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Novel $Sm(PPh_2)_2$ initiator for the synthesis of poly(ε-caprolactone) with linear and star-shaped structures §

Lina Xu[1], Liming Jiang (✉)[1], Weilin Sun[1], Zhiquan Shen[1], Shengming Ma[2]

[1] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P.R.China
[2] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P.R.China
e-mail: lmjiang@mail.hz.zj.cn, Tel: 86-571-87951059, Fax: 86-571-87951773

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Summary

Divalent samarium bis(phosphido) complex $Sm(PPh_2)_2$ was first applied as an initiator for the ring-opening polymerization of ε-caprolactone (ε-CL). In comparison to samarium diiodide (SmI_2), this Sm(II) complex exhibited much higher activity and yielded poly(ε-CL) with higher molecular weight. At the same time, an in-situ generated tetrafunctional samarium enolate from the reduction of 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane with $Sm(PPh_2)_2$ or SmI_2 has proven to initiate the polymerization of ε-CL under mild conditions. The resulting linear and star-shaped poly(ε-CL)s have been characterized by ^1H NMR, GPC, and SLS.

Introduction

Aliphatic polyesters with high molecular weight and/or star-shaped structure are of great interest as biodegradable and biocompatible materials [1-3]. Ring-opening polymerization (ROP) of lactones provides a convenient and efficient route to prepare these polymers. Initiators such as aluminum porphyrins, alkylaluminum alkoxides, tin(2-ethyl-hexanoate), and transition metal complexes have been developed for the ring-opening polymerization of lactones [4-7]. On the other hand, rare earth metal complexes have attracted increasing attention due to their excellent catalytic performance in the ROP of cyclic esters [8-11].

In recent years, our group has been worked on the rare earth-based catalysts for ring-opening polymerization of lactones and lactides. These catalyst systems showed high activity and initiated the polymerization in a living fashion in some cases [12-14]. Advantage of these catalysts over lanthanide metallocene complexes is that they are easily available and relatively stable. In the course of developing new rare-earth catalysts for the ROP of cyclic esters, our interest in readily accessible samarium(II) compounds stems not only from their single-electron-transfer property, but also from the oxophilicity of the central metal. This oxophilicity should be favorable to the coordination of oxygen-containing monomers with active sites and hence their ring-opening polymerization. Especially for $Sm(PPh_2)_2$, its structural characteristic due to containing "soft" phosphido ligands would be anticipated to have particular properties

different from that of the corresponding complexes with “hard” nitrogen and oxygen ligands. To the best of our knowledge, there were few studies on the catalytic activity of this species except for its synthesis and structural characterization described in the literature [15].

This paper reports the preliminary results on ring-opening polymerization of ε-caprolactone initiated with the new complex $Sm(PPh_2)_2$ and the samarium enolate *in situ* formed by the reduction of tetrafunctional 2-bromoisobutyric ester. Resulting linear and tetra-armed poly(ε-caprolactone)s are characterized by ^{1}H NMR , GPC, and SLS. The initiation mechanism of polymerization is also discussed briefly.

Experimental

Materials: ε-Caprolactone obtained commercially was dried over calcium dihydride and fractionally distilled under reduced nitrogen pressure. Tetrahydrofuran (THF) was dried over a benzophenone-sodium complex for 3 days and distilled prior to use. Pentaerythritol (chemical grade) was used after recrystallization from ethanol. A 0.1M THF solution of SmI_2 was prepared according to the reference [16]. $Sm(PPh_2)_2$ was synthesized as a dark green powder by the reaction of SmI_2 with 2 equiv of $KPPh_2$ (ACROS) in THF according to the previous report [15].

Measurements: ^{1}H NMR spectra were recorded on a Bruker Avance AMX-500 NMR instrument in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. A Bruker Vector 22 Fourier Transform Infrared (FT-IR) spectrometer was used for recording spectra in KBr pellets or films. The molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) using a Waters 208 GPC apparatus (THF as eluent at a flow rate of 1.0 ml/ min). The GPC chromatogram was calibrated against standard polystyrene samples. Static light scattering (SLS) measurements were conducted in THF at 30°C on an 18-angular DAWN DSP laser photometer with a He-Ne laser (633 nm) as the light source.

