Undecyltin Trichloride Grafted onto Cross-Linked Polystyrene: An Efficient Catalyst for Ring-Opening Polymerization of ε-Caprolactone

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The activity, recyclability, and chemical stability as a catalyst of undecyltin trichloride grafted to cross-linked polystyrene, $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnCl}_3]_t$, with $[\mathbf{P}\text{-H}]$ the monomeric unit of the nonfunctionalized polymer and t the organotin-functionalized monomer fraction, are assessed in the ring-opening polymerization (ROP) of ε-caprolactone. Quantitative conversion is obtained within 2 h under conditions in which conversion is by far incomplete for two other organotin grafts, $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnBuCl}_2]_t$ and $[\mathbf{P}\text{-H}]_{(1-t)}\{[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnBuCl}]_2\text{O}\}_{t/2}$. Even after 15 min of reaction, conversions of at least 70% are achieved for the grafted tin trichloride. The catalytic reactions of the grafted undecyltin trichloride, more particularly its chemical integrity and recycling ability, are monitored, *in situ*, at the solid–liquid interface, using high-resolution magic angle spinning (HR-MAS) ^{1}H and ^{119}Sn NMR. Residual tin contents in the reaction products were assessed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The polydispersity index of the synthesized poly(ε-caprolactone), investigated with size exclusion chromatography, is closer to unity than for grafted tin dichloride catalysts.

Introduction

(Trans)esterifications are widely applied in industry,[1] e.g., in the synthesis of aspirin (acetylsalicylic acid), fatty acid esters,[2,3] polyesters,[4–9] and macrolides.[10] More specifically, polylactones and polylactides are multipurpose, biocompatible, and biodegradable polyesters, used in biomedical and pharmaceutical applications.[11–14]

(Trans)esterifications generally need to be catalyzed. Tin-based Lewis acids such as mono- and dialkyltin compounds[4,15–19] and tetraalkyldistannoxanes[8,20–22] are good examples of efficient catalysts for transesterifications under mild conditions. Their toxicity and difficult removal from reaction mixtures remain, however, drawbacks to their use in organic synthesis and limit their exploitation in industrial, biomedical, and pharmaceutical applications.[23,24] Less toxic nonstannylated catalysts have been the subject of extensive investigations; for example, organic amino calcium derivatives,[25] homoleptic lanthanide amidinate,[26]

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titanium, zinc, and magnesium alkoxide complexes,[27–32] zirconium oxide derivatives,[33–36] organocatalytic systems such as heterocyclic carbenes,[37,38] triazabicyclodecene[38,39] and guanidine and amidine organocatalysts,[38,40] and/or improvements of workup procedures of homogeneous organotin catalysts were explored. More recently, however, Otera et al. reported on perfluoroalkyl distannoxanes, which combine the advantages of organotin catalysis with fluorous biphasic technology.[21,41] Complete removal from the reaction mixture, as well as high recyclability of the latter catalysts, can be easily achieved owing to their temperature-dependent phase behavior. In view of their high solubility in fluorocarbon solvents, these perfluoroalkyl distannoxanes become fully miscible with the reaction mixture upon heating. Upon cooling, however, phase separation occurs and the catalyst can be easily recovered from the fluorous reaction phase. Another strategy to alleviate toxicity and tin leaching into the environment consists of grafting the organotin reagent onto an insoluble carrier.[24,42–47] In this way, organotin reagents can be easily removed from the desired reaction products by simple filtration of the insoluble support to which they are grafted. In previous studies, our group reported on the catalytic properties of cross-linked polystyrene-grafted organotins of the type $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_n\text{-SnBuX}_2]_t$,[14,45–48]

$[\mathbf{P}\text{-H}]_{(1-t)}\{[\mathbf{P}\text{-}(CH_2)_n\text{-SnBuY}]_2O\}_{t/2}$ ($n = 4$, 6, or 11),[46,47] and $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_n\text{-SnCl}_3]_t$ ($n = 4$),[47] in which $[\mathbf{P}\text{-H}]$ represents the monomer unit of the cross-linked polystyrene matrix, X = Ph, Cl, OH, OOCCH₃, Y = Cl, OH, OOCCH₃, and t is the molar fraction of organotin-functionalized styrene monomers' functionalization degree. Recently, investigations on $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_n\text{-SnCl}_3]_t$ ($n = 11$) evidenced the benefits of using C11 rather than C4 spacers for model transesterifications, showing high catalytic activity, stable catalytic performances, good recyclability, and limited tin leaching.[49]

