

Ring-Opening Polymerization of ϵ -Caprolactone with a Divalent Samarium Bis(phosphido) Complex

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ABSTRACT: The ring-opening polymerization of ϵ -caprolactone initiated with a divalent samarium bis(phosphido) complex [Sm(PPh₂)₂] is reported. The polymerization proceeded under mild reaction conditions and resulted in polyesters with number-average molecular weights of 8.2×10^3 to 12.5×10^3 . The yield and molecular weight of poly(ϵ -caprolactone)s were dependent on the experimental parameters, such as the monomer/initiator molar ratio, the monomer concentration, the reaction temperature, and the polymerization time. The obtained polymers were characterized

with Fourier transform infrared, NMR, gel permeation chromatography, and differential scanning calorimetry. On the basis of an end-group analysis of low-molecular-weight polymers by NMR spectroscopy, a coordination–insertion mechanism is proposed for the polymerization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1558–1564, 2005

Key words: polyesters; ring-opening polymerization; synthesis

INTRODUCTION

The synthesis of aliphatic polyesters has been a field of intense study because of their potential applications as biodegradable and biocompatible materials.^{1–5} The ring-opening polymerization (ROP) of lactones and lactides is the most convenient route for obtaining such polymers. Various tin and aluminum alkoxides have been widely used as initiators for the ROP of cyclic esters.^{6–11} Some others, such as aluminum porphyrins,¹² decamolybdate anion,¹³ and rare-earth-based catalysts,¹⁴ have also been reported.

Recently, we have successfully prepared star-shaped poly(ϵ -caprolactone)s (PCLs) based on an *in situ* formed tetrafunctional samarium enolate in the presence of a divalent samarium complex {SmI₂ or samarium(II) bis(phosphido) [Sm(PPh₂)₂]}.¹⁵ The synthetic procedure allows four-armed PCL with a well-defined architecture to be obtained under mild reaction conditions. In addition, the divalent samarium bis(phosphido) complex is highly active as a single-component catalyst for the ROP of ϵ -caprolactone (CL). These findings motivated us to carry on with the

matter to obtain insight into this new polymerization system. In this article, we describe the polymerization features in detail, and the reaction mechanism is also discussed briefly.

EXPERIMENTAL

Materials

CL (Aldrich Chemicals Co., Milwaukee, WI) was dried over calcium hydride and distilled under reduced pressure. Toluene and tetrahydrofuran (THF) were dried over a benzophenone–sodium complex for 3 days and distilled before use. A 0.1M THF solution of SmI₂ was prepared according to ref. 16. Sm(PPh₂)₂ was synthesized as a dark powder through the reaction of SmI₂ with 2 equiv of KPPH₂.¹⁷ For the sake of removing KPPH₂ residue, the collected powder product was washed with THF several times in a nitrogen atmosphere.

Polymerization procedure

The polymerization was carried out with Schlenk techniques in a dry nitrogen atmosphere. The given amount of CL was introduced by a syringe into Schlenk tubes containing a THF solution of Sm(PPh₂)₂ (0.1 mmol; CL/Sm molar ratio = 600–1600) with vigorous stirring. The dark green color of the Sm(PPh₂)₂ solution disappeared immediately, and the viscosity of the mixture increased as the reaction proceeded. After a certain time, the polymerization was terminated with methanol or ethanol containing a small

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TABLE I
Effect of the Monomer/ $\text{Sm}(\text{PPh}_2)_2$ Molar Ratio
on the ROP of CL in Bulk^a

No.	$[\text{CL}]_0/[\text{Sm}(\text{PPh}_2)_2]$	Yield (%)	M_v (10^4) ^b	M_n ^c	M_w/M_n ^c
1	600	94.7	2.92	8,500	1.59
2	800	98.8	4.39	10,100	1.67
3	1000	95.7	5.01	10,800	2.01
4	1200	82.0	5.24	12,500	2.11
5	1400	54.6	3.33	9,700	1.62
6	1600	32.5	2.63	8,200	1.50

^a Polymerization was carried out at room temperature ($\approx 25^\circ\text{C}$) for 1 h.

