Ring-Opening Polymerization of ϵ-Caprolactone by Benzylalkoxybis(2,4,6-triisopropylphenyl)tin Compounds: Observation of the Insertion Product into the Sn−OMe Bond

Daniela Pappalardo,*,† Liana Annunziata,‡ Claudio Pellecchia,‡ Monique Biesemans,§ and Rudolph Willem§

Dipartimento di Studi Geologici ed Ambientali, Università del Sannio, Via Port'Arsa, I-82100, Benevento, Italy; Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, I-84084 Fisciano (SA), Italy; and High Resolution NMR Centre, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium

Received October 12, 2006; Revised Manuscript Received January 10, 2007

ABSTRACT: Benzylmethoxybis(2,4,6-triisopropylphenyl)tin **(1)** and benzylisopropoxybis(2,4,6-triisopropylphenyl)tin **(2)** were synthesized and characterized. Compound **1** exhibited good activity in the ring-opening polymerization of ϵ-caprolactone, in a *living* fashion, under mild conditions. The polymerization was demonstrated to proceed via ring-opening of the monomer at the acyl−oxygen bond. The ϵ-caprolactone insertion product into the Sn−OCH_3 of the initiator was characterized, providing support for a "coordination−insertion" mechanism.

Introduction

The polymerization of cyclic esters is a convenient method for the synthesis of biodegradable and biocompatible polyesters, which have many applications in various areas such as agriculture and medicine.[1] Polycaprolactone (PCL) is one of the most promising synthetic polymers prone to degradation in aqueous medium or by microorganisms, and therefore it can been used to make polymeric devices.[2]

Various species including alkoxide and alkyl complexes of aluminum,[3] tin,[4,5] lanthanides,[6] and transition metals[7] have been used as initiators for the ring-opening polymerization (ROP) of ϵ-caprolactone, some having the ability to initiate a living polymerization. Current interest has been devoted to the design of well-defined ROP initiators, with the aim to control the molecular weight and the polymer microstructure, enhance the catalytic activity, and limit deleterious transesterification reactions. Single-site catalysts can be represented by the general formula L_nMX, where M is the active center, X is the initiating group, generally an alkoxide, and L_n are ancillary ligands not directly involved in the polymerization but able to tune the properties of the metallic center and minimize the aggregation processes and side reactions.

In principle, the process is believed to occur via a coordination−insertion mechanism, whereby the initiation proceeds by insertion of a monomer unit into the metal−alkoxide bond with cleavage of the acyl−oxygen bond of the monomer. As already pointed out, despite the huge amount of catalytic systems for cyclic esters polymerization, there is a paucity of structurally authenticated intermediate species.[8,9] To our knowledge, only for cyclic diesters a few examples have been reported as direct evidence of the coordination−insertion mechanism, i.e., the ^{1}H NMR characterization of the insertion product of D-lactide into the Al−OCH_3 bond of a porphyrin supported initiator[8] and the X-ray crystal structure of the intermediate formed by insertion of lactide into the Al−alkoxide bond of an organometallic initiator.[9] Theoretical works further support the mechanism for the ROP of cyclic diesters in the presence of a stannous 2-ethylhexanoate-based system.[10]

Interestingly, the product formed by the reaction of two ring-opened β-butyrolactones and a hexameric alumoxane has been structurally characterized.[11]

Several studies have also been devoted to the elucidation of the polymerization mechanism of ϵ-caprolactone.[5,12−14] The crystal structures of rare earth metal complexes with ϵ-caprolactone[12,13] and of a methylaluminium(bisphenoxide)−ϵ-caprolactone complex[14] have been reported; the latter compound formed an efficient catalytic system only upon addition of dry air. NMR studies of model reactions between a chelating diamide aluminum initiator and ϵ-caprolactone showed that the initiation involves monomer insertion into the Al−N bond.[15] For tin-containing initiators, NMR analysis of the polymer end groups has been so far the only *indirect* proof to support the coordination−insertion mechanism.[16]

We recently reported the synthesis of tin(IV) compounds of general formula Tip_2SnR_2 (Tip = 2,4,6-triisopropylbenzene; R = alkyl, halogen) and studied their reactivity toward ionizing agents and toward 1,4-butadiene, propylene oxide, and ϵ-caprolactone.[17] The obtained cationic species were able to act as initiator in the ROP of ϵ-caprolactone. In order to establish whether a "coordination−insertion" mechanism could be active in this kind of system, we substituted an alkyl group for an alkoxy group and studied the reactivity of the compounds in the ϵ-caprolactone ring-opening polymerization. The results of these studies are presented herein. Advanced NMR analysis of the polymer end groups and the characterization of the monomer insertion product into the Sn−OMe bond both converge to the conclusion that the polymerization mechanism is a polyinsertion proceeding via acyl−oxygen bond cleavage of the monomer.

Results and Discussion

Synthesis of the Complexes. The novel compounds benzylmethoxybis(2,4,6-triisopropylphenyl)tin **(1)** and benzylisopropoxybis(2,4,6-triisopropylphenyl)tin **(2)** were synthesized by reaction of benzylbromobis(2,4,6-triisopropylphenyl)tin[17] re-

* Corresponding author. E-mail: pappalardo@unisannio.it.
† Università del Sannio.
‡ Università di Salerno.
§ Vrije Universiteit Brussel.