Poly(ϵ-caprolactone), hereafter PCL, is readily synthesized from ϵ-caprolactone (CL) by ring-opening polymerization (ROP).[50–52] The associated living polymerization mechanism usually enables one to achieve a good control over its polydispersity index, at least when appropriate catalysts are used.[14,53] Their bioavailability and biodegradability through enzymatic and/or hydrolytic chain cleavage of their ester functions make them suitable for biomedical and pharmaceutical applications, e.g., as temporary implant materials and resorbable carriers for controlled drug delivery.[54–56] Previous studies evidenced that grafted dialkyltin dichlorides of the type $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_n\text{-SnBuCl}_2]_t$, with $n = 6$ or 11, are fair catalysts for the ROP of CL.[14] Furthermore, the need for a longer spacer length containing 11 rather than 6 methylene moieties has been demonstrated, reducing the polydispersity index of the synthesized PCL.[14]

In the present work, the catalytic properties of grafted undecyltin trichloride, $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_{11}\text{-SnCl}_3]_t$ (hereafter C11SnCl₃), are investigated in the ROP of CL. Focus hereon is dictated by the facts that (i) the latter catalyst, together with its C4 spacer analogue, C4SnCl₃, recently appeared to display the highest catalytic activity noted so far for grafted organotins in transesterification model reactions[49] and (ii) the C11 spacer-based diorganotin dichloride graft provides better polymer properties and catalyst recyclability in ROPs than the C4- and/or C6-based analogues;[14] in particular, the C6 spacer-grafted tin dichloride gives rise to catalyst bead burst in ROPs, while this problem is effectively overcome using the C11 analogue.[14]

¹H and ¹¹⁹Sn high-resolution magic angle spinning (HR-MAS) NMR spectroscopy is used to monitor the C11SnCl₃ graft directly *in situ* at the solid–liquid interface during or after the catalytic processes. Tin trace leaching from C11SnCl₃ into the polymerization products under these reaction conditions is assessed using inductively coupled plasma/atomic emission spectroscopy (ICP/AES).

Results and Discussion

Catalytic Activity in the Ring-Opening Polymerization of ϵ-Caprolactone. The catalytic efficiency of the grafted C11SnCl₃ catalyst, the synthesis and characterization of which were described previously (Scheme 1),[49] is explored in ROP experiments of CL initiated by 10 mol % *n*-propanol (Scheme 2), using 0.5 mol % tin catalyst with respect to CL monomer.

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Scheme 1. Synthetic Scheme of the Grafted Tin Trichloride with the C11 Spacer
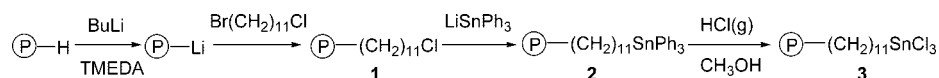
Scheme 2. Reaction Scheme of the Ring-Opening Polymerization of ε-Caprolactone Initiated by 10 mol % *n*-Propanol and Catalyzed by 0.5 mol % of Grafted C11SnCl₃ with Respect to the Initial Amount of CL Monomer
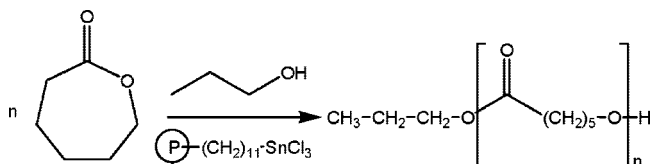
In a first set of experiments, the reaction was carried out for 2 h in dry toluene under moisture-free nitrogen at 100 °C. This study emphasizes the possibility to recycle the catalyst throughout a number of polymerization runs without significant loss of activity, striving to limit recycling constraints (such as extensive washings) between two runs to the strict minimum. The supported catalyst was retrieved from the reaction medium by simple filtration and briefly washed with toluene. Subsequently, its state was analyzed by HR-MAS NMR spectroscopy after each catalytic run. The conversion of CL and the degree of polymerization in the reaction mixture were likewise analyzed after each run. The catalyst was then dried and reused in a subsequent reaction run.

