)	114.99(14)	O(1)–Sm(1)–O(4)	124.36(13)
O(5)–Sm(1)–O(4)	100.80(14)	O(3)–Sm(1)–O(4)	63.29(15)
O(6)–Sm(1)–O(4)	70.43(13)	C(57)–B(1)–C(39)	109.7(4)
C(57)–B(1)–C(51)	110.4(4)	C(39)–B(1)–C(51)	108.7(4)
C(57)–B(1)–C(45)	110.0(4)	C(39)–B(1)–C(45)	108.5(4)
C(51)–B(1)–C(45)	109.5(4)		

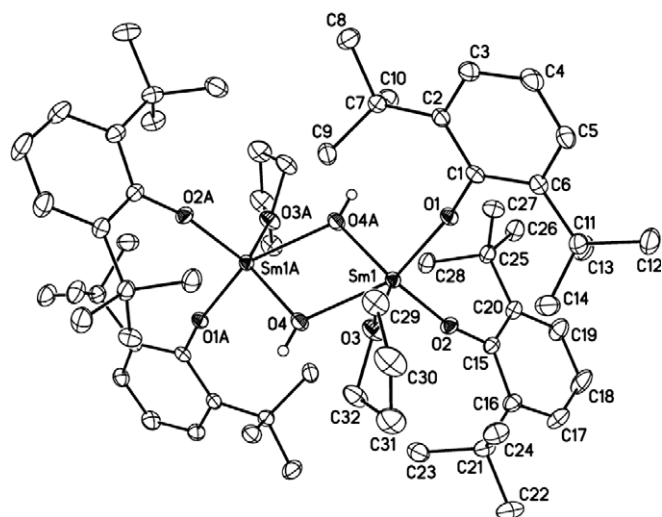


Fig. 2. ORTEP diagram of complex **2** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°) are as follows: Sm(1)–O(1) 2.1686(18); Sm(1)–O(2) 2.1352(19); Sm(1)–O(3) 2.456(2); Sm(1)–O(4) 2.3281(19); Sm(1)–O(4)A 2.291(2); Sm(1)–Sm(1)A 3.8052(3); O(2)–Sm(1)–O(1) 107.82(7); O(2)–Sm(1)–O(4)A 106.21(8); O(1)–Sm(1)–O(4)A 104.94(7); O(2)–Sm(1)–O(4) 105.04(8).

Anyhow, the result indicated the structure of Ar'O has an influence on the synthesis of cationic lanthanide phenoxide complex.

Complex **2** is a centrosymmetric five-coordinated dimer with two bridging hydroxide ligands (Fig. 2). The low-coordinate hydroxolanthanide complexes, which were structurally characterized, are rare [28,29]. This is the first example for samarium complex. The solid-state structure of **2** is quite similar to those of [(2,4,6-*t*Bu₃-C₆H₂O)₂Yb(μ-OH)(THF)₂] [28] and [(Ar'O)₂Yb(μ-OH)(THF)₂] [29].

2.2. Catalytic activity of **1** for the polymerization of ϵ -CL

The cationic alkyl complexes have been known to show the improved catalytic behaviors in homogeneous catalysis, therefore, it should be of interest to examine the catalytic behavior of complex **1**. Thus the ring-opening polymerization of ϵ -CL with complex **1** was conducted, as homoleptic lanthanide triphenoxide complexes are known to be the efficient catalysts for the ring-opening polymerization of ϵ -CL. The results are listed in Table 3. In comparison, the same polymerizations with the neutral samarium (III) triphenoxide (ArO)₃Sm(THF)₂ were also conducted. The representative results are shown in Table 3. From Table 3, it can be seen that complex **1** shows very high activity under mild conditions. The polymerization was completed within 3 min at 20 °C with the catalyst loading of 1.0 × 10^{−3} mol/mol monomer, while the same polymerization with neutral species (ArO)₃Sm(THF)₂ yielded only trace of conversion (Table 3, entries 1 and 9). The polymerization with **1** still went smoothly and yielded the conversion as high as 96.7% when the catalyst loading

Table 3

Polymerization of ϵ -CL initiated by cationic complex **1** and neutral complex $(\text{ArO})_3\text{Sm}(\text{THF})_2^{\text{a}}$