10.1021/ma0623486 CCC: $37.00
Published on Web 02/20/2007

Table 1. Polymerization of ϵ-Caprolactone (CL) by Compound 1

run[a]	time [h]	yield [g]	conv [%]	M_w[b]	M_w/M_n[b]	$M_{n,NMR}$[c]
I	3	0.050	6.1	4 756	1.1	4 467
II	12	0.312	37.9	10 984	1.2	9 721
III	18	0.400	48.5	18 341	1.3	14 965
IV	24	0.710	86.2	27 377	1.4	19 753

[a] Polymerization conditions: compound **1** = 60 μmol; toluene = 10 mL; CL = 0.8 mL; temperature = 75 °C. [b] Determined by gel permeation chromatography (GPC); M_w = weight-average molecular weight, M_n = number-average molecular weight, M_w/M_n = molecular weight distribution. [c] Determined by ^{1}H NMR $M_{n,NMR} = [(1 + (I_{CH_2OCO}/I_{CH_2OH}))M_{wCL}] + M_{wOCH_3}$.

spectively with sodium methoxide and sodium isoproproxide in tetrahydrofuran (THF) solution with good yield. The compounds were fully characterized by 1D ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy in solution and mass spectroscopy (see Experimental Section).

Compound **1** is very stable as a solid in an inert atmosphere but easily undergoes hydrolysis in solution in the presence of adventitious water to give the species $Tip_2BzSnOH$. The latter species was characterized by NMR and IR analysis (see Experimental Section).

Polymerization of ϵ-Caprolactone. Living Character. The reactivity of compounds **1** and **2** in the ring-opening polymerization of ϵ-caprolactone was studied. Polymerization screening was performed under a nitrogen atmosphere by dissolving the proper amount of the initiator in a solution of the selected amount of ϵ-caprolactone in dry toluene.

Compound **2** was inactive as an initiator for ϵ-caprolactone even at high temperature (110 °C). Probably the bulky isopropyl aryl substituents and the bulky isopropoxy group prevent the coordination of the monomer to the metal center.

The main results of the polymerization studies using compound **1** as the initiator are summarized in Table 1. Compound **1** appeared poorly active at room temperature, but the activity increases upon temperature increase, affording almost complete monomer conversion in 24 h at 75 °C (dry toluene; 1:120 tin: monomer molar ratio). The polymers, precipitated from the reaction solution by addition of hexane, were analyzed by gel permeation chromatography (GPC) and by NMR ($CDCl_3$). The number of monomer units in the polymers was also assessed by ^{1}H NMR analysis from the ratio between the methylene resonance areas of the repeating units (ϵ) at 4.04 ppm and those of the end group units $-CH_2CH_2OH$ (ϵ′) at 3.62 ppm (Figure 1). The M_n evaluated by NMR and the M_n measured by GPC agreed well (see Table 1). The obtained PCL showed always narrow molecular weight distributions ($M_w/M_n = 1.1-1.4$). The molecular weight distribution is kept narrow until almost complete monomer conversion and only broadens for longer reaction times, when transesterification reactions become significant. Such a behavior is compatible with the presence of a highly selective active species. Consistently, polymerization screenings performed at 75 °C displayed a linear correlation between the polymer molecular weight and the conversion, evidencing the "living" character of the polymerization (Figure 2).

Mechanism of Ring-Opening of the Monomer. Nature of the End Groups. As generally assumed,[16] the first step of ϵ-caprolactone ROP "coordination−insertion" mechanism is the formation of a coordination complex between the cyclic ester and the initiator, through the interaction of the carbonyl group of the monomer with the metal. The second step is the insertion of the monomer into the metal−(initiating group) bond with selective cleavage of the acyl−oxygen bond of the monomer.

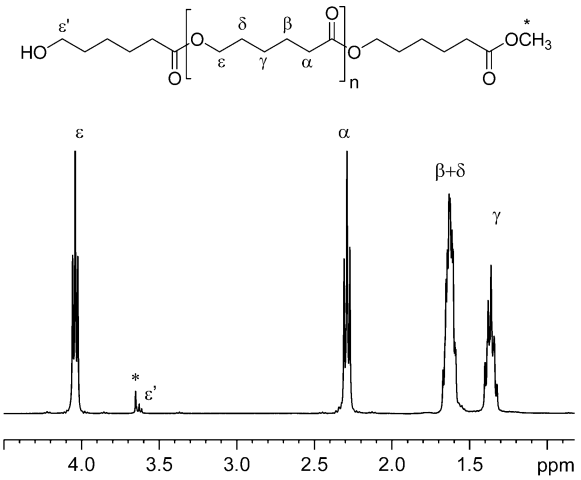


Figure 1. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of polycaprolactone sample obtained using compound **1** (Table 1, run II).

