FULL PAPER

Mechanistic Study of Bu$_2$SnCl$_2$-Mediated Ring-Opening Polymerization of ε-Caprolactone by Multinuclear NMR Spectroscopy

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Abstract: The ring-opening polymerization (ROP) of ε-caprolactone (CL) was carried out in toluene at 100 °C with *n*-propanol (*n*PrOH) in the presence of Bu$_2$SnCl$_2$. It comes out that the molar mass of the polyester chains can be predicted from the initial monomer-to-alcohol molar ratio in accordance with a controlled ROP mechanism involving an O-acyl cleavage of the monomer to selectively form (α-propyloxy)(ω-hydroxy)poly(ε-caprolactone) chains. In order to gain fundamental understanding of the mechanistic factors governing the polyester chain growth, advanced ^{1}H, ^{13}C, and ^{119}Sn NMR investigations were performed in situ in [D$_8$]toluene, as well as with model solutions that contained Bu$_2$SnCl$_2$ and binary mixtures of the components at various concentrations and temperatures. This has enabled us to propose a mechanism in which Bu$_2$SnCl$_2$ behaves as a catalyst, while *n*PrOH is the actual initiator. It involves non-aggregated, six-coordinate Bu$_2$SnCl$_2$ complexes in which ligands exchange fast on the ^{119}Sn NMR observational timescale, and the simultaneous interactions of CL and alcohol function in such a way that it favors insertion/propagation reactions over transesterification ones, up to high monomer conversion.

Keywords: lactones · NMR spectroscopy · reaction mechanism · ring-opening polymerization · tin

Introduction

The majority of polymers used in the biomedical field to develop implants, sutures, and controlled drug-delivery systems are resorbable aliphatic polyesters. They are synthesized by ring-opening polymerization (ROP) of cyclic (di)esters such as ε-caprolactone (CL), lactides, and glycolide. The most widely used initiators for the ROP of cyclic (di)esters are aluminum alkoxides[1–9] and tin alkoxides[10] or carboxylates[11–17] (the latter coupled with alcohols as co-initiators). The predominance of these activators is due to their ability to produce stereoregular polymers of narrow molecular-weight distribution and predictable molar mass with well-defined end groups. Such a control of the molecular parameters can only be achieved by a comprehensive study of the polymerization mechanism and the factors governing the reactivity of active species.

As far as aluminum and tin alkoxides are concerned, the polymerization proceeds through a coordination–insertion mechanism with acyl–oxygen cleavage of the monomer and insertion into the metal–oxygen bond of the initiator (Scheme 1).

A major difference between aluminum- and tin-based initiators is that tin derivatives, and more particularly tin(IV) compounds, are known as good transesterification catalysts.[18, 19] In fact, there are two possibilities of transesterification side reactions in ROP of (di)lactones: monomolecular (intramolecular) chain transfer with macrocyclics formation [Eq. (1)][20] and bimolecular (intermolecular) chain transfer, leading to macromolecular chain-length redistribution and thus broadening of molecular weight distribution [Eq. (2)].[20]

The extent of inter- and intramolecular transfer reactions depends on the monomer conversion and on the structure of the active sites so that less reactive species are more discriminating and characterized by higher selectivity parameters, $\beta = k_p/k_{tr(1)}$ and $\gamma = k_p/k_{tr(2)}$ in which k_p, $k_{tr(1)}$, and $k_{tr(2)}$ are the kinetic constants of propagation, monomolecular, and bimolecular transfer reactions, respectively.[21] The formation of cyclic compounds is thermodynamically inevitable for polyesters, but kinetic conditions can be found out to prepare linear macromolecules almost free of ring structures. Due to

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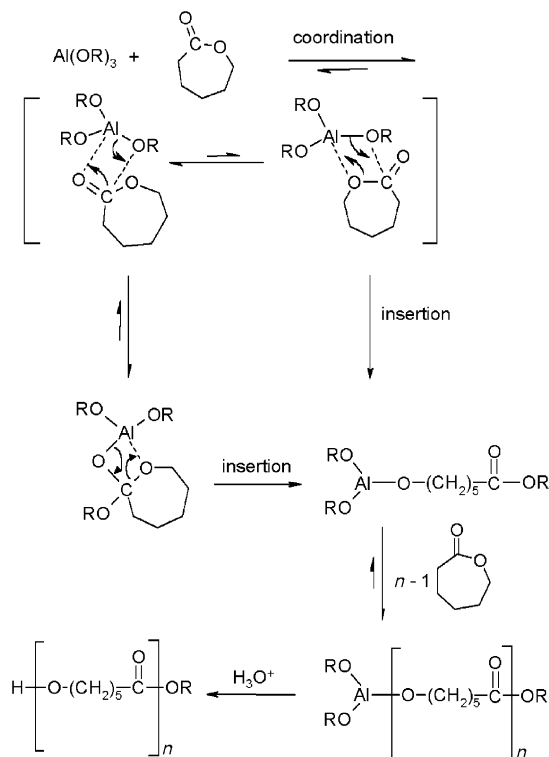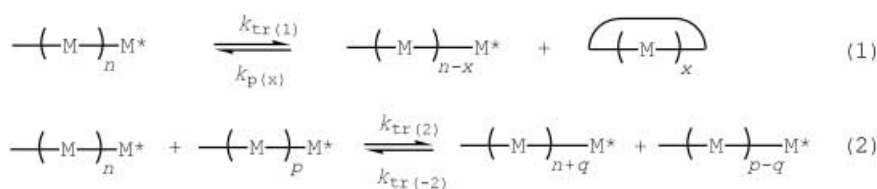
Scheme 1. Coordination–insertion mechanism as illustrated for the polymerization of ε-caprolactone, initiated by trialkoxy aluminum.[5]