After the first polymerization run, the ^{119}Sn HR-MAS resonance of C11SnCl₃ is shifted to lower frequency by ca. 57 ppm (Figure 1b) with respect to nonused catalyst (3 ppm; line width 1200 Hz) (Figure 1a). The signal has basically collapsed into the noise, being hardly visible and extremely broad (Figure 1b). The low-frequency shift of the ^{119}Sn resonance can be explained by a coordination change of the tin atom from pure four-coordination to a dynamic equilibrium state involving the latter and five- and/or six-coordination, caused by residual polymerization residues still present in the pores of the material and interacting with the tin atom. The presence of a single, coalescing broad band is explained by the exchange averaging equilibrium between these various organotin coordination species or transients being moderately fast on the ^{119}Sn NMR time scale. This interpretation is confirmed by the presence, after the reaction, of additional ^{1}H HR-MAS resonances all assigned to residual PCL left behind in the catalyst beads. Subsequently, the used catalyst was subjected to a thorough Soxhlet extraction at refluxing temperature of methylene chloride, after which the HR-MAS ^{1}H spectrum only shows minor resonances of residual PCL being left. The ^{119}Sn HR-MAS resonance recovered nearly its original chemical shift, however with a signal-to-noise reduction by ca. 1/2, an increased line width equal to ca. 2050 Hz, and a significant additional shoulder at the low-frequency side of the resonance under the same acquisition conditions (Figure 1c). The signal-to-noise ratio shows further decrease with increasing number of runs (Figure 1, for the third (d), fifth (e), and 10th (f) run). This is explained by additional cross-linking of organotin moieties at the interface resulting in a restricted local rotational molecular mobility of the graft, such that an essential prerequisite to the HR-MAS technique is no longer fulfilled. This, in turn, unavoidably results in signal collapse for that fraction of organotin grafts that underwent loss of rotational mobility as a consequence of their interfacial cross-linking. This chemical modification does not affect the efficiency of the catalyst since quantitative conversions remain further obtained upon repetitive reuse during 2 h of reaction time. After

9-fold recycling, the C11SnCl₃ catalyst is again subjected to a thorough Soxhlet extraction with methylene chloride. The ^{119}Sn HR-MAS resonance reappears at its original chemical shift (3 ppm) with practically the same line width (1350 Hz) as for the intact, nonused catalyst, however with an important signal-to-noise reduction by nearly a factor of 4 with respect to the nonused catalyst and a significant additional shoulder at the low-frequency side of the resonance (Figure 1g). A part of the SnCl₃ moiety is clearly regenerated, while the remaining tin that is no longer visible by HR-MAS NMR is chemically modified to a more cross-linked organotin moiety, explaining the loss of signal-to-noise. Tin leaching, being negligible as shown below, is not responsible for the major signal-to-noise reduction of the ^{119}Sn HR-MAS resonance.

This cross-linking phenomenon was likewise observed for C11SnCl₃ in model transesterifications and thoroughly analyzed by modulated temperature differential scanning calorimetry (MTDSC).[49] MTDSC experiments in this work on the nonused and recycled C11SnCl₃ aimed at providing further evidence for organotin cross-linking at the interface, and for the associated loss in molecular chain mobility as assessed by their glass transition temperature (T_g). The temperature derivative of the MTDSC heat capacity signal, in which the glass transition appears as a marked peak, is used for efficiently evidencing small changes in the shape and position of T_g.[57,58] Altered peak shapes are clearly observed after one or more polymerization run(s) (Figure 2): along with a progressive decrease in the intensity of the main glass transition around 50 °C, a significant shoulder appears at the high-temperature side of T_g (at ca. 80 °C). This convincingly evidences that part of the polystyrene grafted organotin compound undergoes a progressive loss in segmental mobility after use in the ROP of CL, in full agreement with the conclusion formulated from the ^{119}Sn HR-MAS NMR spectra.