Entry	Init	$[M]/[I]$	Temperature ($^{\circ}\text{C}$)	Time (min)	Yield ^b (%)	M_n ($\times 10^4$)	M_w/M_n ^c
1	1	1000	20	3	100	5.45	1.93
2	1	1500	20	3	75.3	6.12	2.07
3	1	2500	20	3	61.6	5.39	2.14
4	1	3000	20	5	37.7	6.32	1.84
5	1	3000	20	7	45.3	7.64	2.00
6	1	3000	20	10	63.4	9.60	1.91
7	1	3000	20	15	96.7	12.0	1.94
8 ^d	1	1000	20	30	45.2	–	–
9	$(\text{ArO})_3\text{Sm}(\text{THF})_2$	1000	20	30	36.6	–	–
10	$(\text{ArO})_3\text{Sm}(\text{THF})_2$	700	20	3	23.3	5.05	1.75
11	$(\text{ArO})_3\text{Sm}(\text{THF})_2$	700	20	10	55.1	5.88	1.78
12	$(\text{ArO})_3\text{Sm}(\text{THF})_2$	700	20	15	72.5	7.02	1.87
13	$(\text{ArO})_3\text{Sm}(\text{THF})_2$	700	20	30	100	8.41	1.99
14	$(\text{ArO})_2\text{Sm}(\text{THF})_3$	1000	20	5	100	26.5	1.41

^a Conditions: toluene as solvent, $V_{\text{sol}}/V_{[\text{M}]} = 5:1$.^b Yield: weight of polymer obtained/weight of monomer used.^c Measured by GPC calibrated with standard polystyrene samples.^d THF as solvent.

decreased to 3.3×10^{-4} mol/mol monomer in 15 min at 20°C (Table 3, entry 7). The dependence of conversion on the polymerization time for the systems of **1** and $(\text{ArO})_3\text{Sm}(\text{THF})_2$, respectively, at different catalyst loading is shown in Fig. 3. It can be seen obviously that the complex **1** is much more efficient than the parent neutral complex $(\text{ArO})_3\text{Sm}(\text{THF})_2$. The comparison of the activity between complex **1** and the divalent complex $(\text{ArO})_2\text{Sm}(\text{THF})_3$ can also be made. The polymerizations with $(\text{ArO})_2\text{Sm}(\text{THF})_3$ were reported to complete at room temperature in 5 min at the catalyst loading of 1.0×10^{-3} mol/mol monomer, and even at 5.0×10^{-4} mol/mol monomer [16]. Therefore, the activity of **1** is almost as high as that of $(\text{ArO})_2\text{Sm}(\text{THF})_3$.

The polymerization system with **1** yielded the polymers with high molecular weights and moderate molecular

weight distributions (Table 3). A unimodal molecular weight distribution for all the polymers obtained with complex **1** indicates that complex **1** plays the role of a single-component catalyst in the polymerization of ϵ -CL. The conversion increased with the polymerization time. The molecular weight of the resulting polymers increased almost linearly with the conversion, except the early stage of the polymerization, while little changes in the molecular weight distributions of the polymers were observed for both cationic and neutral systems (entries 4–7 and 10–13; Table 3; see also Figs. 3 and 4).

The polymerization in toluene yielded higher conversion and the polymers with higher molecular weights than that in THF (Table 3, entries 1 and 8). The same effect of solvent on the polymer yield and molecular weight is also observed in the polymerization systems with neutral lanthanide (III)

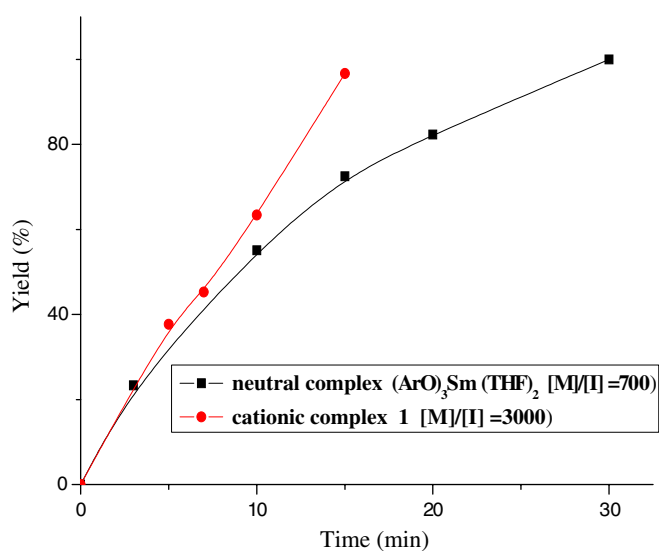


Fig. 3. Plot of the poly (ϵ -CL) yield vs. the polymerization time. Conditions: $V_{\text{sol}}/V_{[\text{M}]} = 5:1$, 20°C , toluene.

