Ring-Opening Polymerization of ε -Caprolactone and δ -Valerolactone Using New Sm(III) μ -Halo-bis(trimethylsilyl)amido Complexes

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ABSTRACT: New Sm(III) μ -halo-bis(trimethylsily)amido complexes [Sm(μ -X) {N(SiMe₃)₂}₂(THF)]₂ (X = Cl, Br) were synthesized and their crystal structures were analyzed. These complexes were used as catalysts for the homopolymerization of ε -caprolactone and δ -valerolactone and found to initiate ring-opening polymerization (ROP) of these monomers in high conversion over a short period, giving homopolymers with a moderate polydispersity index (~ 2.0). The effect of temperature and the catalyst amount on the molecular weight distribution was also studied. Mechanistic studies were conducted using 1 : 1 and 1 : 6 molar ratios of μ -halo-bis-(trimethylsily)amido complexes and ε -caprolactone by ¹H-NMR and ¹³C-NMR spectroscopic techniques and revealed the presence of more than one initiating species. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1669–1674, 1999

Key words: samarium; catalysis; ring-opening polymerization; lactones

INTRODUCTION

Organolanthanides are useful catalysts for the synthesis of polylactones by the ring-opening polymerization (ROP) method. Polylactones are of interest as biodegradable material for various medical applications.¹⁻⁶ The applications of new initiators, based on the lanthanide elements, has led to the production of several new macromolecular architectures like telechelic and block polymers incorporating poly(ε -caprolactone) (PCL) segments.⁷⁻¹⁰. Therefore, the development of improved structurally defined initiators of high efficiency for polylactones is of interest and, in particular, for the understanding for the design of

new catalyst systems. Our long-term goal is the understanding of lanthanoid chemistry in ROPs.

In this article, we report the synthesis and characterization of novel Sm(III) μ -halo-bis(trimethylsilyl)amido complexes and their catalytic activity for the ROP of ε -caprolactone (ε -CL) and δ -valerolactone (δ -VL). An attempt was also made to determine the nature of the initiating species for ROP of lactones using these catalysts.

EXPERIMENTAL

 ε -CL (Aldrich) and toluene were dried by refluxing over CaH₂ and distilled under reduced pressure. THF was purified by distillation over potassium. Samariumtrichloride (**1a**) and samariumtribromide (**1b**) were obtained following a published procedure by the thermolysis of ammonium hexahalogeno samarates¹¹ and tris(bis-tri-

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methylsilyl) amido samarium (2) was obtained as described in the literature. 12

Preparation and Characterization of Samarium μ -Chloro-bis(trimethylsilyl)amido tetrahydrofuran (3a) (Scheme 1)

Compound **1a** (1.1 g, 3.9 mmol) was suspended in 25 mL THF and cooled to -15° C. Compound **2** (4.98 g, 7.8 mmol), dissolved in 20 mL THF, was added dropwise. The pale yellow solution was slowly heated to 20°C. After 2 h, the solvent was removed completely by reduced pressure. The crude yellow product (6.51 g; yield: 95%) was dissolved in 80 mL of *n*-pentane and filtered. The volume of the filtrate was reduced to 65 mL under a vacuum. After 3 days at 7°C, 4.6 g of yellow crystals were isolated. Yield: 67%.

 $IR \ (cm^{-1}): 1250 vt, \ 1180 m, \ 1093 m, \ 1018 m, \ 986 st, \ 936 st, \ 833 vt, \ \ 770 w, \ \ 665 st, \ \ 606 st, \ \ 403 sh, \ \ 383 st, \ \ 309 w, \ 287 m, \ 238 m, \ 205 sh, \ 190 vst, \ 145 w, \ 114 w.$

Anal. Calcd for $C_{16}H_{44}ClN_2OSi_4Sm(578.69)$: C, 33.21%; H, 7.66%; N, 4.84%; Cl, 6.13%. Found: C, 31.97%; H, 6.92%; N, 4.43%; Cl, 6.52%.

Preparation and Characterization of Samarium μ -Bromo-bis(trimethylsilyl)amido tetrahydrofurane (3b)

The procedure was adopted as described for **3a** using 2.25 g (5.7 mmol) of **1b**, 25 mL of THF, and 7.20 g (11.4 mmol) of **2** in 30 mL of THF. The crude product (9.8 g; yield: 91%) was isolated as described above. The crude product was dissolved in 70 mL of *n*-pentane and the volume of the solution was reduced to 50 mL. After cooling for 3 days to 7°C, 5.1 g of yellow crystals was isolated. Yield: 51%.