Preparation of 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane. A dichloromethane (5ml) solution of 2-bromoisobutyryl bromide (2.52 ml, 20.4 mmol) was added into dichloromethane solution of pentaerythritol (0.681g, 5.0 mmol) and pyridine (0.4 ml) at 0°C. The resulting mixture was stirred for 8 hours at room temperature, then washed with 1M HCl, saturated solution of $NaHCO_3$ and brine in order. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by recrystallization 2 times from absolute ethanol. Yield 1.937g (63.3%). mp:124.5-125.5°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.92 ppm (-C(C**H**$_3$)$_2$Br,s, 24H), δ 4.33 ppm (-C**H**$_2$OCO-,s, 8H). IR (neat): 3006, 2980, 2866, 1739, 1476.0, 1495.4, 1393.4, 1372.2, 1272.8, 1166.5, 1103.9, 1012.4, 983.5, 934.9 and 646.2 cm^{-1}.

Synthesis of linear poly(ε-caprolactone): The polymerization was carried out using Schlenk techniques in a dry nitrogen atmosphere. The given amount of ε-CL was introduced by a syringe into Schlenk tubes contained a THF solution of $Sm(PPh_2)_2$ (0.1 mmol; ε-CL/Sm=300-1000 in molar ratio) with vigorous stirring. The dark green color of $Sm(PPh_2)_2$ solution disappeared immediately and the viscosity of the mixture increased as the reaction proceeding. After a certain time, the polymerization was terminated with methanol containing a small amount of HCl. The product was then dissolved in CH_2Cl_2 and recovered by precipitation in excess methanol. Finally, the purified polymers were dried under vacuum at 30°C for 48 h.

Synthesis of star-shaped poly(ε -caprolactone): In a typical process, a solution of $Sm(PPh_2)_2$ or SmI_2 (0.48 mmol in 4.43ml THF) was added into a dried Schlenk tube containing 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane (0.029g, 0.043 mmol) at ambient temperature. After 2 h (15 minutes for SmI_2), the given amount of ε -caprolactone was injected into the resulting suspension and then the mixture was stirred at room temperature for a certain time. The treatment for polymeric products was the same as the procedure described above. A bulk polymerization was performed analogously, but the solvent of the resulting samarium enolate solution was evaporated under a reduced pressure prior to introducing monomer.

Results and discussion

The ring-opening polymerization of ε -CL with $Sm(PPh_2)_2$ was carried out in THF solution or bulk at different monomer/initiator ratios and the results are summarized in Table 1. For comparison, SmI_2 was also examined as an initiator for the polymerization and gave the observation similar to that reported by Evans et al [17]. It can be seen that $Sm(PPh_2)_2$ was an effective initiator for the ring-opening polymerization of ε -caprolactone. The variation of monomer/initiator ratio from 300 to 800 greatly influenced the molecular weight and polydispersity index (PDI) of polymer while a nearly quantitative yield remained. The observed molecular weights were not in accordance with the initial monomer/initiator ratio. This may be ascribed to transesterification reactions or coordinative competition between active polymer chain end and monomer [18]. Both yield and molecular weight of polymers increased with the elongation of reaction time at $[\varepsilon\text{-CL}]_0/[Sm]_0=1000$. GPC pattern of poly(ε -CL)s obtained by $Sm(PPh_2)_2$ displayed a unimodal curve, which means the presence of a single propagation species. Under adequate conditions, the $Sm(PPh_2)_2$ initiating polymerization proceeded steadily and gave the polymer with a relative narrower molecular distribution (No.6, Table 1).The results suggest that the samarium complex

Table 1. Polymerization of ε -caprolactone initiated with $Sm(PPh_2)_2$ or SmI_2 in THF or bulk [a]