^b Measured in DMF at 30°C .

^c Determined by GPC with polystyrene standards.

amount of hydrochloric acid to remove the samarium salts in the polymer. The product was then dissolved in CH_2Cl_2 and recovered by precipitation in excess methanol. Finally, the purified polymer samples were dried *in vacuo* at 30°C for 48 h. The yield was calculated on the basis of the polymer weight. The low-molecular-weight PCL sample used for end-group analysis was prepared with the same procedures, except that the molar ratio of CL to $\text{Sm}(\text{PPh}_2)_2$ equaled 200.

Measurements

$^1\text{H-NMR}$ spectra were recorded on a Bruker Avance DMX-500 NMR instrument in CDCl_3 with tetramethylsilane as an internal standard. A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used for recording spectra in KBr pellets or films. Ultraviolet–visible (UV–vis) measurements were carried out with a Cary 100 Bio UV–vis spectrophotometer operating at a fixed wavelength of 480 nm. The molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with a Waters 2410 GPC apparatus equipped with a set of Styragel columns (HT-3, HT-4, and HT-5) and a differential refractometer. THF was used as an eluent at a flow rate of 1.0 mL/min at 25°C , and the molecular weights were calibrated against polystyrene standards. Differential scanning calorimetry (DSC) curves were taken on a PerkinElmer DSC Pyris-1 apparatus from 0 to 80°C at a heating rate of $10^\circ\text{C}/\text{min}$.

The intrinsic viscosity ($[\eta]$) of PCL was measured with an Ubbelohde viscometer at $30.0 \pm 0.1^\circ\text{C}$ with *N,N*-dimethylformamide (DMF) as a solvent. The corresponding viscosity-average molecular weight (M_v) was calculated according to the following equation: $[\eta] = 1.94 \times 10^{-4} M_v^{0.73}$.¹⁸

RESULTS AND DISCUSSION

Polymerization features

$\text{Sm}(\text{PPh}_2)_2$ was prepared readily in a high yield as a dark green powder from the reaction of SmI_2 with 2 equiv of KPPH_2 in THF. The washing of the powder product with THF gave the pure solvated adduct $\text{Sm}(\text{PPh}_2)_2(\text{THF})_4$. In our previous report, both $\text{Sm}(\text{II})$ complexes [SmI_2 and $\text{Sm}(\text{PPh}_2)_2$] were examined to compare their relative activity for the ROP of CL.¹⁵ Just as reported by Evans and Katsumata,¹⁹ SmI_2 showed no reactivity for the polymerization at the ambient temperature over 6 h. However, polymerization occurred in THF at the reflux temperature or, in the case of a low monomer/ Sm ratio, with a longer reaction period.²⁰ On the other hand, we found that $\text{Sm}(\text{PPh}_2)_2$ could initiate the ROP of CL effectively at room temperature, giving polyesters with a higher molecular weight.

Table I summarizes the results of the bulk polymerization of CL by $\text{Sm}(\text{PPh}_2)_2$. The monomer/ Sm relationship is directly related to the molecular weights of the resultant polymers. There was an increase in both the number-average molecular weight (M_n) and the polydispersity index as the ratio increased from 600 to 1200 (samples 1–4, Table I). With a further increase in this ratio (samples 5 and 6, Table I), the polymer yield, M_n , and the weight-average molecular weight/number-average molecular weight ratio (M_w/M_n) dropped. The observed molecular weights were not in accordance with the initial monomer/ Sm ratio, and this may be ascribed to transesterification reactions or coordinative competition between the active polymer chain end and monomer.^{20,21}

With the other parameters fixed, the effect of the initial monomer concentration ($[\text{CL}]_0$) on the polymerization is shown in Table II. The data indicate that the catalytic activity and molecular weight of the polyesters have nearly the same dependence on $[\text{CL}]_0$. An increase in the concentration of the monomer first caused an increase in the yield and M_v (see samples

TABLE II
Effect of the Initial Monomer Concentration
on the Polymerization^a

No.	$[\text{CL}]_0$ (mol/L)	Yield (%)	M_v (10^4)
1	1.2	31.5	2.47
2	1.6	60.8	2.66
3	2.0	75.9	3.86
4	2.5	96.0	4.58
5	2.8	90.5	4.20
6	3.3	92.2	5.21
7	4.9	91.2	4.42
8	6.6	92.9	4.58

^a $[\text{CL}]_0/[\text{Sm}(\text{PPh}_2)_2] = 1000$. The other conditions were the same as those listed in Table I.