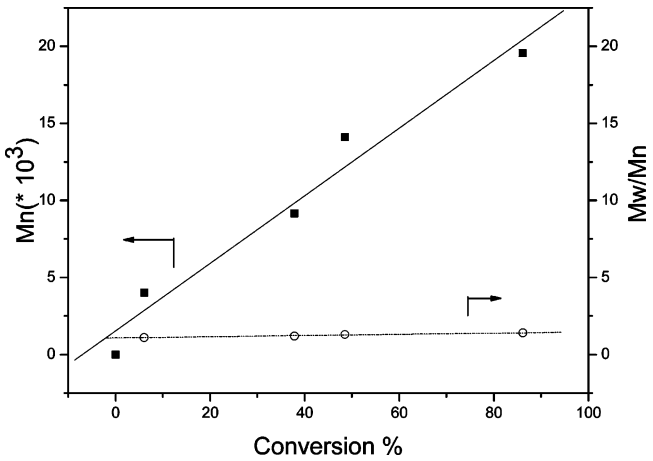
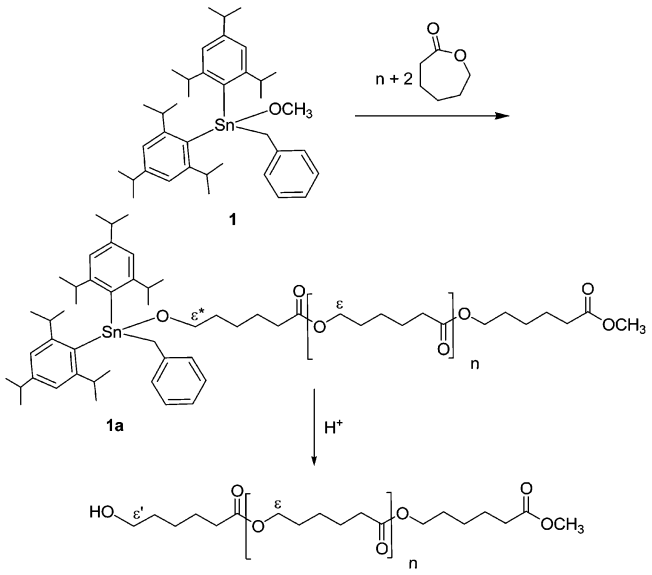


Figure 2. Polymerization of ϵ-caprolactone initiated with compound **1** (for polymerization conditions see Table 1). Relationship between number-average molecular weight M_n (■) and molecular weight distribution M_w/M_n (○) and conversion. M_n and M_w/M_n were determined by gel permeation chromatography GPC (30 °C, tetrahydrofuran, 1 mL/min).

For instance, if the initiating group is an alkoxide, an ester functionality will be generated as the polymer end group. The presence of the "initiating group" as the end group of the polymer is therefore a clue for the insertion mechanism.

In order to check this issue, we investigated the polymer end groups by NMR analysis of a suitable sample. In the ^{1}H NMR spectrum of a typical PCL sample (Figure 1, $CDCl_3$), in addition to intense resonances assignable to the opened ϵ-caprolactone units, minor resonances were assigned, according to literature data, to the polymer end groups. Diagnostic signals are a singlet at 3.65 ppm, assigned to the methyl group of a methyl ester function $-COOCH_3$, generated via insertion of the monomer unit into the $Sn-OCH_3$ bond with cleavage of the acyl−oxygen bond of the monomer, and a triplet at 3.62 ppm, associated with the methylene group at the hydroxyl end group $-CH_2CH_2OH$ (ϵ′), generated by hydrolysis of the polymer chain (Scheme 1). Protic reagents were not added to the reaction mixture, but the air moisture was enough to perform this hydrolysis. ^{13}C NMR data confirmed these assignments.[16] The NMR analysis did not show any other end groups, such as benzylic or arylic. The PCL was formed by exclusive insertion of the monomer molecule into the Sn−OMe bond, while the Sn−C bonds remain intact. Therefore, a single polymer chain can grow for each molecule of tin-containing initiator. The presence of such end groups

Scheme 1



therefore constitutes an indirect proof for the monomer insertion step of the mechanism.