Finally, ^{117}Sn CP-MAS spectra show an anisotropy pattern with an isotropic shift around 6 ppm for nonused C11SnCl₃ catalyst; after a single run already, without washing, the latter pattern vanishes, while another broad, ill-defined, and noisy pattern extending from −270 to −500 ppm becomes visible. Upon Soxhlet extraction, the original pattern is only partially restored, being in turn very noisy. This observation is in line with the assumed chemical cross-linking modification (apparently coupled to coordination expansion), as was concluded above on the basis of MTDSC experiments and the loss of signal-to-noise ratio in ^{119}Sn HR-MAS NMR spectra.

The low-frequency shoulder of the ^{119}Sn HR-MAS resonance can be assigned to residual ROP components that cannot be fully extracted from the catalyst pores by Soxhlet extraction and that still interact with the tin atom of the fraction of the chemically unaltered SnCl₃ moiety. Residual chemical shift anisotropy distortion is considered unlikely, since it is not observed for nonused catalyst.

A number of additional experiments were performed in an attempt to characterize further this phenomenon of interface modification of the catalyst upon increasing the number of

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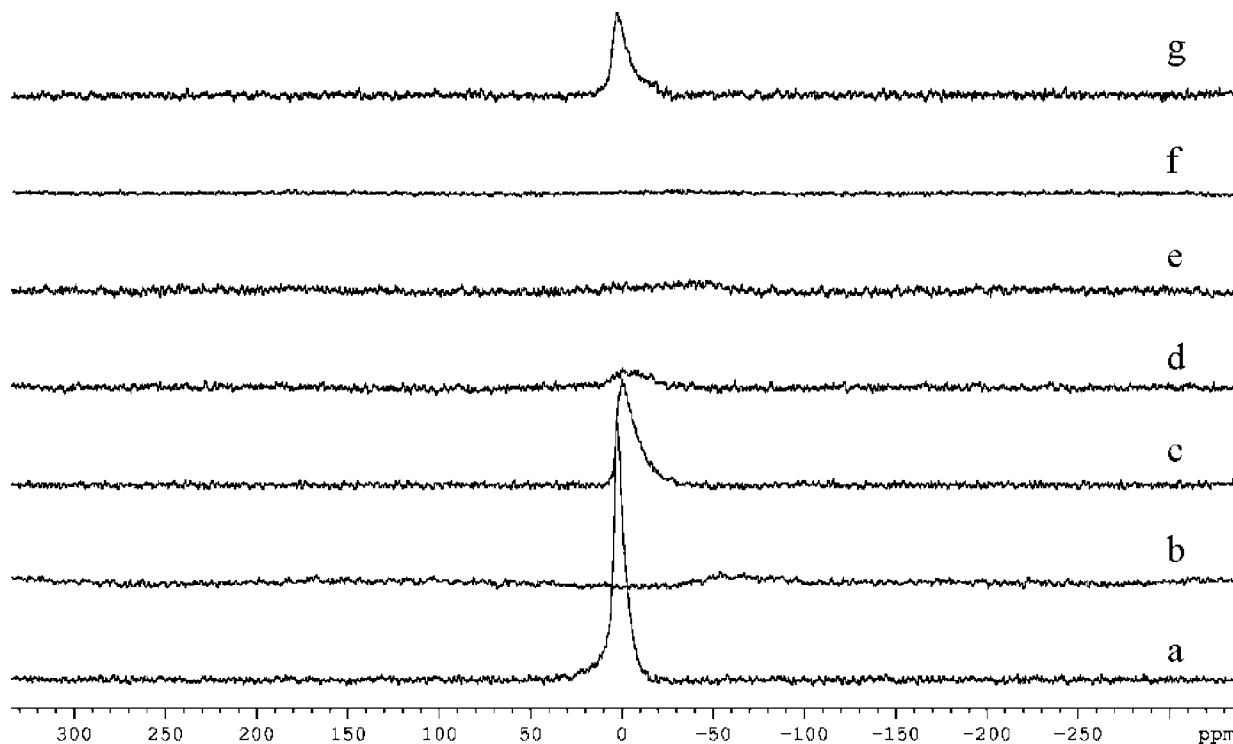
Figure 1. ^{119}Sn HR-MAS NMR spectra of grafted C11SnCl₃ catalyst in CDCl₃ in different states: nonused (a), after the first polymerization run (b), after thorough Soxhlet extraction with CH₂Cl₂ of the catalyst after this first ROP run (c), after the third run (d), after the fifth run (e), after the 10th run (f), and after Soxhlet CH₂Cl₂ extraction after the latter 10 successive runs (g).
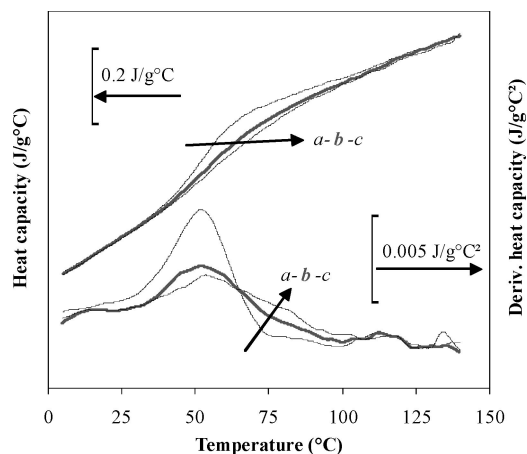