TABLE III
Effect of Reaction Temperature on the Polymerization^a

No.	Temperature (°C)	CL/Sm (molar ratio)	Yield (%)	M_v (10^4)
1	50	1000	94.6	2.12
2	50	1000 ^b	98.1	1.79
3	30	1000	97.3	2.79
4	15	1000	100	8.28
5	15	800	100	7.43
6	15	1200 ^c	99	9.90
7	15	1000 ^b	100	4.37
8	4	1000	81.2	6.72
9	-20	1000	70.1	3.24

^a Sm(PPh₂)₂ 0.01 mmol; [CL]₀ = 2.50 mol/L; [CL]/[Sm] = 1000; THF, 1 h.

^b Polymerization time = 24 h.

^c Monomer addition was done in two batches: first batch = 8 mmol and second batch = 4 mmol; the total reaction time was 6 h.

1–4, Table II) but had little effect on either when [CL]₀ was greater than or equal to 2.5 mol/L.

As shown in Table III, the reaction temperature has a strong influence on the polymerization. A polymer with a high molecular weight could be obtained in a quantitative yield at 15°C. The deviation of this temperature seems not to be favorable for the formation of high-molecular-weight PCLs under these conditions.

In an attempt to check whether this polymerization system has a living character, a polymerization experiment was carried out by the addition of the monomer in two batches. The growing polymer chain was active for the further polymerization of the second batch of

the monomer (see sample 6, Table III). Not only was the yield of the prepared polymer quantitative after the completion of the polymerization of the second batch of the monomer, but an increase in the molecular weight also was obtained in comparison with sample 4 in Table III. However, we failed to synthesize the block copolymer incorporating CL and propylene oxide units into the chain backbone with this polymerization system. The reason for this is not yet clear.

The variations of the yield and M_v of PCL versus the reaction time are depicted in Figure 1, with CL/Sm = 1000 at 15°C. The rate of polymerization was very fast, and a yield of more than 90% was achieved within 20 min. Although a linear increase in the molecular weight was observed in the early reaction stage, an elongation of the reaction time resulted in a decrease in the molecular weights, especially for the polymerizations at higher temperatures (see samples 7 and 2 in Table III). This decrease in the molecular weight was probably due to transesterification reactions. Similar behavior was observed for the ROP of cyclic esters by other lanthanide catalysts.^{20,22}

FTIR spectroscopy was used to characterize the obtained PCL; the bands at 2945, 1723, and 1192 cm⁻¹ correspond to the stretching vibrations of —CH₂—, —CO—, and —COO— linkages, respectively.²³ A typical GPC pattern of PCL displayed a unimodal curve (Fig. 2) with a tail from the high-elution-volume side, corresponding to macromolecules with a low molecular weight. Figure 3 shows the DSC trace of PCL with M_v = 5.84 × 10⁴; the sample had a melting temperature (T_m) of 60.6°C and a crystallization temperature of 37.3°C.