intermolecular transfer reactions, the polydispersity index (M_w/M_n) increases more or less rapidly with the monomer conversion, eventually reaching the value predicted by the most probable distribution ($M_w/M_n = 2$) in case of initiators characterized by low selectivity. In contrast, for highly selective active species, the molecular distribution can be kept narrow until almost complete monomer conversion is achieved and only broadens for a much longer reaction time actually well above the monomer-to-polymer conversion.

Next to the aforementioned tin alkoxides and carboxylates, other tin(IV) derivatives, such as $SnPh_4$,[22] $SnBu_4$,[23] SnX_4 (where X = Cl and Br),[24] and 1-alkoxy-3-oxyacyl tetrabutyl distannoxane,[25] have also been reported to promote the ROP of cyclic esters. The polymerization is often carried out in bulk (i.e., in the absence of solvent) at temperatures ranging from 100 to 180 °C. So far, these tin(IV) derivatives have been mostly compared to each other in terms of polymerization kinetics, but poorly investigated from the viewpoint of the activation mechanism. Actually, the only information available is the necessity to have hydroxyl-containing compounds within the reaction medium for (co-) initiating the polymerization. In order to shed some more light onto the efficiency and the selectivity of such tin(IV)-based activators, Bu_2SnCl_2

was taken into consideration for mediating the ROP of CL. For this purpose, Bu_2SnCl_2 was added with *n*-propanol while the CL polymerization was carried in toluene at 100 °C.

This paper shows that such conditions allow for controlling the polymerization mechanism to yield polyester chains of predetermined molar mass from the initial monomer-to-alcohol molar ratio. Confirming previous statements, transesterification reactions, however, occur at higher monomer conversion leading to a broadening of molecular-weight distribution. Interestingly, multinuclear NMR spectroscopy was utilized in order to get a better insight into the polymerization mechanism, and the parameters responsible for the polydispersity increase as the polymerization proceeds. In particular, ^{119}Sn NMR spectroscopy has been used as a powerful tool for monitoring the coordination of the organotin catalyst as a function of the degree of polymerization.

Results and Discussion

Polymerization of ε-caprolactone (CL): In a first set of experiments, the ring-opening polymerization (ROP) of ε-caprolactone ([CL]₀ = 4.51 mol L⁻¹) was initiated with *n*-propanol ([nPrOH]₀ = 4.51 × 10⁻² mol L⁻¹) in the presence of dibutyltin dichloride ([Bu₂SnCl₂]₀ = 2.25 × 10⁻³ mol L⁻¹) in toluene at 100 °C. Table 1 shows the time dependence of the monomer conversion, the number average molecular weight (M_n), and the molecular-weight distribution (M_w/M_n).

Table 1. Time dependence of monomer conversion, number average molecular weight (M_n) and polydispersity index (M_w/M_n).

	Time [h]	Conversion [%]	M_{ntheor}[a]	M_{nNMR}[b]	M_{nSEC}[c]	M_w/M_n
1	24	~1	–	–	–	–
2	48	24	2700	2200	2600	1.04
3	72	47	5400	6300	6100	1.05
4	94	98	11200	12400	9800	1.77

[a] $M_{ntheor} = ([CL]_0[nPrOH]_0 \times conv. \times M_{WCL}) + M_{WnPrOH}$. [b] $M_{nNMR} = [(1 + (I_{CH2-O-CO}/I_{CH2-OH})) \times M_{WCL}] + M_{WnPrOH}$, as determined by ^{1}H NMR spectroscopy. [c] M_{nSEC}, as determined by SEC.

The monomer conversion was determined gravimetrically by weighing the precipitated polyester chains. It comes out that Bu_2SnCl_2-mediated polymerization of CL is quite slow compared to that initiated by aluminum and tin alkoxides.[5–10] Indeed, a reaction time of 94 h at 100 °C is required to reach a monomer conversion close to completion (entry 4 in Table 1).