IR (cm^{-1}) : 1250vst, 1182m, 1097m, 989st, 933m, 841vst, br, 769w, 678m, 660m, 603st, 483w, 386vst, 374sh, 282m, 254sh, 247m, 190st, 105w.

Anal. Calcd for $C_{16}H_{44}BrN_2OSi_4Sm(623.13)$: C, 30.84%; H, 7.12%; N, 4.50%; Br, 12.82%. Found: C, 29.36%; H, 7.62%; N, 4.10%; Br,13.14%.

Polymerization (General Procedure)

The complexes described in this article are airand moisture-sensitive. Therefore, all the polymerization reactions were carried out under dry nitrogen using a Schlenk, vacuum line and glovebox techniques. In a typical polymerization reaction, the required quantity of the catalyst is weighed in a Schlenk tube in a glovebox. Addition of the corresponding amounts of the solvent and monomer is done through a rubber septum with a syringe. The reaction contents are stirred at 20°C until completion of the reaction. Afterward, the reaction mixture is precipitated in excess methanol and filtered through a G-3 sintered crucible. Purification of the polymers is done by dissolution in CHCl₃ and reprecipitation in methanol. The purification procedure is repeated three times and, finally, the polymer is dried in a vacuum at room temperature.

Characterization

GPC was used to determine the molecular weights and molecular weight distributions (M_w/M_n) . A Knauer GPC apparatus equipped with two 10- μ polymer mixed-gel columns (600 × 8 mm, PSS) and a Knauer-differential refractometer/viscometer K200 was used. Molecular weights were corrected by universal calibration relative to polystyrene standards. The polymers were dissolved in THF and elution was performed at a flow rate of 0.63 mL/min.

¹H-NMR spectra (300 MHz) were obtained on a Brucker AC-300 spectrometer in CDCl_3 as a solvent. The ¹H-NMR and ¹³C NMR spectra used for end-group analysis were measured in C_6D_6 with a Brucker AMX-500 spectrometer. The IR spectra were recorded using a Bruker IFS-88 with Nujol suspensions between CsBr or polyethylene plates.

RESULTS AND DISCUSSION

Synthesis and Structure of Catalysts

Suspensions of anhydrous samariumtrichloride (1a) and samariumtribromide (1b) were reacted with two equimolar amounts of tris(bis-trimethylsilyl)amido samarium¹³ (2) in THF at -15° C (Scheme 1). The samariumtrihalides were dissolved rapidly by adding the solution of 2 in THF to give a yellow solution of **3a**,**b**. After evacuation to dryness, the yellow crystals of **3** were isolated by crystallization from *n*-pentane by cooling to 7°C.

 $2SmX_{3} + 4Sm(NSi(Me_{3})_{2})_{3} \xrightarrow{\text{THF}} 3[Sm(\mu - X)(NSi(Me_{3})_{2})_{2}(\text{THF})]_{2}$ (1a,1b)
(2) $X = CI \quad (3a)$ $= Br \quad (3b)$

Scheme 1



Figure 1 ORTEP drawing of **3a** in the crystal. Displacement ellipsoids at the 50% probability level.



Figure 2 ORTEP drawing of 3b in the crystal. Displacement ellipsoids at the 50% probability level.

The crystal structures of **3a** and **3b** were determined by an X-ray single-crystal structure (Figs. 1 and 2). Based on the crystal structure, three mechanisms are possible for the first reaction step involving the interaction of the metal-substrate:

- 1. Increase of the coordination number to 6, preserving the dimeric structure.
- 2. Coordination of a polymerizable donor molecule, for example, ε -CL, in exchange for a THF ligand.
- Coordination involving the loosening of the Sm₂X₂ bridging bonds.