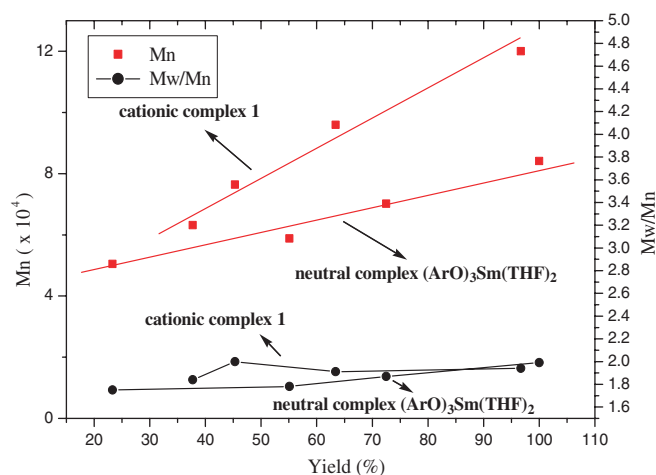
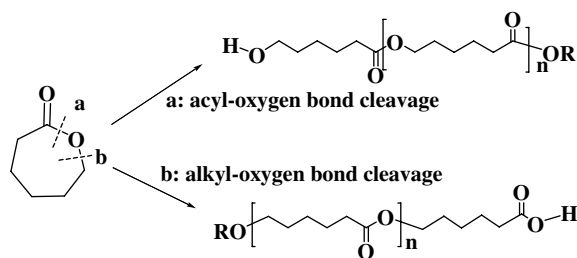


Fig. 4. Plot of the poly (ϵ -CL) M_n , (M_w/M_n) vs. the conversion with cationic complex **1** and neutral complex $(\text{ArO})_3\text{Sm}(\text{THF})_2$ as initiators in toluene at 20°C . Conditions: (cationic complex) $[M]/[I] = 3000$; (neutral complex) $[M]/[I] = 700$.

Scheme 1. Ring-opening modes of ϵ -CL.

phenoxide (alkoxide). Such a solvent dependence indicates the present polymerization to be coordination-insertion process. All the results indicate that the catalytic behavior for both systems of cationic and neutral complexes is quite similar except the difference in catalytic activity.

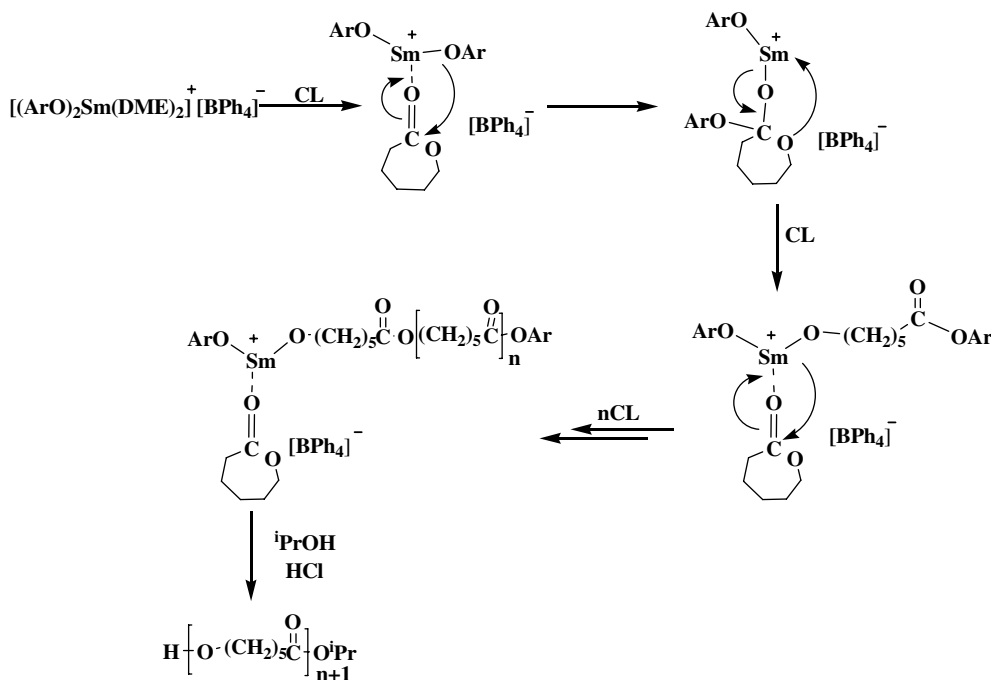
As we know, the ring-opening polymerization of ϵ -caprolactone can be proceeded by either acyl-oxygen bond cleavage or alkyl-oxygen bond cleavage (Scheme 1) depending on the catalyst used. If the reaction goes by the former way, the end group of the polymer should be connected with ROCOO⁻ group, while with RO⁻ group by the later one. In order to elucidate the polymerization mechanism, an end-group analysis was measured by ¹H NMR. Thus, an oligomer of ϵ -CL was prepared by the oligomerization of ϵ -CL with a [ϵ -CL]/[initiator] of 10 and terminated by isopropyl alcohol. The analysis of ¹H NMR spectroscopy revealed that the polymer contained an isopropoxy end group appeared at 5.0 ppm as a multiple peak and at 1.3 ppm as a double peak. No signal at about 3.5 and 1.1 ppm assigned to the CH and CH₃ of