Assuming that each chain is end-capped by a propyloxycarbonyl function at one end and a hydroxyl group at the other, according to the coordination-insertion mechanism (Scheme 1), the experimental molar mass can be calculated by ^{1}H NMR spectroscopy (M_{nNMR}) from the relative intensity of the methylene protons of the main chain at 3.95 ppm (-C*H₂*-O-C(O)-) and α-hydroxy methylene protons at 3.35 ppm
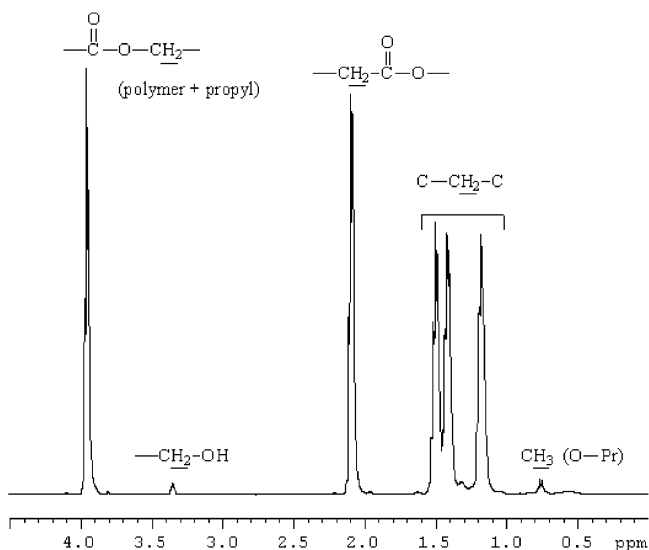
Figure 1. ^{1}H NMR spectrum of poly(ε-caprolactone) as obtained by polymerization of ε-caprolactone initiated by n-propanol in the presence of Bu$_2$SnCl$_2$ in toluene at 100 °C for 72 h (entry 3 in Table 1).
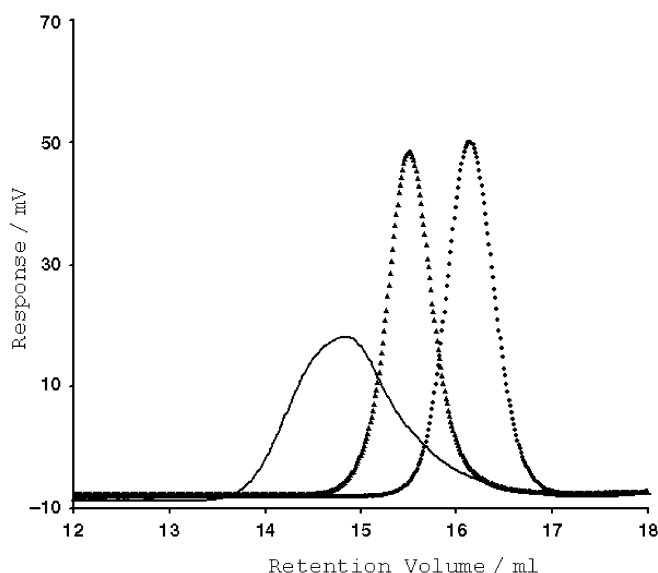

Figure 2. SEC traces of poly(ε-caprolactone) as obtained by polymerization of ε-caprolactone initiated by n-propanol in the presence of Bu$_2$SnCl$_2$ in toluene at 100 °C for various reaction times: 48 h ($\bullet$), 72 h ($\blacktriangle$) and 94 h (——).

($-CH_2$-OH) (Figure 1). It is worth noting that there is a good agreement between the experimental average molar masses (M_{nNMR} and M_{nSEC} determined by size exclusion chromatography) and the theoretical one calculated from the initial monomer-to-alcohol molar ratio ($M_n = ([CL]_0/[nPrOH]_0 \times$ conv. $\times M_{\mathrm{WCL}}) + M_{\mathrm{W}n\mathrm{PrOH}}$), whereby conv. denotes monomer conversion, and M_{WCL} and $M_{\mathrm{W}n\mathrm{PrOH}}$ are the molecular weights of monomer and n-propanol, respectively). Such a behavior is consistent with a polymerization mechanism involving an O-acyl rupture of the monomer to selectively form (α-propyloxy)(ω-hydroxyl)poly(ε-caprolactone) chains in the absence of any transfer and irreversible termination reactions. As far as the molecular-weight distribution is concerned, it is remarkably narrow ($M_w/M_n < 1.1$), at least up to monomer conversion of 50% (entries 2 and 3 in Table 1). When the reaction time exceeds 72 h, transfer reactions start to happen that lead to a broadening of the molecular-weight distribution (Figure 2).

In another experiment, the initial monomer-to-alcohol molar ratio was decreased to 50 for an initial $[nPrOH]_0/[Bu_2SnCl_2]_0$ molar ratio of 50. After 24 h at 100 °C, complete monomer conversion was reached, and the polyester chains were analyzed by size exclusion chromatography (SEC). Again, a quite good agreement exists between M_{nSEC} (6100) and the expected molar mass ($M_{\mathrm{ntheor}} = 5750$). The polydispersity index reached 1.4.

Last but not least, an attempt to polymerize CL with Bu$_2$SnCl$_2$ in the absence of n-propanol was carried out in toluene at 100 °C ($[CL]_0 = 4.512 \ \mathrm{mol\,L^{-1}}$ and $[CL]_0/[Bu_2SnCl_2]_0 = 2000$). After 94 h, monomer conversion was lower than 0.5%; this definitely demonstrates that n-propanol is the actual and exclusive initiator of the polymerization. To gain a better insight into the polymerization mechanism and the parameters governing the reactivity of the active species, a multinuclear NMR study of Bu$_2$SnCl$_2$ in various chemical environments was conducted.