Figure 2. Modulated temperature differential scanning calorimetry profiles showing the glass transition region of nonused catalyst (a), the catalyst after one polymerization run (b), and after 10 runs (c).

catalytic runs and to refine insights into the issue of the catalytic mechanism. Several previous studies[4,14,49,59] led to the convergent conclusion that organotins, either in homogeneous solution[4,59] or grafted at a liquid–solid interface,[14,49] find the origin of their catalytic activity in transesterification reactions in coordination expansion of the tin atom by the nucleophilic reaction components, the ester and the alcohol. This results in a fast equilibrium between noncoordinated alkyltin chloride and its complexes resulting from weak interactions of the tin atom with the esters and alcohols.[4,14,49,59] To the best of our knowledge, no evidence is available from the literature that, in the presence of an alcohol as a polymerization initiator, the organotin would act as an initiator of ring-opening polymerization, and none of our own studies provided evidence for this.[4,14,46,47,49] Organotins do act as an initiator only in the absence of alcohol, as documented recently.[60] In spite of these data, the question arises whether the catalytic activity could result from hydrogen chloride generated *in situ* upon alcoholysis of the alkyltin trichloride due to heating of the reaction mixture in toluene at 100 °C. This issue is now addressed. Mimicking the ROP reaction conditions used (2 h, toluene at 100 °C), BuSnCl₃ was refluxed for 3 h in toluene in the presence of *n*-propanol in the molar ratio 1:20. [1]H and [119]Sn spectra recorded after complete evaporation of the solvent mixture were identical to those of a freshly prepared BuSnCl₃ solution in CDCl₃, excluding any detectable irreversible formation of a *n*-PrO−Sn bond, meaning unambiguously that alcoholysis converting BuSnCl₃ into a butyltin alkoxide and HCl does not take place under the reaction conditions used. Refluxing the grafted C11SnCl₃ catalyst in toluene for 3 h in the presence of *n*-propanol in the molar ratio 1:20 (comparable to catalytic reaction conditions), followed by complete evaporation and a ^{119}Sn HR-MAS NMR spectrum recording in CDCl₃ provided a similar result, only a single resonance with a [119]Sn chemical shift at +2 ppm, to be compared to that of the initial fresh, nonused catalyst at +3 ppm,[49] confirming the lack of evidence for the formation of any tin alkoxide under HCl elimination or any other tin species that would result from chlorine substitution.

Further indirect evidence for noninvolvement of HCl generated *in situ* in the catalytic process is provided by the fact that, while 98% of ε-caprolactone is converted into polymer within 15 min during the first catalytic run when grafted 0.5 mol % of C11SnCl₃ is used, only 71% of conversion was observed in the presence of 0.1 mol % of added HCl instead of C11SnCl₃, indicating a slightly lower catalytic efficiency of the latter; this