end group OCH(CH₃)₂ were found in the ¹H NMR spectra. The results of end-group analysis are consistent with those published previously for the system with Ln(OAr)₃ [15a,15b]. The presence of these end groups indicates that the acyl-oxygen bond cleavage should occur.

The coordination-insertion and acyl-oxygen bond cleavage mechanism might be suggested according to the polymerization results and the end-groups analysis. As shown in Scheme 2, the ϵ -CL molecule coordinated to Sm of the cation, followed by ring-opening *via* the cleavage of acyl-oxygen bond to form the real active species. The improved catalytic activity observed for cationic complex may be attributed to the enhanced electrophilicity of the Sm metal bearing a formal positive charge, which makes both the coordination of ϵ -CL and the cleavage of acyl-oxygen bond more favorable. Both phenoxide groups in **1** may initiate ϵ -CL polymerization, which leads to rather broad molecular weight distributions of the resulting polymers.

3. Conclusion

Cationic samarium phenoxide complex **1** has been synthesized by the one-electron oxidation reaction of (ArO)₂Sm(THF)₃ with AgBPh₄. Complex **1** is found to be an efficient single-component initiator for the ring-opening polymerization of ϵ -CL. Its activity is much higher than that of the corresponding trivalent complex (ArO)₃Sm(THF)₂. The results presented indicate that the enhanced electrophilicity of the central metal bearing a formal positive charge is favorable for homogeneous catalysis.

Scheme 2. Postulated mechanism of the ring-opening polymerization of ϵ -CL.

4. Experimental

4.1. General procedures

All the manipulations are conducted under pure Ar atmosphere with rigorous exclusion of air and moisture using Schlenk tube and vacuum-line technique. Anhydrous SmCl_3 [19], $(\text{ArO})_2\text{Sm}(\text{THF})_3$ [20], $(\text{ArO})_3\text{Sm}(\text{THF})_2$ [22], and $(\text{Ar}'\text{O})_2\text{Sm}(\text{DME})_2$ [24] were synthesized according to the literature methods. AgBPh_4 was prepared from NaBPh_4 and AgNO_3 [18]. Deuterated benzene (C_6D_6) was purchased from Acros, dried over sodium and transferred by vacuum. $\varepsilon\text{-CL}$ was purchased from Acros, dried over CaH_2 and distilled at reduced pressure. Toluene, dimethoxy-ethane (DME), and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. A metal analysis was carried out by complexometric titration. Carbon, hydrogen, and nitrogen analysis were performed by direct combustion on a Carlo-Erba EA = 1110 instrument. Melting points were determined on a Yanaco MP-500 melting point apparatus and were uncorrected. The ^1H NMR spectra was measured on a Unity Inova-400 spectrometer in CDCl_3 at 25 °C. The number-average (M_n), weight-average (M_w) molecular weights and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC) with THF as an eluant and polystyrene as a standard on a Waters 1515 apparatus equipped with three HR columns (HR-1, HR-2, and HR-4) and an ultraviolet visible detector.