NMR investigations: The ^{119}Sn NMR spectra of purified Bu$_2$SnCl$_2$ in [D$_8$]toluene at 303 K for concentrations of 0.13 and 0.65 mol L^{-1} display a single narrow resonance at 124.2 and 123.4 ppm, respectively. Varying the temperature from 363 to 233 K has negligible effect on the ^{119}Sn chemical shifts, which range from 126.2 to 120.7 ppm and from 125.8 to 120.6 ppm for diluted and concentrated Bu$_2$SnCl$_2$ solutions, respectively. Such observations are consistent with a four-coordinate tin atom and the virtual absence of coordinating expansion by auto-aggregation upon concentration and temperature decrease. Interestingly, the ^{119}Sn chemical shift decreases to 29 ppm at 303 K when CL and nPrOH are added to a solution of Bu$_2$SnCl$_2$ in [D$_8$]toluene ($[CL] = 4.5 \ \mathrm{mol\,L^{-1}}$, $[nPrOH] = 0.045 \ \mathrm{mol\,L^{-1}}$, and $[Bu_2SnCl_2] = 0.1125 \ \mathrm{mol\,L^{-1}}$). It is worth noting that the concentrations in both monomer and alcohol are identical to those prevailing for the polymerization conducted at 373 K, while the concentration in Bu$_2$SnCl$_2$ is 50-fold higher to achieve acceptable ^{119}Sn signal-to-noise response. Table 2 shows the temperature dependence of the ^{119}Sn chemical shift for various ternary and binary compositions containing Bu$_2$SnCl$_2$, CL, and nPrOH. A single ^{119}Sn resonance is observed whatever the temperature and composition; this means that several coordinated tin config-

Table 2. Temperature dependence of the ^{119}Sn chemical shift for various binary and ternary compositions in [D$_8$]toluene ($[Bu_2SnCl_2] = 0.1125 \ \mathrm{mol\,L^{-1}}$, $[CL] = 4.5 \ \mathrm{mol\,L^{-1}}$, $[nPrOH]_1 = 0.045 \ \mathrm{mol\,L^{-1}}$ and $[nPrOH]_2 = 0.225 \ \mathrm{mol\,L^{-1}}$).

T [K]	Bu$_2$SnCl$_2$/ CL/nPrOH$_1$	Bu$_2$SnCl$_2$/CL	Bu$_2$SnCl$_2$/ nPrOH$_1$	Bu$_2$SnCl$_2$/ nPrOH$_2$
233	-19.1	-20.0	$+85.4$	$+24.3$
253	-7.2	-2.9	$+101.7$	$+63.2$
273	$+8.7$	$+13.8$	$+114.8$	$+92.7$
303	$+29.0$	$+32.2$	$+120.9$	$+113.1$
363	$+64.9$	$+66.5$	$+120.3$	$+119.2$

urations coexist with an exchange rate that is fast on the ^{119}Sn NMR timescale. The decrease of the ^{119}Sn chemical shift upon temperature decrease, whatever the composition, evidences the existence of equilibrated mixtures in which a coordination expansion occurs upon temperature lowering.[27, 28]

To get a better insight into the relative effectiveness of CL and *n*PrOH to coordinate Bu$_2$SnCl$_2$, binary compositions were studied. Similarly to the ternary mixture, the temperature dependence of the ^{119}Sn chemical shift for Bu$_2$SnCl$_2$/CL binary mixture is roughly linear and passes from 66.5 ppm at 363 K to -20.0 ppm at 233 K (Figure 3).

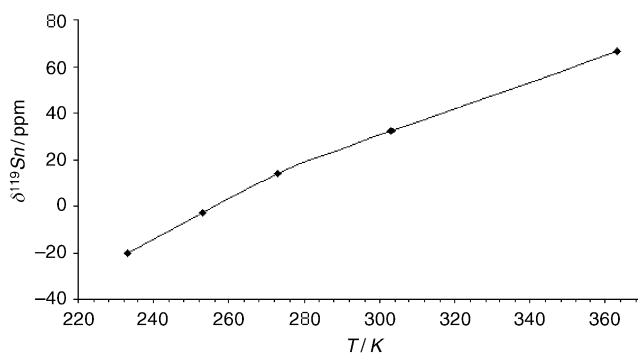Figure 3. Temperature dependence of the ^{119}Sn chemical shift of the binary mixture containing Bu$_2$SnCl$_2$ (0.1125 mol L^{-1}) and CL (4.5 mol L^{-1}) in [D$_8$]toluene.

In the absence of CL, the addition of *n*-propanol to Bu$_2$SnCl$_2$ also affects the temperature dependence of the ^{119}Sn chemical shift. As might be expected, the variation is more pronounced for a [*n*PrOH]/[Bu$_2$SnCl$_2$] molar ratio of 2 as compared to 0.4, but the most striking feature is that the ^{119}Sn chemical shift varies almost asymptotically with temperature to reach a value close to that of the purified Bu$_2$SnCl$_2$ in [D$_8$]toluene at 363 K, that is, $\sim$120 ppm (Figure 4). In other terms, although *n*-propanol apparently coordinates more
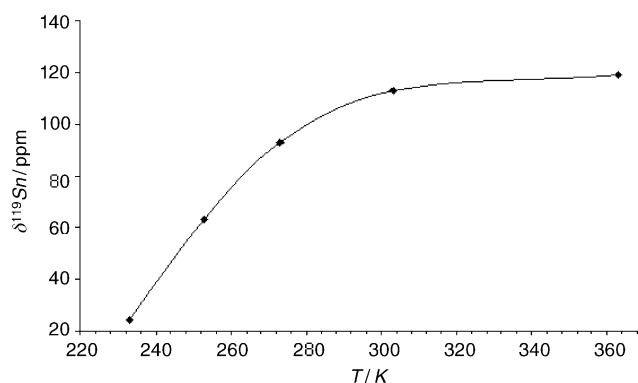