Oligomerization of ϵ-Caprolactone. Observation of the Insertion Product into the Sn−OMe Bond. In order to obtain a low molecular weight sample, ϵ-caprolactone was polymerized in the presence of compound **1** at 75 °C in dry toluene in a 1:60 tin:monomer molar ratio for 17 h. In order to avoid deleterious hydrolysis reaction (see above), the quenching was performed with dry hexane, and all the manipulations were performed under nitrogen (see Experimental Section). In this case, no precipitation was observed, but upon solvent removing in vacuo, an oily product was obtained. Its ^{1}H NMR spectrum displayed, in addition to the main resonances assignable to PCL, minor resonances due to tin(IV)-containing species with benzyl and triisopropylphenyl ligands, the aromatic resonances of which are shifted upfield compared to those of **1**. The ^{119}Sn NMR spectrum no longer displays the signal at −37.8 ppm belonging to the initiator **1**, but three new resonances, all in the expected range for tetrahedral tin species, among which the one at −50.2 ppm is the major one. Its resonance pattern appears compatible with the formulation benzylbis[2,4,6-triisopropylphenyl](L)tin-(IV) (**1a**), where "L" is a monoanionic ligand, replacing the methoxy group of compound **1**. In order to obtain more information on the nature of the fourth ligand L in compound **1a**, 2D spectra were recorded. The 2D ^{1}H−^{119}Sn heteronuclear multiple-bond-correlation (HMBC) spectrum[18] exhibits a correlation peak between the ^{119}Sn resonance at −50.2 ppm and a ^{1}H signal at 3.67 ppm, with a ^{1}H−^{119}Sn coupling splitting of 24.2 Hz (Figure 3). The 2D ^{1}H−^{13}C heteronuclear multiple quantum correlation (HMQC) NMR spectrum (Figure 4) reveals that the intricate signal at 3.6−3.7 ppm in the ^{1}H NMR spectrum is a composite one, correlating with three ^{13}C NMR signals at 51.7 ppm (^{1}H at 3.65 ppm), 62.7 ppm (^{1}H at 3.62 ppm), and 65.7 ppm (^{1}H at 3.67 ppm). The resonances at 51.7 and 62.7 ppm are assigned respectively to the methyl ester end group (−C(O)O*C*H$_3$) and to the −*C*H$_2$OH end group of PCL, and therefore the corresponding protons do not show a correlation cross-peak in the ^{1}H−^{119}Sn HMBC spectrum. The third signal at 65.7 ppm, correlating with a ^{1}H signal at 3.67 ppm, belongs, according to a distortionless enhancement by polarization transfer DEPT-135 NMR analysis, to a methylene carbon, adjacent to an oxygen atom as suggested from the value of its chemical shift. This correlation peak is thus assigned to the

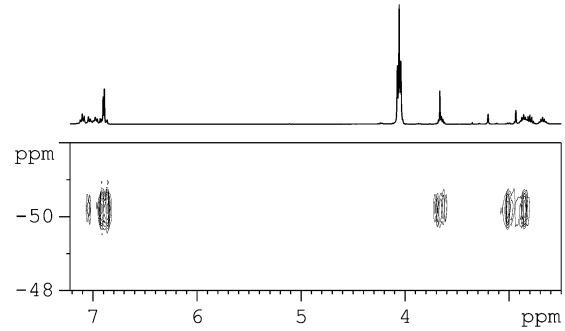


Figure 3. Part of ^{1}H−^{119}Sn heteronuclear multiple bond correlation (HMBC) NMR spectrum ($CDCl_3$, 25 °C, $1/(2J_{H-Sn})$ delay = 10.0 ms) of the ϵ-caprolactone oligomerization mixture containing **1a**.

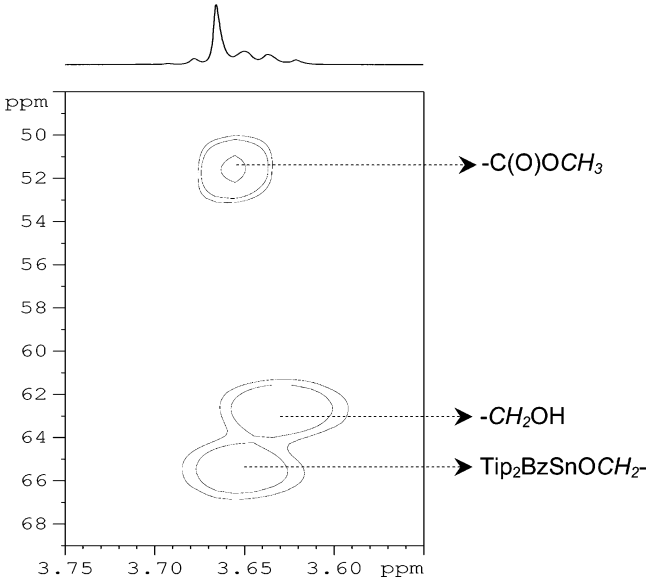


Figure 4. Part of ^{1}H−^{13}C heteronuclear multiple quantum correlation (HMQC) NMR spectrum ($CDCl_3$, 25 °C) of the ϵ-caprolactone oligomerization mixture containing **1a**.

methylene group (ϵ*) bound to the oxygen atom in the last inserted unit (Sn−O−C*H*$_2$−) and provides unambiguous evidence for ϵ-caprolactone insertion into the Sn−OCH$_3$ bond of compound **1**, prior to hydrolysis (Scheme 1). This species **1a** with ^{119}Sn resonance at −50.2 ppm exhibits in the ^{1}H−^{119}Sn HMBC spectrum additional correlation peaks with a singlet at 2.93 ppm, assigned to the benzylic protons of the SnC*H*$_2$Ph moiety, and the resonance around 6.9 ppm arising from the hydrogen atoms of triisopropylphenyl groups, further proving its identity.

To our knowledge this is the first direct observation of the product of the insertion of ϵ-caprolactone into a Sn−alkoxide bond of a ROP initiator. This result constitutes a *direct* proof that the insertion mechanism via acyl−oxygen bond cleavage is operating in such a system.