4.2. Synthesis of $[(\text{ArO})_2\text{Sm}(\text{DME})_2][\text{BPh}_4] \cdot \text{THF}$ (**1**)

A black solution of $(\text{ArO})_2\text{Sm}(\text{THF})_3$ (2.16 g, 2.69 mmol) in 30 ml of THF was slowly added to a solution of slight excess AgBPh_4 (1.41 g, 3.31 mmol) in THF in dark at r.t. The reaction mixture turned black immediately and was stirred in dark at 50 °C for 24 h until the whole blackish silver deposit was precipitated. The solvent was removed by vacuum and the residue was extracted with DME and then centrifugalized to remove Ag. After the extract was concentrated, orange–yellow crystals of **1** (2.12 g, 68%) were obtained at room temperate. Crystals suitable for X-ray analysis were grown from THF solution with a small amount of DME at r.t. Melting Point (Dec.): 150–153 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ 6.90–7.25 (m, 20H, $\text{BPh}_4\text{-H}$), 6.70–6.80 (m, 4H, Ph-H), 3.54 (t, 8H, CH_2CH_2), 3.24 (s, 12H, O-CH_3), 2.35 (s, 6H, $\text{CH}_3\text{-Ph}$), 1.32 (s, 36H, $\text{C}(\text{CH}_3)_3$). Anal. Calc. for $\text{C}_{66}\text{H}_{94}\text{O}_7\text{BSm}$ (1160.57): C, 68.30; H, 8.16; Sm, 12.96. Found: C, 67.82; H, 8.52; Sm, 12.73%.

4.3. Synthesis of $[(\text{Ar}'\text{O})_2\text{Sm}(\mu\text{-OH})(\text{THF})]_2 \cdot 2\text{THF}$ (**2**)

A black solution of $(\text{Ar}'\text{O})_2\text{Sm}(\text{DME})_2$ (1.85 g, 2.50 mmol) in 30 ml of THF was slowly added to a solution of slight excess AgBPh_4 (1.32 g, 3.08 mmol) in THF in dark at r.t. The reaction mixture turned black and was stirred in

dark at 50 °C for 24 h. The solvent was removed by vacuum and the residue was extracted with DME. After the extract was concentrated, yellow crystals of **2** (0.18 g, 10%) were obtained at room temperate. Crystals suitable for X-ray analysis were grown from DME solution with a small amount of THF at r.t. Melting Point (Dec.): 122–125 °C. Anal. Calc. for $\text{C}_{72}\text{H}_{118}\text{O}_{10}\text{Sm}_2$ (1444.36): C, 59.87; H, 8.23; Sm, 20.82. Found: C, 59.26; H, 8.47; Sm, 21.00%.

4.4. X-ray structural determination of **1** and **2**

Suitable crystals of complexes **1** and **2** were sealed in a thin-walled glass capillary for single-crystal structural determination. Diffraction data for both complexes **1** and **2** were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structure was solved by direct methods and refined by full-matrix least squares procedures based on F^2 . All non-hydrogen atoms were refined with isotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXL-97 program. Crystal data and collection and main refinement parameters are given in Table 1.

4.5. Polymerization

To a stirred solution of initiator in toluene, $\varepsilon\text{-CL}$ was added with a syringe. The polymerization mixture was stirred for a definite time at the desired temperature and then quenched with an ethanol solution containing a small amount of hydrochloric acid. The polymer was precipitated from ethanol and washed with ethanol three times and dried under vacuum.

4.6. The synthesis of oligomer for end group analysis

The oligomerization of $\varepsilon\text{-CL}$ was carried out with **1** in toluene at 20 °C under the condition of $[\varepsilon\text{-CL}]/[\text{initiator}]$ (mole ratio) of 10 for 3 min. The reaction was terminated by adding 1 ml of 5% HCl/PrOH . The oligomer was precipitated from ethanol. The product was dissolved in THF, followed by precipitation in ethanol. The procedure was repeated two times. The white product was dried in vacuum.

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Appendix A. Supplementary data

CCDC 619499 and 619500 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crys-

talographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.013.

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