Figure 4. Temperature dependence of the ^{119}Sn chemical shift of the binary mixture containing Bu$_2$SnCl$_2$ (0.1125 mol L^{-1}) and *n*PrOH (0.225 mol L^{-1}) in [D$_8$]toluene.

strongly the tin atom than CL, as can be deduced from both the respective temperature dependence of the chemical shifts (ca. 95 ppm over 130 K for *n*PrOH and about 85 over 130 K for CL) in conjunction with their important concentration

differences (0.225 mol L^{-1} for *n*PrOH and 4.5 mol L^{-1} for CL), coordination of *n*-propanol to tin(IV) can be considered as negligible at higher temperature. Actually this indicates at most that at high temperatures the fast dynamic equilibrium between tin species coordinating *n*-propanol and those that do not are by far in favor of the latter, without actually excluding that *n*-propanol does interact with tin. As an intermediate conclusion, it can be stated that CL coordinates the tin atom and brings, at least partially, the four-coordinate Bu$_2$SnCl$_2$ in more favorable five- and/or six-coordinate configurations to initiate the coordination-insertion polymerization as illustrated above with aluminum alkoxides (Scheme 1). Though *n*-propanol is the actual initiator, it is prone neither to coordinate irreversibly and even reversibly to the tin atom at the polymerization temperature (373 K), nor to substantially react with Bu$_2$SnCl$_2$ to form tin alkoxide species such as Bu$_2$Sn(Cl)$_{2-n}$(OC$_3$H$_7$)$_n$. Indeed, no additional single resonance accounting for tin(IV) alkoxide can be detected by ^{119}Sn NMR spectroscopy, at least within the NMR timescale.

In a subsequent series of experiments mimicking the polymerization conditions, the ternary mixture of CL, *n*-propanol and Bu$_2$SnCl$_2$ in [D$_8$]toluene was heated up to 353 K by immersing the NMR tube directly in a thermostated oil bath ([CL] = 4.5 mol L^{-1}, [*n*PrOH] = 0.145 mol L^{-1} and [Bu$_2$SnCl$_2$] = 0.1125 mol L^{-1}). After various polymerization times, the NMR tube was cooled down to 303 K in order to record the ^{1}H, ^{13}C and ^{119}Sn spectra of the reaction mixture. It allowed monitoring the ^{119}Sn chemical shift as a function of the monomer-to-polymer conversion. Monomer conversion was monitored by ^{1}H NMR spectroscopy from the relative intensities of the methylene protons of the residual monomer at 2.33 ppm and the ones of the polyester repetitive units at 2.10 ppm. Table 3 shows that the single narrow ^{119}Sn resonance drifts to higher chemical shift as the polymerization

Table 3. Time dependence of the ^{119}Sn chemical shift and monomer conversion as determined by NMR spectroscopy at 303 K ([CL] = 4.5 mol L^{-1}, [*n*PrOH] = 0.145 mol L^{-1} and [Bu$_2$SnCl$_2$] = 0.1125 mol L^{-1}).

	Time [h]	Conversion [%]	^{119}Sn chemical shift [ppm]
1	0.0	0.0	26.2
2	68.0	29.3	34.7
3	91.0	43.0	37.6
4	140.0	73.3	49.7
5	166.5	81.6	54.5
6	236.0	98.6	71.8
7	260.0	99.4	72.4
8	284.0	99.8	72.2

proceeds. For instance, it increases from 26.2 ppm for the initial ternary mixture up to 72.2 ppm at almost complete monomer conversion (entries 1 and 8 in Table 3). It is worth noting that the ^{119}Sn chemical shift at the end of the polymerization process remains far from 120 ppm, which excludes a pure four-coordinate tin(IV) configuration.

After evaporation under reduced pressure of the solvent and any other volatile components (for instance, residual monomer and/or low molecular-weight macrocyclics) from

the polymerization medium, the resulting solid, which can only be a combination of higher molecular weight poly(ε-caprolactone) (PCL) and tin derivatives, was dissolved in [D$_8$]toluene, and the solution was analyzed by ^{119}Sn NMR spectroscopy. As evidenced by the shift to higher frequency of the ^{119}Sn signal up to 86.0 ppm, it turns out that the tin atom is partially coordinated by one (tin coordination number, CN = 5) and/or two (CN = 6) carbonyl groups from the PCL chains. Such inter- and/or intramolecular coordination of the polyester chains onto the metal is likely to be weaker than the coordination of CL monomer, because of the higher thermal instability of the tin–ligand interaction; this explains the drift to high frequency of the ^{119}Sn signal as the polymerization proceeds. In order to confirm that PCL chains are able to coordinate to the tin atoms, a mixture of Bu$_2$SnCl$_2$ and previously prepared (α-propyloxy)(ω-hydroxyl)poly(ε-caprolactone) was prepared in [D$_8$]toluene so as to reach a concentration very similar to the polymerization experiment ([Bu$_2$SnCl$_2$] = 0.1125 mol L^{-1} and [CL repetitive unit] = 4.5 mol L^{-1}). The ^{119}Sn NMR spectrum shows a single narrow signal with a chemical shift of 83.6 ppm, which is very close to the value observed after the evaporation treatment of the crude polymerization medium.