A second organotin species was also identified at −67.5 ppm in the ^{119}Sn NMR spectrum. This latter species was the prevalent one in an oligomeric sample prepared in the presence of initiator **1** contaminated by Tip$_2$BzSnOH. By the analysis of combined ^{1}H, ^{13}C, and ^{119}Sn NMR spectra, the resonance at −67.5 ppm in the ^{119}Sn NMR spectrum has been assigned to the species Tip$_2$BzSn−OOC(CH$_2$)$_5$O(CO(CH$_2$)$_5$)$_n$−OOC(CH$_2$)$_4$CH$_2$OH (**1b**). The assignments were confirmed by ^{1}H−^{13}C and ^{1}H−^{119}Sn 2D NMR spectra. The tin species at −67.5 ppm showed, apart from correlations with benzyl and triisopylphenyl protons, a correlation with protons at 2.25 ppm in its ^{1}H−^{119}Sn HMBC NMR

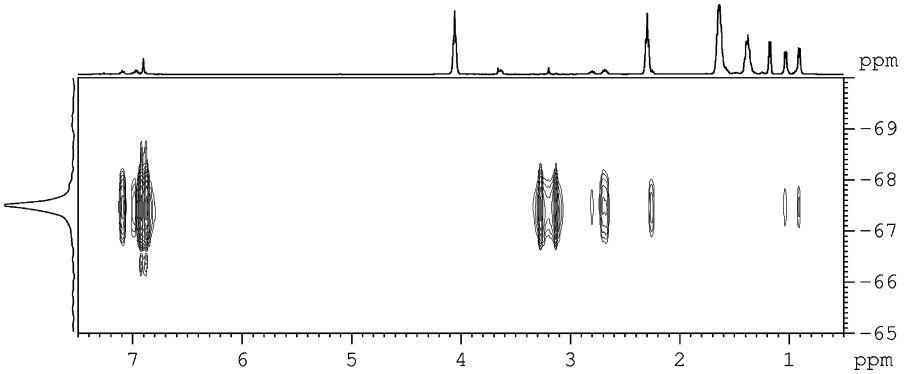
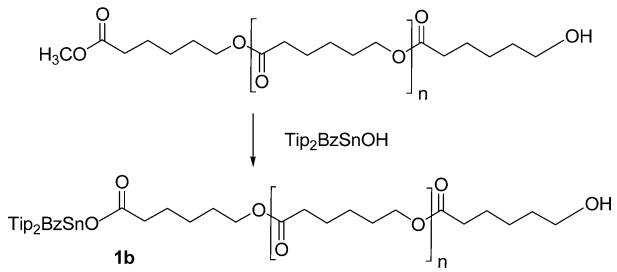


Figure 5. Part of $^{1}H-^{119}Sn$ heteronuclear multiple bond correlation (HMBC) NMR spectrum ($CDCl_3$, 25 °C, $1/(2J_{H-Sn})$ delay = 62.5 ms) of the ϵ-caprolactone oligomerization mixture containing **1b**.

Scheme 2



spectrum (Figure 5). These protons had a correlation in the $^{1}H-^{13}C$ HMBC spectrum with a C=O resonance at 177.8 ppm, meaning that they belonged to a methylene groups directly bound to a carbonyl $-CH_2CO-$, thus confirming the structure **1b** (see Supporting Information). Species **1b** can reasonably be assumed to be generated by the transesterification reaction of the polymer methyl ester end group with the $Tip_2BzSnOH$ impurity, formed by hydrolysis of the initiator (Scheme 2).[19] $Tip_2BzSnOH$ was also identified as the third product in the oily reaction mixture.

Conclusions

Benzylmethoxybis(2,4,6-triisopropylphenyl)tin(IV) was synthesized and screened as an initiator in the ring-opening polymerization of ϵ-caprolactone. The catalytic activity appeared satisfactory, and the polymerization showed a *living* behavior. NMR analysis of the polymer end groups suggested that the polymerization is achieved with a polyinsertion mechanism via acyl−oxygen bond cleavage of the monomer. The insertion product of ϵ-caprolactone into the Sn−OMe bond of the initiator was observed, unambiguously confirming the insertion mechanism. This product could be a model complex for the design of new high-performance single-site ROP catalyst systems. The presence of different reactive/functional groups at both polymer chain ends also makes it a versatile macroinitiator for the synthesis of new block copolymers of ϵ-caprolactone. Work is in progress in order to develop these promising issues.

Experimental Section

General Procedure. Sensitive materials were manipulated under nitrogen using Schlenk or glovebox techniques. Toluene, hexane, and tetrahydrofuran (THF) were refluxed over sodium/benzophenone and distilled under nitrogen prior to use. $CDCl_3$ was distilled from CaH_2 and stored over molecular sieves in a glovebox. All reagents were purchased from Aldrich and used as received. ϵ-Caprolactone was distilled in vacuum from CaH_2 prior to use. The benzylbromobis(2,4,6-triisopropylphenyl)tin was synthesized according to a previously reported procedure.[17] NMR spectra were recorded on Bruker Avance 400 (Avance 1) and 500 (Avance 2) MHz spectrometers (^{1}H, 400.00 MHz; ^{13}C, 100.57 MHz; ^{119}Sn, 149.09 MHz and ^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz; ^{119}Sn, 186.49 MHz, respectively). The ^{119}Sn resonances were measured relative to $Sn(CH_3)_4$. EI MS data were obtained with a Finnigan Thermoquest GCQ Plus 200 spectrometer using a direct insertion probe. Molecular weight and molar mass distribution of polymers were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, flow rate of eluant 1 mL/min, and narrow polystyrene standards as reference. The measurement were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000−1 000 000 Å). FTIR spectra with a resolution of 1 cm^{-1} were recorded on a Bruker Vector 22 spectrometer, using solid samples in KBr pellets.