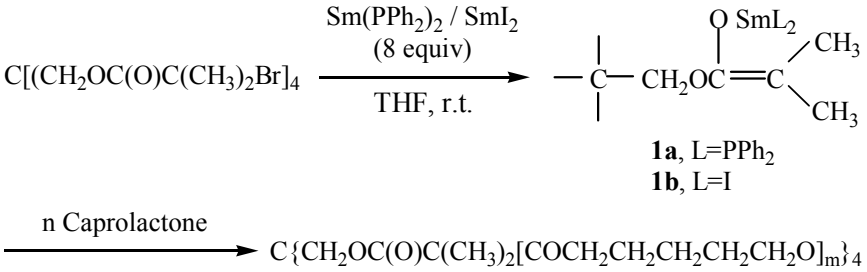
No	Samarium Complex	$[M]_0/[I]_0$	$[M]_0$ (mol/L)	Time (min)	Temp (°C)	Conv (%)	$\overline{Mw}$ [b]	PDI [b]
1	$Sm(PPh_2)_2$	300	2.5	5	20	95.7	12000	2.10
2	$Sm(PPh_2)_2$	500	2.5	5	20	94.2	23300	2.55
3	$Sm(PPh_2)_2$	800	2.5	5	20	89.9	33100	2.71
4	$Sm(PPh_2)_2$	1000	3.0	5	20	74.8	31300	2.50
5	$Sm(PPh_2)_2$	1000	3.0	30	20	85.8	45800	1.57
6	$Sm(PPh_2)_2$	1000	3.0	45	20	93.3	57400	1.42
7	$Sm(PPh_2)_2$	1000	bulk	30	20	92.2	20600	2.00
8	SmI_2	100	3.0	360	r.t.	0	--	--
9	SmI_2	100	3.0	360	reflux	84.7	3200	1.81

[a] $Sm(PPh_2)_2$ (0.071 mmol) or SmI_2 (0.1 mmol), THF

[b] Polydispersity index (PDI) was determined by GPC analysis

containing bulky groups effectively stabilized the propagating species through coordination, which prevented the propagating species from the possible side reactions to a certain extent. It should be noted that $Sm(PPh_2)_2$ has high solubility in THF and ε-CL. Thus, the bulk polymerization could be carried out smoothly giving the polymer with PDI of around 2.0 in a good yield (No.7, Table 1).

Endo et al have recently reported that samarium enolates, which are formed *in situ* by the reduction of 2-bromoisobutyric esters with SmI_2, can initiate the living polymerization of MMA in the presence of diethylpivalamide at -78℃[19,20]. In the present work, we examined the capability of $Sm(PPh_2)_2$ and SmI_2 to form a multifunctional samarium enolate for initiating the polymerization of ε-CL. We designed and synthesized 1,1,1,1-tetra(2-bromoisobutyryloxymethyl)methane as a precursor of the tetrafunctional samarium enolate (Scheme 1).



Scheme 1

As described in the Experimental, the characteristic color of divalent samarium reagents faded with the reaction between 2-bromoisobutyric ester and $Sm(PPh_2)_2$ or SmI_2 proceeded and a suspension was obtained simultaneously.

Table 2. Polymerization of ε-CL initiated with *in-situ* generated tetrafunctional samarium enolates **1a** and **1b** at room temperature in THF or bulk [a]

No	Samarium Complex	$[M]_0/[\mathbf{1}]_0$	$[M]_0$ mol/L	Time (min)	Conv (%)	$\overline{Mw}$ [b]	PDI [b]
1	SmI_2	1000	3.10	85	100	28800	3.00
2	SmI_2	1000	3.16	120	100	25200	2.64
3	SmI_2	1000	2.24	120	100	36700	1.86
4	$Sm(PPh_2)_2$	1000	3.31	120	56.6	44200	1.24
5	$Sm(PPh_2)_2$	1000	bulk	120	100	70600	1.52
6	$Sm(PPh_2)_2$	1300	bulk	120	95.9	162800	1.79
7	$Sm(PPh_2)_2$	1600	bulk	120	96.9	244800	1.65
8	SmI_2	1000	bulk	120	100	27800	1.25

[a] $Sm(PPh_2)_2$ (0.071 mmol) or SmI_2 (0.1 mmol), THF

[b] Determined by GPC analysis

caprolactone, the reaction mixture became homogeneous and the solution viscosity increased apparently. Table 2 shows the data of ε-caprolactone polymerization with

in situ generated tetrafunctional samarium enolates. It can be seen that a complete monomer convers After addition of ε- ion was achieved within 2 h for the solution polymerization with SmI_2-forming samarium enolate (**1b**) (Scheme 1). In comparison to **1b**, the rate of solution polymerization was found to be slower (56.6% yield in 2 h) with the $Sm(PPh_2)_2$-forming enolate (**1a**) and gave PCL of quite low PDI (No 4, Tab.2). On the other hand, in the case of **1a** initiating bulk polymerization the molecular weight increased with an increase in the ratio of monomer to samarium enolate and reached $\overline{M}w$ of 24×10^4 at $[\varepsilon\text{-CL}]_0/[Sm]_0$ of 1600. For **1b** system, resulted poly(ε -CL) has relatively low molecular weight and narrower molecular weight distribution. However, the nature of GPC traces exhibited unimodal for polymers obtained by both samarium enolates in solution or bulk polymerization (Tab.2 and Fig.1).