At this stage, the question still to be addressed concerns the exact origin of the difference in ^{119}Sn chemical shifts before and after evaporation treatment (72.2 and 86.0 ppm, respectively). As stated above, such a discrepancy can only be explained by the presence of volatiles, that is, 0.2% residual monomer and/or macrocyclics formed by intramolecular transesterification reactions [see Eq. (1)]. To evidence the presence or absence of macrocyclics, the crude polymerization product was analyzed before the evaporation treatment by size exclusion chromatography (SEC) and ^{13}C NMR spectroscopy. No trace of low molecular-weight oligomers could be detected by SEC, which diplays a quite narrow polydispersity index (M_n = 4200 and M_w/M_n = 1.31, Figure 5).
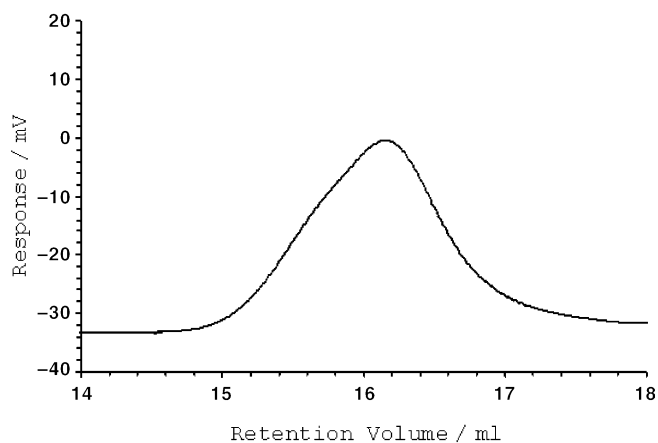
Figure 5. SEC trace of poly(ε-caprolactone) as obtained by direct polymerization of ε-caprolactone in a NMR tube (entry 8 in Table 3).

The ^{13}C NMR spectrum shows three well-separated signals in the carbonyl region; these can be assigned to the carbonyl groups of PCL repetitive units at 173.1 ppm, the propyloxy-carbonyl end-group at 173.3 ppm, and the carbonyl function

of residual monomer at 175.2 ppm, respectively. Confirming this chemical shift assignment, Figure 6 shows the dependence of these specific ^{13}C signals on the monomer conversion.
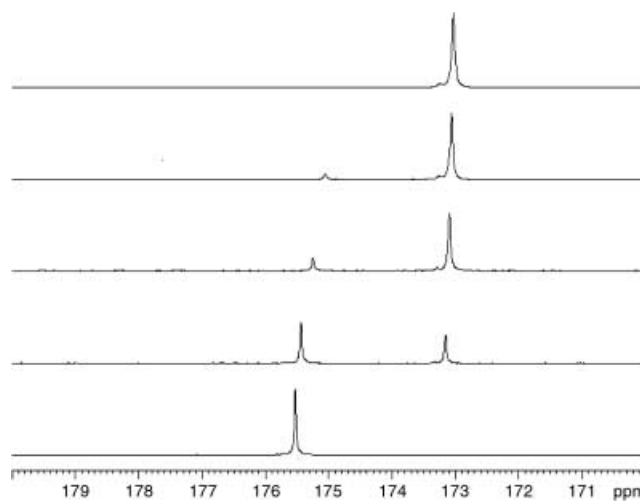
Figure 6. Time dependence of ^{13}C NMR spectra of poly(ε-caprolactone) as obtained by direct polymerization of ε-caprolactone in a NMR tube. From bottom to top; 1) t = 0; 2) t = 42 h; 3) t = 90 h; 4) t = 160 h; and 5) t = 258 h.

As a result, the formation of cyclic oligomers can be excluded, at least within the time required to reach maximum monomer conversion, and the difference in ^{119}Sn chemical shift is then only attributable to the presence of residual monomer. Scheme 2 illustrates the evolution of a tin configuration that likely prevails as the polymerization proceeds. It
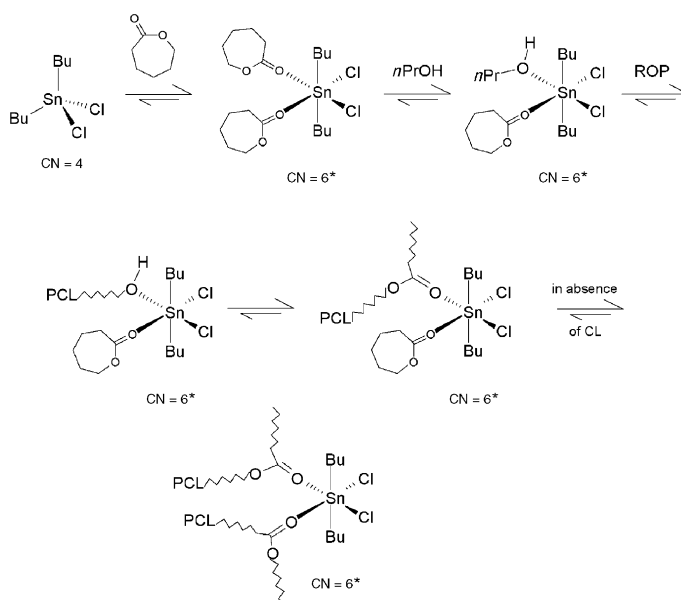
Scheme 2. Tin configuration as the polymerization of CL proceeds (* CN = 4 and 5 are also present).

is worth recalling that a fast dynamic equilibrium between coordinated tin species exists at the polymerization temperature, especially for tin species coordinating n-propanol.