Benzylmethoxidebis(2,4,6-triisopropylphenyl)tin (1). Sodium methoxide (100 mg, 1.85 mmol) was added to a stirred solution of benzylbromobis(2,4,6-triisopropylphenyl)tin (750 mg, 1.08 mmol) in dry THF (50 mL) at room temperature. The solution was warmed to 50 °C and stirred for 18 h. The solvent was removed in vacuo, and the product was extracted with dry hexane. The solvent was removed in vacuo, and a white powder was obtained. Yield = 500 mg, 72%. ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.94 (12H, d, $CH(CH_3)_2$), 0.98 (12H, d, $CH(CH_3)_2$), 1.18 (12H, d, $CH(CH_3)_2$), 2.75−2.85 (6H, m, $CH(CH_3)_2$), 2.96 (2H, s, $^{2}J^{119}Sn-^{1}H$ = 63.4 Hz, CH_2Ph), 3.62 (3H, s, $^{3}J^{119}Sn-^{1}H$ = 44.5 Hz, OCH_3), 6.90 (4H, s, $^{4}J^{119}Sn-^{1}H$ = 22.0 Hz, Ar*H*), 6.9−7.1 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, 293 K): δ = 24.1, 24.4, 25.0 ($CH(CH_3)_2$), 32.2 (CH_2Ph), 34.3 (*p*-$CH(CH_3)_2$), 37.5 (*o*-$CH(CH_3)_2$), 54.7 (OCH_3), 121.7 (Ar*C*H), 124.4, 128.3, 128.5 (Ph-*C*), 139.2, 150.5, 155.0 (Ar-*C*). ^{119}Sn ($CDCl_3$, 293 K): δ = −37.8. EI MS *m*/*z* = 647 $[M]^+$.

The species $Tip_2BzSnOH$, derived from the hydrolysis of **1**, was identified as side product. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.37 (1H, s, $^{2}J^{119}Sn-^{1}H$ = 26.4 Hz, SnO*H*, $CH(CH_3)_2$), 1.05 (12H, d, $CH(CH_3)_2$), 1.19 (12H, d, $CH(CH_3)_2$), 2.80−2.87 (6H, m, $CH(CH_3)_2$), 2.95 (2H, s, $^{2}J^{119}Sn-^{1}H$ = 63.1 Hz, CH_2Ph), 6.93 (4H, s, $^{4}J^{119}Sn-^{1}H$ = 22.4 Hz, Ar*H*), 7.0−7.1 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, 293 K): δ = 24.1, 24.5, 25.1 ($CH(CH_3)_2$), 31.3 (CH_2Ph), 37.5 (*o*-$CH(CH_3)_2$), 121.8 (Ar*C*H), 124.6, 128.1, 128.7 (Ph-*C*), 139.4, 139.8, 150.5, 154.7 (Ar-*C*). ^{119}Sn ($CDCl_3$, 293 K): δ = −59.9. IR (KBr), characteristic bands: ν = 3599 cm^{-1} (stretching −OH); 563 cm^{-1} (stretching Sn−O).[20]

Benzylisopropoxidebis(2,4,6-triisopropylphenyl)tin (2). Sodium isoproproxide (THF solution, 0.261 M, 3.5 mL, 0.91 mmol) was added to a stirred solution of benzylbromobis(2,4,6-triisopropylphenyl)tin (582 mg, 0.76 mmol) in THF dry (40 mL) at 0 °C. The resulting solution was allowed to reach room temperature and stirred for 18 h. The solvent was removed, and the product was extracted with hexane. The solvent was removed by rotary evaporation, and a light orange oil was obtained, crystallized in methyl alcohol at −20 °C (yield = 383 mg; 75%). ^{1}H NMR ($CDCl_3$, 293 K): δ = (24H, m, $CH(CH_3)_2$), 1.03 (6H, d, $OCH(CH_3)_2$), 1.19 (12H, d, $CH(CH_3)_2$), 2.78−2.88 (6H, m, $CH(CH_3)_2$), 2.95 (2H, s, $^{2}J^{119}Sn-^{1}H$ = 64.04 Hz, CH_2Ph), 4.04 (1H, m, $OCH(CH_3)_2$), 6.86

(4H, s, $^4J^{119}$Sn−^{1}H = 21.5 Hz, Ar*H*), 6.9−7.0 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, 293 K): δ = 24.1, 24.5, 24.9 (CH(CH_3)$_2$), 27.6 (OCH(CH_3)$_2$), 32.2 (CH_2Ph), 34.3 (*p*-*C*H(CH_3)$_2$), 37.1 (*o*-*C*H-(CH_3)$_2$), 66.4 (O*C*H(CH_3)$_2$), 121.7 (Ar*C*H), 124.3, 128.3, 128.6 (Ph-*C*), 141.0, 142.1, 150.3, 155.4 (Ar-*C*). ^{119}Sn (CD_2Cl_2, 293 K): δ = −62.0. EI MS *m*/*z* = 617 [M−OCH(CH_3)$_2$]$^+$.