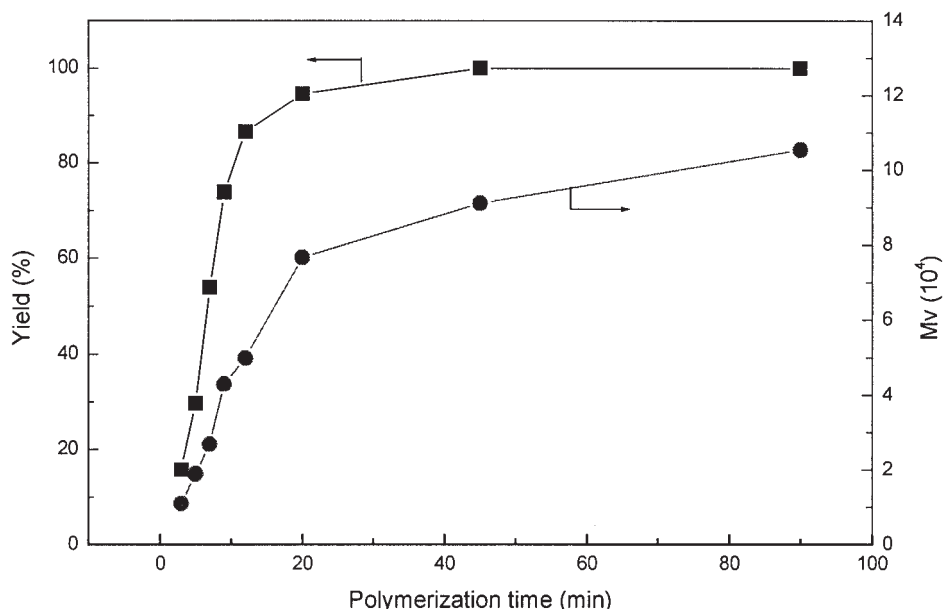


Figure 1 Plot of the PCL yield and M_v versus the reaction time. The polymerization was carried out in THF at 15°C ([CL]/Sm = 1000, [CL]₀ = 2.50 mol/L).

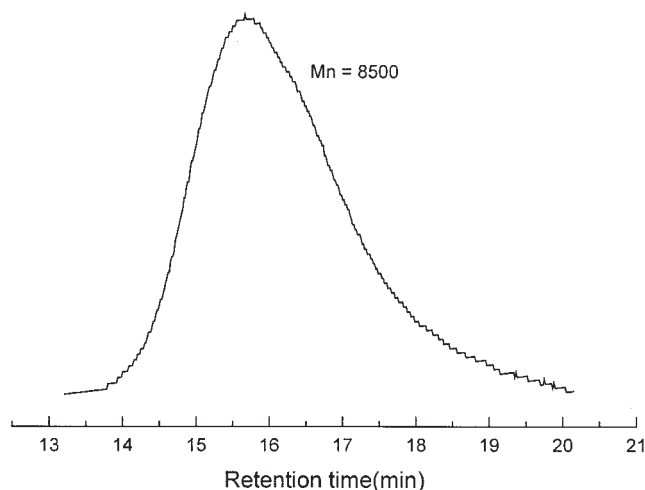


Figure 2 Typical GPC profile for PCL (see sample 1 in Table I).

Mechanistic aspects

The polymerization mechanism of lactones has been investigated for many years, and the coordination–insertion fashion is commonly accepted now.¹¹ A divalent samarium reagent has the characteristic of strong oxophilicity, besides its single-electron-transfer property. This oxophilicity should be favorable for the coordination of oxygen-containing monomers with active sites and hence for their polymerization. As a model for the initially formed samarium complex in the polymerization, Figure 4 shows the UV–vis spectra of a reaction mixture of $\text{Sm}(\text{PPh}_2)_2$ or SmI_2 with equiv-

alent CL along with corresponding $\text{Sm}(\text{II})$ complexes. The significant difference between the $\text{Sm}(\text{II})$ reagent and $\text{Sm}(\text{II})$ –CL mixture in the absorption fashion indicates the strong coordination interaction among these components, although it is difficult to give an exact explanation for this.