The first part of the initiation/propagation involves the coordination of the monomer to Bu$_2$SnCl$_2$ with a partial extension of the tin coordination number up to six. With the coordination of the monomer, the nucleophilic attack of the oxygen of *n*-propanol onto the monomer carbonyl carbon atom is activated. The formation of the new C–O bond between the monomer and the alcohol probably occurs via a four-center transition state (**2** in Scheme 3). In the intermediate, the former carbonyl oxygen is coordinated to tin through
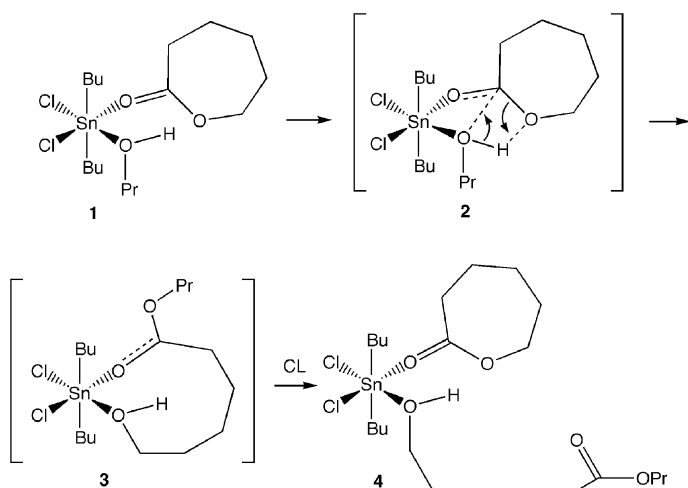
Scheme 3. Plausible mechanism detailing the insertion propagation.

an alkoxide bond (**3** in Scheme 3), but it is rapidly replaced by the coordination of a new monomer molecule with formation of **4** (analogue of **1**). At high monomer conversion, the polyester remains partially coordinated to the tin atom as evidenced by the value of the ^{119}Sn chemical shift close to 72 ppm, while the very labile coordination of the primary hydroxyl group that end-caps the PCL chains is responsible for the occurrence of intermolecular transesterification reactions and the broadening of the molecular-weight distribution. According to such a mechanism, Bu$_2$SnCl$_2$ behaves as a catalyst activating the carbonyl group of the monomer, while the actual initiator is *n*-propanol. The electrophilicity of the metal center plays an important role in the controlled character of the ROP sequence through the higher stability of the tin lowest unoccupied molecular orbital with the monomer highest occupied molecular orbital rather than that of the hydroxyl group. This in turn leads to a control of the polyester molecular parameters: predictable average molar mass from the initial monomer-to-initiator molar ratio and remarkably narrow polydispersity index ($M_w/M_n < 1.1$), even up to high monomer conversion.

Figure 7 shows that the experimental PCL molar mass (M_{nNMR}) increases linearly with monomer conversion meaning that the number of active species remains constant all along the ROP. The M_{nNMR} value was determined by ^{1}H NMR spectroscopy from the relative intensity of methylene protons of the repetitive units at 3.95 ppm (-CH$_2$-O-CO-) and α-hydroxyl methylene protons at 3.35 ppm (-CH$_2$-OH). An excellent agreement exists between the M_{nNMR} at complete
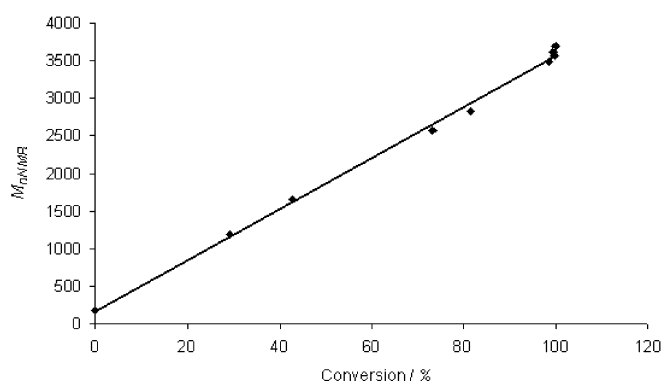

Figure 7. Dependence of poly(ε-caprolactone) molar mass on monomer conversion in [D$_8$]toluene at 353 K ([CL] = 4.5 mol L^{-1}, [*n*PrOH] = 0.145 mol L^{-1} and [Bu$_2$SnCl$_2$] = 0.1125 mol L^{-1}).

monomer conversion (3600) and the theoretical value (3600) calculated by $M_{ntheor} = ([CL]_0/[nPrOH]_0 \times \text{conv.} \times M_{wCL}) + M_{wnPrOH}$, whereby [CL]$_0$ and [*n*PrOH]$_0$ are the initial concentrations of the monomer and the initiator, respectively; M_{wCL} and M_{wnPrOH} are the molecular weights of the monomer and initiator, respectively; and conv. is the monomer conversion.