Polymerization Screening. The main results of the polymerization tests are summarized in Table 1. Polymerization tests were carried out in dry nitrogen by dissolving the appropriate amount of compound **1** in dry toluene and the selected amount of ϵ-caprolactone. The reaction mixture was quenched by addition of hexane. The polymer was filtered and dried in vacuo.

A typical polymerization test (Table 1, run II) was conducted by dissolving 40 mg (60 μmol) of compound **1** in a mixture of dry toluene (10 mL) and of ϵ-caprolactone (0.8 mL, 7.2 mmol). The solution was warmed to 75 °C and stirred for 12 h. After this time, the solution was cooled to room temperature, and 60 mL of hexane was added. The polymer was filtered and dried in vacuo (yield = 0.312 g). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2H, −CH_2−), 1.62 (m, 4H, −CH_2−), 2.29 (t, 2H, −CH_2C(O)O−), 4.04 (t, 2H, −CH_2OC(O)−), 3.62 (t, 2H, −CH_2OH), 3.65 (s, 3H, -C(O)-OCH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 24.7, 25.7, 28.5, 34.3, 64.3 (−OCO(CH_2)$_5$−), 51.7 (−C(O)O*C*H$_3$), 62.7 (−CH_2OH), 173.7 (−COO−). GPC data: M_w = 10 984; M_w/M_n = 1.2.

Oligomerization Reaction. The reaction was performed as above, but using 49 mg (76 μmol) of compound **1** at 75 °C in a mixture of dry toluene (10 mL) and 0.5 mL of ϵ-caprolactone for 17 h. After addition of dry hexane (60 mL), no insoluble products were observed. The solvent was removed in vacuo from the polymerization solution, obtaining an oily white product (70 mg), which was further characterized by NMR. All the manipulations were performed under nitrogen, using Schlenk or glovebox techniques.

Species 1a. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.92 (12H, d, CH-(C*H*$_3$)$_2$), 0.96 (12H, d, CH(C*H*$_3$)$_2$), 1.19 (12H, d, CH(C*H*$_3$)$_2$), 2.80−2.85 (6H, m, C*H*(CH_3)$_2$), 2.93 (2H, s, $^2J^{119}$Sn−^{1}H = 63.1 Hz, CH_2Ph), 3.67 (2H, m, $^3J^{119}$Sn−^{1}H = 24.2 Hz, SnOCH_2−), 6.89 (4H, s, $^4J^{119}$Sn−^{1}H = 21.9 Hz, Ar*H*), 6.9−7.1 (5H, m, Ph). ^{13}C NMR ($CDCl_3$, 293 K): δ = 24.3, 24.8 (CH(*C*H$_3$)$_2$), 30.2 (*C*H_2Ph), 37.3 (*o*-*C*H(CH_3)$_2$), 65.1 (SnO*C*H_2−), 121.7 (Ar*C*H), 124.4, 128.3, 128.5 (Ph-*C*), 139.3, 150.3, 155.0 (Ar−*C*). ^{119}Sn ($CDCl_3$, 293 K): δ = −50.2.

Species 1b. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.90, (12H, d, CH-(C*H*$_3$)$_2$), 1.02 (12H, d, CH(C*H*$_3$)$_2$), 1.16 (12H, d, CH(C*H*$_3$)$_2$), 2.25 (2H, m, Sn−OOCC*H*$_2$(CH_2)$_4$−), 2.69 and 2.80 (6H, m, C*H*(CH_3)$_2$), 3.20 (2H, s, $^2J^{119}$Sn−^{1}H = 69.4 Hz, CH_2Ph), 6.90 (4H, s, Ar*H*), 7.00−7.15 (5H, m, Ph). ^{13}C NMR, selected resonances ($CDCl_3$, 293 K): δ = 33.0 (*C*H_2Ph), 35.9 (Sn−OOC*C*H$_2$(CH_2)$_4$−), 38.0 (*C*H(CH_3)$_2$), 122.0 (Ar*C*H), 124.8, 128.2, 128.5 (Ph−*C*), 138.9, 140.0, 154.3 (Ar−*C*), 177.8 (Sn−OO*C*CH$_2$(CH_2)$_4$−). ^{119}Sn ($CDCl_3$, 293 K): δ = −67.5.

Acknowledgment. This work was supported by the fund of Scientific Research Flanders (Belgium) (FWO) (Grants G 0016.02 & G.0469.06), the Research Council (Onderzoeksraad) of the Vrije Universiteit Brussel (Concerted Reseach Action, Grant GOA31), and the fund of Università del Sannio (FAR 2005). The authors are grateful to Dr. Patrizia Oliva and Eng. Ingrid Verbruggen for acquiring ^{119}Sn NMR data.

Supporting Information Available: ^{1}H, ^{13}C, and ^{19}Sn NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For recent reviews on polymerization of cyclic esters see: (a) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602−626. (b) Gibson, C.; Marshall, E. L. In *Comprehensive Coordination Chemistry II*; Elsevier: Amsterdam, 2004; Vol. 9, p 1. (c) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176.