Polymerization

ROP of ε -CL and δ -VL in the presence of catalytic amounts (cat : monomer 1 : 150) of Sm(III)-based halo (X = Cl, Br) bridged complexes (Figs. 1 and 2; sample designation is given in the Experimental section) was carried out in the presence of toluene as a solvent. The results of ε -CL and δ -VL homopolymerizations at room temperature (20°C) are given in Table I. These complexes were found to initiate the ROP of ε -CL and δ -VL in high conversion over a short period, giving a high molecular weight ($M_n > 10,000$ g/mol) PCL and $poly(\delta-VL)$ (PVL) with a moderate polydispersity index $(M_w/M_n \sim 2.0)$ up to very high conversions and long polymerization times. In spite of the moderate polydispersity, the presence of living chains was proved which enabled the synthesis of block copolymers.¹⁴ The trivalent tris(bis-trimethylsilyl)amidosamarium was so reactive that the viscosity of the solution increased very rapidly and the reaction was complete in <1 min, which may be due to the monodentate nature of the ligands as reported earlier by Evans and Katsumata also for the bis(bis-trimethylsilyl)amido samarium(II) catalyst.⁴

Polymerizations were carried out at various monomer-to-initiator ratios (Table II). No systematic correlation between the monomer/initiator ratio and the molecular weight of the polymer was found. In fact, the molecular weight was found to

Table I Homopolymerization of ε -CL and δ -VL at 20°C Using Sm(III) μ -Halo-bis(trimethyl)silylamido Complex

Sm(III) Complex	Monomer	Time (min)	$M_n imes 10^4 \ (m g/mol)$	M_w/M_n	Yield (%)
$Sm(N(SiMe_3)_2)_3$	$\epsilon ext{-CL}$	< 1	2.72	2.38	98
$[Sm\{N(SiMe_{3})_{2}\}_{2}(\mu\text{-}Cl)(THF)]_{2}$	ε-CL δ-VL	$\begin{array}{c} 20\\ 15 \end{array}$	$\begin{array}{c} 1.10\\ 1.62 \end{array}$	$\begin{array}{c} 1.91 \\ 2.02 \end{array}$	98 97
$[Sm\{N(SiMe_{3})_{2}\}_{2}(\mu\text{-}Br)(THF)]_{2}$	$\epsilon ext{-CL} \delta ext{-VL}$	10 8	$1.75 \\ 1.86$	$\begin{array}{c} 1.65\\ 1.62\end{array}$	98 96

Sm(III) Complex	Cat : Monomer	Yield (%)	$\begin{array}{c} M_n \times \ 10^4 \\ (\text{g/mol}) \end{array}$	M_w/M_n
$[Sm{N(SiMe_2)_3}_{2}(\mu-Cl)(THF)]_{2}$	1:75	96	0.97	1.92
	1:150	98	1.10	1.95
	1:300	92	1.33	1.57
$[Sm{N(SiMe_3)_2}_2(\mu-Br)(THF)]_2$	1:75	97	1.66	1.65
	1:150	97	1.77	1.72
	1:200	95	1.71	2.01

Table IIEffect of Cat : Monomer Ratio on Molecular Weight ofResulting PCL

be independent of the initiator amount, which can be explained by the very low initiation rate of the catalyst and the very fast polymerization rate. Understanding of the relation of the initiation/ polymerization rate and the nature of the ligand on the metal is the key issue for tailor-made catalysts heading for living polymerization.

Sm(III) μ -halo-bis(trimethylsilyl)amido complexes are also found to be effective in ROP at low temperature (-10°C). There was an increase in the number-average molecular weight (M_n) from 1.65 \times 10⁴ to 3.1 \times 10⁴ g/mol on reducing the temperature of the polymerization from +50 to -10°C (Table III). This could be due to transesterification reactions leading to the formation of cyclic structures and oligomers at high temperature in contrast to the reaction at room temperature. The suppression of undesired side reactions at low temperature was also suggested by Novak et al.¹⁵

Reaction of ε -CL with Sm(III) μ -halo-bis(trimethylsilyl)amido complexes in 1 : 1 and 1 : 6 (cat : monomer) molar ratios was carried out in an NMR tube in CDCl₃ and C₆D₆ solvents under dry and inert conditions. The contents with 6 equivalents of ε -CL with 1 equivalent of [Sm{N(SiMe_3)_2}_2(μ -Cl)(THF)]₂ was analyzed by GPC and showed an M_n = 5380 g/mol and M_w/M_n = 2.29. In addition to the peaks for PCL, ¹H-NMR showed additional peaks at

0.234 ppm (SiMe₃) (Fig. 3). The ¹H-NMR spectrum of the catalyst was also taken to avoid any confusion of end-group signals with the signals of the unreacted initiator. The reaction was also carried out in the coordinating solvent (THF).