Conclusion

Ring-opening polymerization (ROP) of cyclic esters can be more or less efficiently initiated by a wide range of ionic and non-ionic organometallic compounds. Covalent metal alkoxides and carboxylates (the latter coupled with alcohols as co-initiators) have been demonstrated to initiate cyclic esters polymerization through a coordination–insertion mechanism. This paper shows that activation of the ROP of cyclic esters and control of molecular parameters can also be achieved by using other tin(IV) derivatives, such as Bu$_2$SnCl$_2$ which probably behaves as a catalyst, while *n*-propanol acts as the initiator. Advanced ^{119}Sn NMR spectroscopy has been shown to be a powerful tool for monitoring the coordination of organotin catalysts and elucidating the polymerization mechanism. The electrophilicity of the metal center plays a key role in the ROP reaction sequence, and more particularly, the propensity towards metal–oxygen bond formation as well as its dynamics and thermal stability.

Experimental Section

Materials: ε-Caprolactone (CL, Acros, 99%) and *n*-propanol (*n*PrOH, Aldrich, 99.5+%) were dried over calcium hydride at room temperature for 48 h and then distilled under reduced pressure. As far as polymerization experiments were concerned, dibutyltin(IV) dichloride (Bu$_2$SnCl$_2$, Aldrich, 96%) was dried by three successive azeotropic distillations of toluene, while it was preliminarily crystallized from petroleum ether at 0 °C for NMR mechanistic studies. Toluene (Labscan, 99%) was dried by refluxing over CaH$_2$ and distilled just before use under inert atmosphere. For the sake of accuracy, *n*-propanol and Bu$_2$SnCl$_2$ solutions in dry toluene were prepared just before use ([*n*PrOH] = 0.45 mol L^{-1} and [Bu$_2$SnCl$_2$] = 2.256 × 10^{-2} mol L^{-1}).

Ring-opening polymerization of ε-caprolactone: A typically representative polymerization experiment is reported here. In a preliminarily flamed and nitrogen purged round-bottomed flask equipped with a three-way stopcock

and a rubber septum, ε-caprolactone (5.0 mL, 45.12 mmol), a solution of Bu$_2$SnCl$_2$ in toluene (1.0 mL, 2.256×10^{-2} mmol) and toluene (3.0 mL) were added. The reaction medium was heated up to 100 °C before a solution of *n*-propanol in toluene (1.0 mL, 0.45 mmol) was added. After a reaction time of 48 h, the reaction product was poured into cold heptane (80 mL). The polymer was recovered by filtration and dried under reduced pressure at 40 °C until constant weight was achieved. Yield = 24 %. In order to extract undesired tin(IV) residues, the polymer was dissolved in CHCl$_3$ (1 g in 10 mL) and added to an aqueous solution of HCl (10 mL, 0.1 mol L^{-1}) in a separating funnel. The organic phase was recovered, washed twice over with deionized water, and poured into cold heptane (80 mL). The purified polyester was recovered by filtration and dried under reduced pressure at 40 °C until constant weight. ^{1}H NMR (500 MHz, [D$_8$]toluene): $\delta = 0.81$ (t, 3H; Me in propyloxy), 1.0 – 1.7 (m, 8H; methylene of the repetitive units (6H) and propyloxy (2H)), 2.07 (t, 2H; methylene adjacent to CO-O), 3.35 (t, 2H; methylene adjacent to hydroxyl), 3.95 ppm (t, 4H; methylene adjacent to O-CO (2H) and propyloxycarbonyl (2H)). $M_n = 2600$. $M_w/M_n = 1.04$.

Characterization: ^{1}H, ^{13}C, and ^{119}Sn spectra were acquired on an upgraded AMX 500 spectrometer tuned at 500.13, 62.90, and 186.5 MHz, respectively, with [D$_8$]toluene as a solvent. Chemical shifts were referenced to residual toluene peaks and converted to the standard Me$_4$Si scale by adding 7.00 and 137.9 ppm for ^{1}H and ^{13}C, respectively. For ^{119}Sn nuclei, absolute external referencing with $\Xi = 37.290665$ MHz was used.[25] Typical ^{119}Sn acquisition parameters were: acquisition time: 0.85 s; recycling time: 1 s; number of scans: 2048; digital resolution in the FID: 0.59 Hz per pt; spectral width: 38 461 Hz; pulse length: 15.0 μs; inverse-gated proton broad-band decoupling: Waltz16. Typical ^{13}C acquisition parameters were: acquisition time: 1.25 s; recycling time: 4 s; number of scans: 400; digital resolution in the FID: 0.40 Hz per pt; spectral width: 26 316 Hz; pulse length: 15.0 μs; proton broad-band decoupling: Waltz16. Typical ^{1}H acquisition parameters were: acquisition time: 0.59 s; recycling time: 10 s; number of scans: 32; digital resolution in the FID: 0.85 Hz per pt; spectral width: 6944 Hz; pulse length: 9.9 μs.

Size exclusion chromatography (SEC) was performed in THF at 35 °C by using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL min^{-1}), a Marathon autosampler (loop volume = 200 μL, solution conc. = 1 mg mL^{-1}), a PL-DRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-B 10 μm columns (linear columns for separation of PS molecular weight ranging from 500 to 10^6 Da). Poly(styrene) standards were used for calibration. Molar masses were calculated by reference to a poly(styrene) standard calibration curve, using the Mark – Houwink relationship $[\eta] = KM^a$ for PS and PCL ($K_{PS} = 1.25 \times 10^{-4}$ dL g^{-1}, $a_{PS} = 0.707$, $K_{PCL} = 1.09 \times 10^{-3}$ dL g^{-1}, $a_{PCL} = 0.600$).

Acknowledgement

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