(2) Jarrett, P.; Benedict, C.; Bell, J. P.; Cameron, J. A; Huang, S. J. In *Polymers as Biomaterials*; Shalaby, S. W., et al., Eds.; Plenum Press: New York, 1984; pp 181−192.

(3) (a) Nomura, N.; Aoyama, T.; Ishii, R. Kondo, T. *Macromolecules* **2005**, *38*, 5363−5366. (b) Chen, C.; Huang, C.; Huang, B. *Macromolecules* **2004**, *37*, 7968−7973. (c) Milione, S.; Grisi, F.; Centore, R.; Tuzi, A. *Organometallics* **2006**, *25*, 266−274.

(4) (a) Lecomte, P.; Stassin, F.; Jerome, R. *Macromol. Symp.* **2004**, *215*, 325−338. (b) Deshayes, G.; Poelmans, K.; Verbruggen, I.; Camacho-Camacho, C.; Degée, P.; Pinoie, V.; Martins, J. C.; Piotto, M.; Biesemans, M.; Willem, R.; Dubois, P. *Chem.—Eur. J.* **2005**, *11*, 4552−4561.

(5) Deshayes, G.; Mercier, F.; Degee, P.; Verbruggen, I.; Biesemans, M.; Willem, R.; Dubois, P. *Chem.—Eur. J.* **2003**, *9*, 4346−4352.

(6) Shen, Y.; Shen, Z.; Zhang, Y.; Yao, K. *Macromolecules* **1996**, *29*, 8289−8295. (b) Nishiura, M.; Hou, Z.; Koizumi, T.; Immoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245−8251. (c) Kerton, F.; Withwood, A.; Williams, C. *Dalton Trans.* **2004**, 2237−2244. (d) Barnea, E.; Moradove, D.; Berthet, J.-C.; Ephiritikhine, M.; Eisen, M. S. *Organometallics* **2006**, *25*, 320−322.

(7) (a) Wang, H.; Chan, H.; Okuda, J.; Xie, Z. *Organometallics* **2005**, *24*, 3118−3124. (b) Cayuela, J.; Bounor-Legare, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338−1346. (c) Chmura, A.; Davidson, M.; Jones, M.; Lunn, M.; Mahon, M. *Dalton Trans.* **2006**, *7*, 887−889. (d) Chen, M.; Sun, H.; Li, W.; Wang, Z.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, *691*, 2489−2494.

(8) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991−994.

(9) Lewinski, J.; Horeglad, P.; Wojcik, K.; Justyniak, I. *Organometallics* **2005**, *24*, 4588−4593.

(10) Ryner, M.; Stridsberg, K.; Albertsson, A.; von Schenck, H.; Svensson, M. *Macromolecules* **2001**, *34*, 3877−3881.

(11) Harlan, C. J.; Bott, S. G.; Wu, B.; Lenz, R. W.; Barron, A. R. *Chem. Commun.* **1997**, 2183−2184.

(12) Evans, J. W.; Shreeve, J. L.; Doedens, R. J. *Inorg. Chem.* **1993**, *32*, 245−246.

(13) Evans, J. W.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1995**, *34*, 576−585.

(14) Lewinski, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kolodziejczyk, E. *Macromol. Rapid Commun.* **2004**, *25*, 1939−1942.

(15) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 1438−1442.

(16) (a) Kricheldorf, H. R.; Berl, M.; Kreiser-Saunders, I. *Macromolecules* **1988**, *21*, 286−293. (b) Kricheldorf, H. R.; Sumbel, M. V.; Kreiser-Saunders, I. *Macromolecules* **1991**, *24*, 1944−1949. (c) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419−6424. (d) Nishiura, M.; Hou, Z.; Koizumi, T.-A.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245−8251. (e) Kricheldorf, H. R.; Kreiser-Saunders, I. *Polymer* **2000**, *41*, 3957−3963.

(17) Annunziata, L.; Pappalardo, D.; Tedesco, C.; Antinucci, S.; Pellecchia, C. *J. Organomet. Chem.* **2006**, *691*, 1505−1514.

(18) (a) Martins, J. C.; Biesemans, M.; Willem, R. *Prog. NMR Spectrosc.* **2000**, *36*, 271−322. (b) Willem, R.; Bouhdid, A.; Kayser, F.; Delmotte, A.; Gielen, M.; Martins, J. C.; Biesemans, M.; Mahieu, B.; Tiekink, E. R. T. *Organometallics* **1996**, *15*, 1920−1929.

(19) The formation of tin carboxylate bonds could, in principle, be achieved by the ϵ-caprolactone ring-opening mechanism through the cleavage of the alkyl−oxygen bond. In this case, however, the PCL sample should display carboxylic (−COOH) and ether (−OCH_3) functions as end groups. This is not the case here, since the unambiguously demonstrated pairwise presence of the methyl ester (−COOC*H*$_3$) and the hydroxyl (−CH_2C*H*$_2$OH) functions as unique polymer end groups strictly rules out this assumption.

(20) Bonadi, A.; Cantoni, A.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Organomet. Chem.* **1991**, *402*, 281−288.

MA0623486