To explore the mechanisms for the formation of initiating species and chain growth, an end-group analysis has been carried out by an NMR technique. Figure 5 presents the ^1H -NMR spectrum of a low-molecular-weight PCL sample quenched with ethanol. The peaks at 4.06, 2.32, 1.65, and 1.38 ppm are assigned to the methylene protons (a, b, c + d, and e) of the PCL repeat unit. The triplet at 1.32 ppm (h) and the quartet around 4.23 (g) are attributed to the ethoxy end group. Obviously, the ethoxy groups in these polymers were derived from the acylation of the quenching reagent (i.e., ethanol). This suggests the presence of an electrophilic acyl end group in the original polymer chains, just as discussed by Nishiura et al.^{14(e)} Also observed is multiple absorption in the range of 3.60–3.70 ppm, which is a superposition of a triple and a singlet. Apparently, the triple signal at 3.65 ppm corresponds to the methylene protons adjacent to the hydroxyl group at the terminating chain end (f), whereas the singlet peak (marked with an asterisk in Fig. 5) is due to a $\text{CH}_3\text{O}-\text{CO}-$ end group, which is probably from the reaction with methanol used for the crystallization of the polymer sample.

On the basis of this observation, we propose that CL polymerization with $\text{Sm}(\text{PPh}_2)_2$ takes place according to a coordination–insertion mechanism, as shown in

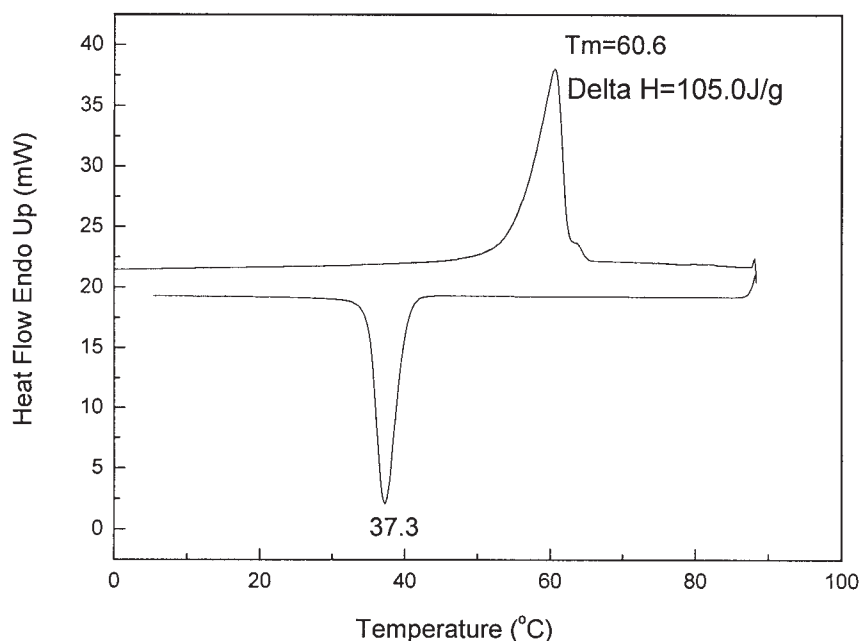


Figure 3 DSC trace of PCL with $M_n = 5.84 \times 10^4$ at a heating rate of $10^\circ\text{C}/\text{min}$.