The rate of the reaction was found to be slow as compared to the rate in the noncoordinating solvent. Based on the ¹H-NMR spectrum and the slowed rate of polymerization in THF, the coordination insertion mechanism is proposed in which ROP proceeds through acyl oxygen cleavage of the lactone ring as suggested by Mclain et al.¹⁶ and Yaal.⁸ with organolanthanides suda \mathbf{et} like [Y(OCH₂CH₂OCH₂CH₃)₃] and Ln(OR)(C₅Me₅), respectively. The 1 : 1 molar reaction of $[Sm{N(SiMe_3)_2}_2(\mu-Br)(THF)]_2$ with ε -CL gives further insight into the nature of the initiating species. This reaction gave a solid product which became insoluble in organic solvents after drying in a vacuum. The insoluble 1:1 adduct of ε -CL and the μ -bromo-bis(trimethylsilyl)amido Sm(III) catalyst was also tried as an initiator for ε -CL polymerization and found to initiate its polymerization (M_n) $= 1.24 \times 10^4$, $M_w/M_n = 2.26$). However, the rate of polymerization is significantly lower compared to the reaction using the original μ -halo-bis(trimethylsilyl)amido Sm(III) catalysts (with a cat : monomer ratio of 1:150). This strongly indicates that the

Table III Effect of Temperature on ROP of PCL

Sm(III) Complex	Temperature (°C)	$\stackrel{M_n \ (\text{g/mol})}{\times \ 10^{-4}}$	M_w/M_n	Yield (%)
$[Sm{N(SiMe_3)_2}_2(\mu-Br)(THF)]_2$	-10	3.10	1.98	98
0227 2	+10	2.88	1.91	98
	+20	1.77	1.72	97
	+50	1.65	2.05	89

Cat(3b) : monomer 1 : 150 (by mol).



Figure 3 ¹H-NMR spectrum of the reaction mixture. Cat (**3a**) : caprolactone 1 : 6 (by mol).

Sm species obtained by the 1 : 1 ratio monomer : catalyst differs from the Sm species obtained in the first reaction step with a catalyst : monomer ratio of 1 : 150. The typical carbonyl band of PCL (1725 \pm 2 cm⁻¹) decreased in intensity and a new very strong band appeared at 1610 cm⁻¹ (Fig. 4) in the IR spectrum.

This shows the strong interaction between the carbonyl oxygen and the samarium atom, resulting in a delocalized π -electron system. The ¹³C-NMR spectrum of the same reaction mixture showed the presence of many additional peaks including one peak for —<u>C</u>H₂Br (Fig. 5). There could be a possibility of the presence of more than one type of initiating species by participation of both samarium–silylamide and samarium–bromide bonds in the Sm(III) μ -halo-bis(trimethyl-



Figure 4 IR spectra of (a) PCL and (b) reaction product of ϵ -CL and cat (3b) (mol ratio 1 : 1).

silyl)amido complexes (Fig. 6). This is also supported by the dissociation of Sm(III) bridged complexes in solution into monomeric species, which



Figure 5 ¹³C-NMR spectrum of the reaction mixture. Cat (3a) : caprolactone 1 : 1 (by mol).



Figure 6 Proposed initiation mechanism.

was proved by osmometric measurements following a published procedure¹⁷:

$$\mathrm{Sm}_2\mathrm{X}_2 \rightleftharpoons 2 \mathrm{Sm}\mathrm{X}_2$$

CONCLUSIONS

Sm(III) μ -halo-bis(trimethylsilyl)amido complexes are found to be effective room-temperature ROP catalysts for ε -CL and δ -VL. The preliminary attempts to elucidate the polymerization mechanism reveals the presence of more than one type of initiating species. From the results available so far, it is most likely that the decoordination of THF in exchange for a lactone molecule is the first reaction step. Loosening of the Sm₂X₂ bridging bonds and participation of both silyamido and bromide groups attached to the Sm metal in the formation of reactive active species for further insertion of lactone units could be the possible initiation step. Future work will focus on ligands, turning toward more efficient catalyst systems, particularly focusing on coordinated ligands and on bridging atoms for a better understanding of the role of ligands in ROP.

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