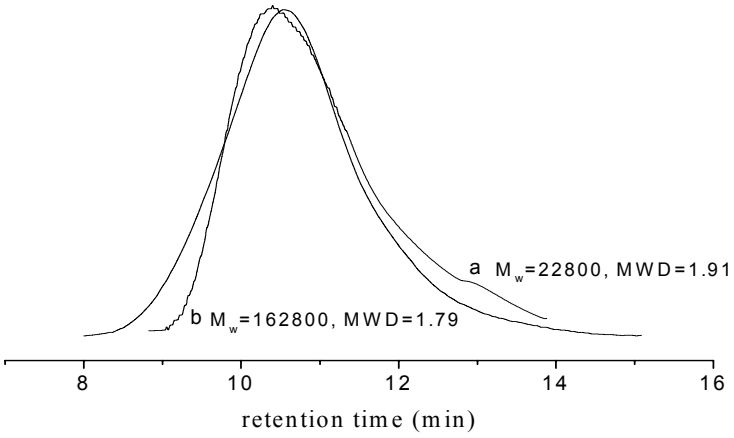


Figure 1. GPC curves of (a) linear poly(ε-CL) prepared with $Sm(PPh_2)_2$ and (b) four-armed poly(ε-CL) prepared with $Sm(PPh_2)_2$-forming samarium enolate (**1a**)

In order to identify the star-shaped structure of poly(ε-caprolactone), an oligomer was prepared at low molar ratio of monomer to samarium enolates for spectrum analysis. The ^{1}H NMR spectra of the four-armed and linear poly(ε -CL)s are given in Figure 2. It is apparent that both polymers exhibit the same absorption and signal characteristics of the polymer [21]. The peak at 1.93 ppm assigned to the methyl groups of the tetraisobutyryloxymethylmethane moieties indicates that the initiating species incorporated into the main chain (Fig.2A). However, the C**H**$_2$ absorption of the core unit is not clearly observed, which may be merged with that of impurities at about 4.30 ppm (h, Fig.2). Further evidence in support of the star-shaped structure comes from the comparison of molecular weights determined by GPC and SLS. Based on the results of GPC, two typical samples were selected for light-scattering tests. Their weight-average molecular weights ($\overline{M}_{w,GPC}$) were 46400 (retention time, R_t=16.242 min) and 49500 (R_t=16.158 min) for linear and star-shaped polymer respectively, which means that both samples have similar hydrodynamic volumes. From SLS measurements, the molecular weight ($\overline{M}_{w,SLS}$) of linear polymer was 17500, while the star-shaped polymer had $\overline{M}_{w,SLS}$ of 54500. On the basis of above

observations, it is reasonable to conclude that the tetrafuctional samarium enolate yielded the anticipated poly(ε -CL) with star-shaped structure. In addition, it must be noted that a triplet signal at 3.63 ppm (g, Fig.2) in ^{1}H NMR spectra is usually ascribed to the methylene protons adjacent to the hydroxyl group at the terminating chain-end [21]. The presence of CH_2OH end-groups indicates either linear or star-shaped polymerization proceeded with an alkoxide propagating species. Consequently, it can be assumed that the initiation of polymerization with $Sm(PPh_2)_2$ or *in situ* generated samarium enolates by ring cleavage at the O-acyl bond as shown in Scheme 1.

In conclusion, we have described the ring-opening polymerization of ε -caprolactone initiated with a novel divalent samarium complex $Sm(PPh_2)_2$ and *in situ* formed tetrafunctional samarium enolates. These catalysts are promising for synthesis of aliphatic polyesters with high molecular weight and/or star-shaped structure.