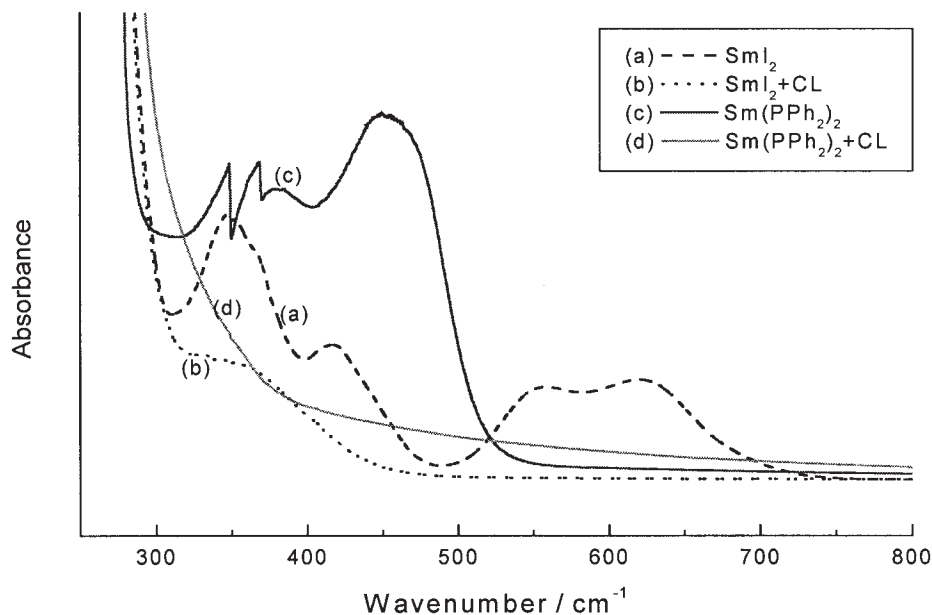


Figure 4 UV-vis spectra of the reaction mixture of $\text{Sm}(\text{PPh}_2)_2$ or SmI_2 with equivalent CL along with corresponding $\text{Sm}(\text{II})$ complexes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 1. In the initiation step, there are two probable ring-opening ways for the $\text{Sm}\text{--}\text{CL}$ complex: acyl-oxygen cleavage (mode a) and alkyl-oxygen cleavage (mode b). The two ways, accompanied by an intramolecular nucleophilic attack of a phosphido group, produce initiating species **1** and **2**, respectively. Meanwhile, the initiation reaction may involve a redox pro-

cess of samarium species. In the chain propagation step, **1** reacts with another molecule of lactone via acyl-oxygen cleavage and chain growth through acyl-oxygen cleavage, yielding product **A**. When the polymerization is quenched by alcohols, the end group $\text{--}\text{COPPh}_2$ in **A** is changed to an ester group, and the active-site $\text{Sm}\text{--}\text{O}$ bond leads to hydrolysis, giving