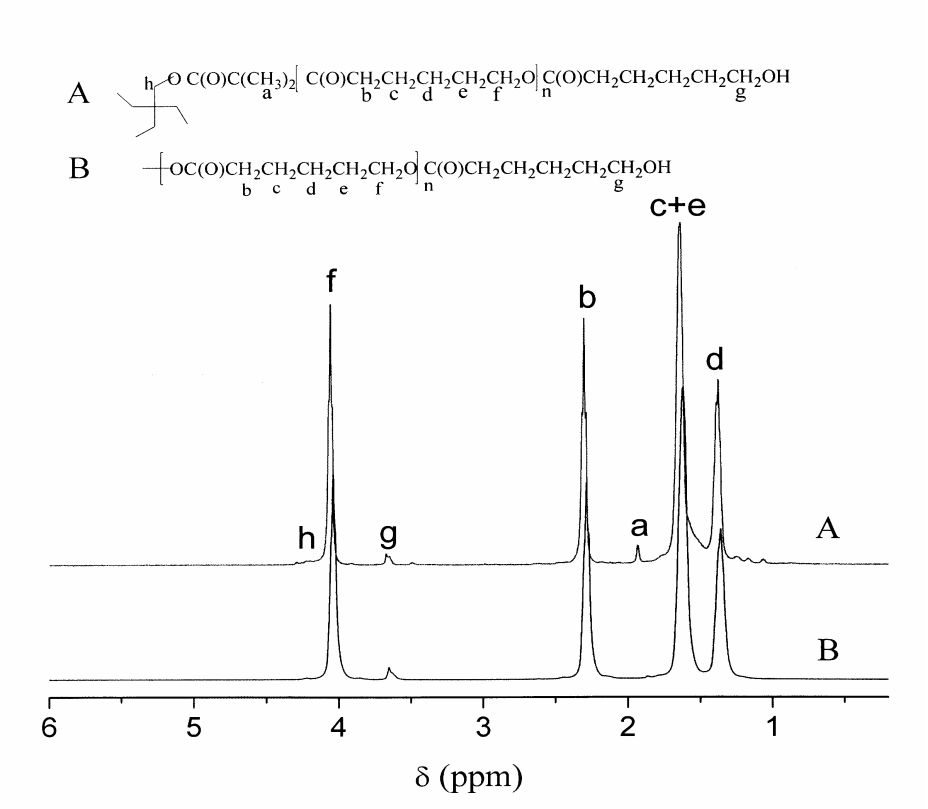


Figure 2. ^{1}H NMR spectra: (A) four-armed poly(ε-CL) prepared with **1a**; (B) linear poly(ε-CL) prepared with $Sm(PPh_2)_2$ in THF

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References:

1. Dubois Ph, Jacobs C, Jerome R, Teyssie Ph (1991) Macromolecules 24:2266
2. Nijenhuis A J, Grijpma D W, Pennings A J (1992) Macromolecules 25:6419
3. Duda A, Penczek S (1990) Macromolecules 23:1636
4. Isoda M, Sugimoto H, Aida T, Inoue S (1997) Macromolecules 30:57
5. Duda A, Penczek S (1994) Macromol.Rapid Commun.15:559
6. Kricheldorf H R, Keiser-Saunders I, Boettcher C (1995) Polymer 36:1253
7. Nomura, R ; Endo, T. (1995) Macromolecules 28:1754
8. Okuda J, Rushkin I L (1993) Macromolecules 26:5530
9. Endo M, Aida T, Inoue A (1987) Macromolecules 20:2982
10. Mclain S J, Drysdale N E (1992) Polym. Prepr. 33:174,463
11. Yasuda H, Ihara E (1997) Adv.Polym.Sci. 53:133
12. Shen Z Q, Shen Y Q (1995) Polym. J. 27:59
13. Shen Y Q, Shen Z Q, Zhang Y F, Yao K M (1996) Macromolecules 29:8289
14. Shen Y Q, Shen Z Q, Zhang Y F (1996) Macromolecules 29:3441
15. Rabe G W, Yap G P A, Rheingold A L (1995) Inorg. Chem. 34:4521
16. Girard P, Namy J L,Kagan H B (1980) J.Am.Chem.Soc. 102:2693
17. Evans W J, Katsumoto H (1994) Macromolecules 27:2330
18. Agarwal S, Brandukova-Szmikowski NE, Greiner A (1999) Macromol.Rapid Commun.20: 274
19. Narita M, Nomura R, Endo T(1998) Macromolecules 31:2774
20. Narita M, Nomura R, Tomita I, Endo T (2000) Polym. Bull. 45:231
21. Zhong Z Y, Ankoné M J K, Dijkstra P J, Birg C, Westerhausen M, Feijen Jan (2001) Polym. Bull. 46:51