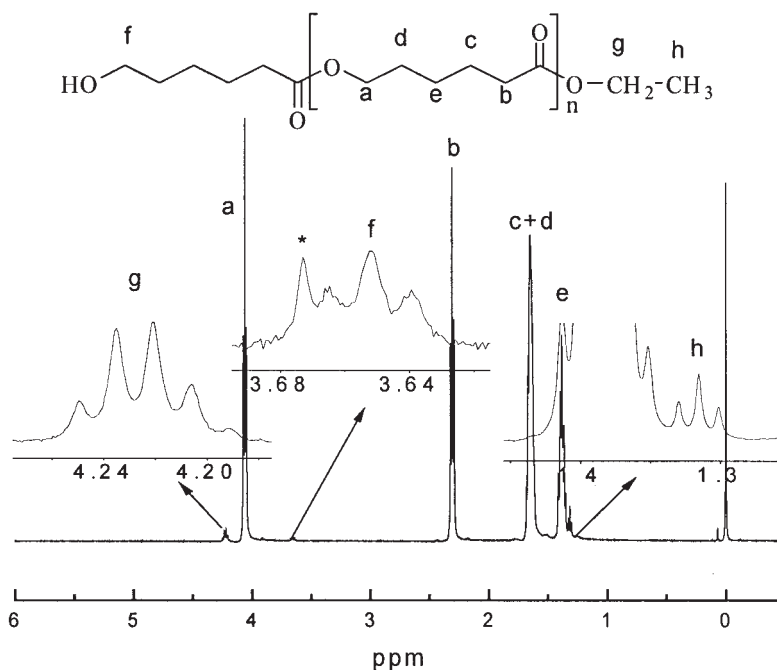
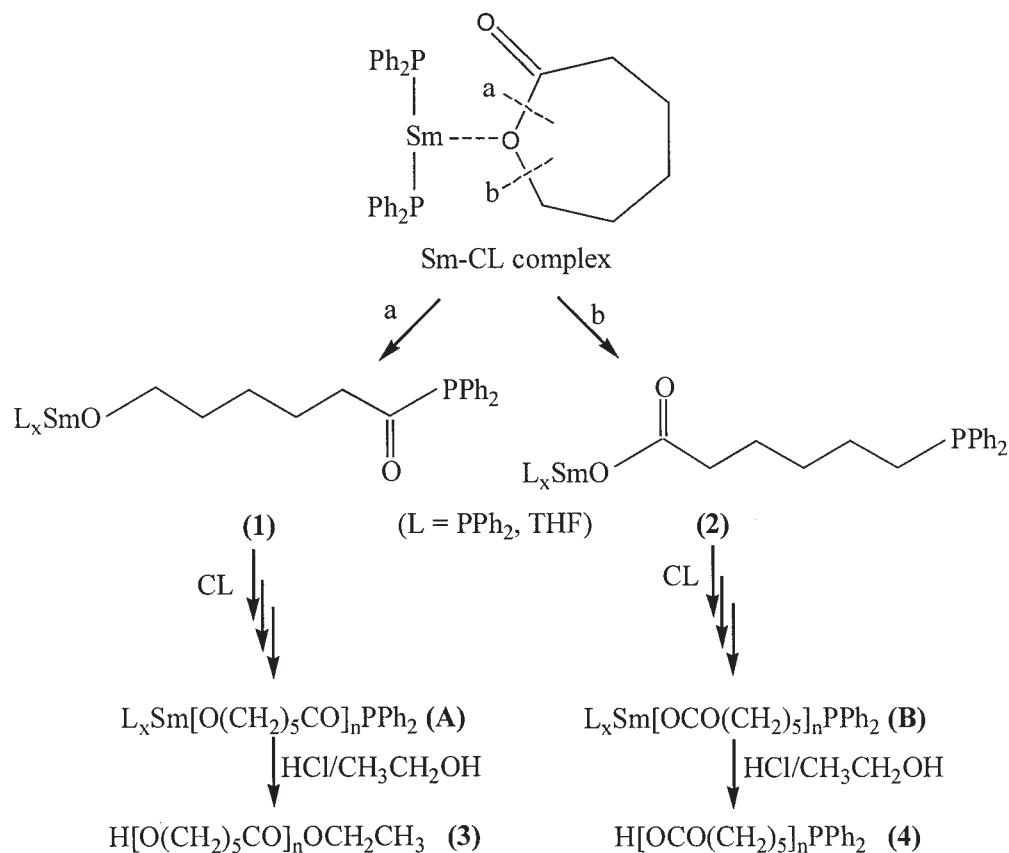


Figure 5 ^1H -NMR spectrum of a low-molecular-weight PCL sample obtained with $\text{Sm}(\text{PPh}_2)_2$ as an initiator and quenching with ethanol ($M_{n,\text{GPC}} = 2500$, $M_w/M_n = 1.46$; $M_{n,\text{NMR}} = 2100$, as estimated from the relative area ratio of peak b to peak f).



Scheme 1 Proposed mechanism for the ROP of CL initiated by Sm(PPh₂)₂.

—CH₂OH. On the other hand, if the polymerization proceeds via **2** in an alkyl–oxygen cleavage mode, the end group —PPh₂ should be detected by NMR spectroscopy in the low-molecular-weight PCL (**4**) because of its relative stability. Mode b has been observed in the polymerization of CL by metal halides such as ZnCl₂, in which a chlorine atom is transferred to carbon in the epsilon position.²⁴ However, there is no evidence from NMR analysis supporting mode b for this polymerization system. Consequently, it may be concluded that the Sm(PPh₂)₂-initiated ROP of CL follows a coordination–insertion mechanism proceeding via acyl–oxygen cleavage of the monomer with insertion into the metal–oxygen bond of the propagating species.

CONCLUSIONS

The easily available samarium bis(phosphido) complex Sm(PPh₂)₂ is an effective initiator for the ROP of CL. This Sm(II)-based polymerization system allows the molecular weights of polyesters to be modulated by reaction parameters such as the monomer/initiator molar ratio, reaction temperature, and polymerization time. On the basis of the end-group analysis of low-molecular-weight polymer samples, the ROP of CL

proceeds most likely by a coordination–insertion mechanism.

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