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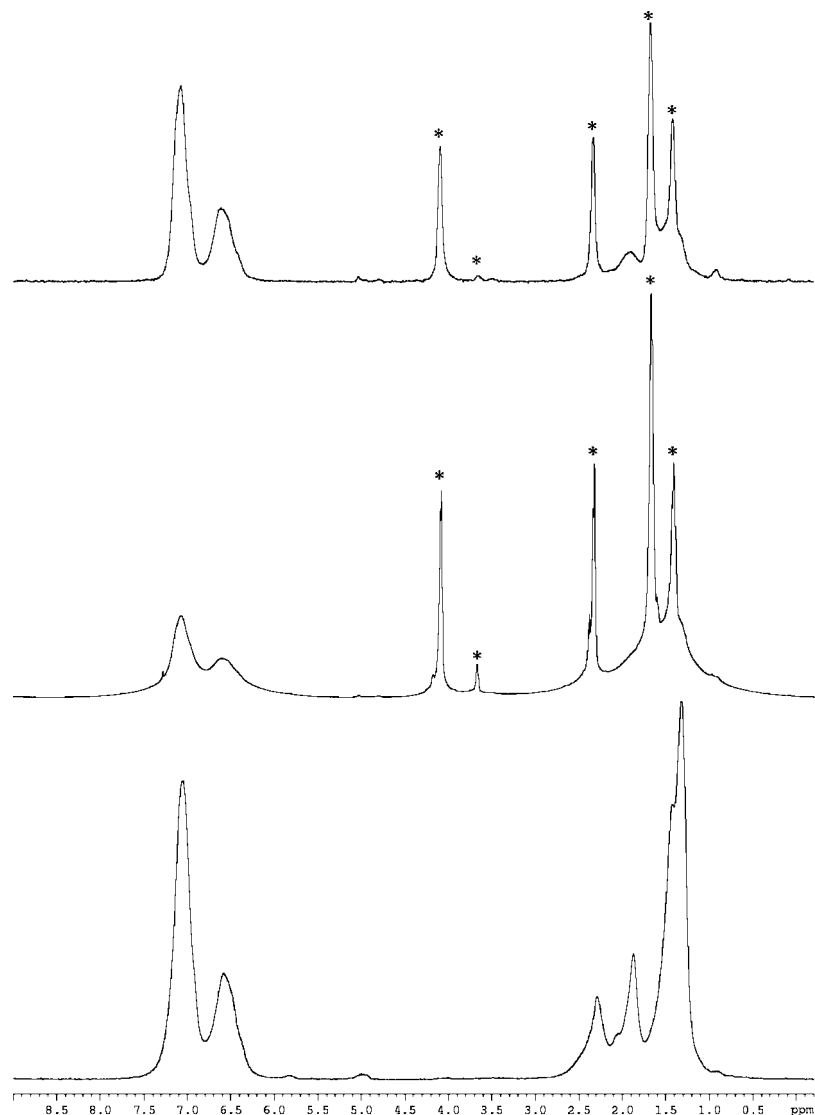
Figure 3. Diffusion filtered ^{1}H HR-MAS NMR spectrum of fresh C11SnCl$_3$ catalyst[49] (bottom), and standard (middle) and diffusion filtered (top) ^{1}H HR-MAS NMR spectrum after use of C11SnCl$_3$ in 10 successive recycling catalytic ROP runs. Resonances marked by an asterisk originate from PCL, as deduced from the ^{1}H NMR spectrum of Figure 4.

shows at least that even if HCl would be generated *in situ*, unlike the above-mentioned evidence against this, it cannot be the most determinant factor for the observed high catalytic activity of C11SnCl$_3$. Interestingly, the grafted C11SnCl$_3$ appears catalytically slightly more efficient than its molecular, nongrafted solution analogue, since using 0.5 mol % of BuSnCl$_3$ under otherwise identical reaction conditions provided a conversion of CL in 15 min of reaction of only 74% instead of 98% with C11SnCl$_3$.

Elemental analysis of the catalytic material after a single run does suggest a loss of chlorine from 10.7% to 8.4%, but this was accompanied by an increase of the carbon content from 66.4% to 67.8%. While, at first glance, this might suggest some split off of chlorine from tin, it must be realized that the interface cross-linking of the tin moiety upon increasing the number of catalytic runs, supported by the carbon content increase and the T_g measurements above, also necessarily results in a relative decrease of the chlorine content, even without chlorine split off.

Altogether these data converge to the reasonably safe conclusion that the partial catalyst alteration upon increasing reaction runs is not due to some grafted tin alkoxide generation under HCl elimination, but does indeed result from the additional cross-linking of tin moieties.

In an effort to precise the nature of this catalyst interface alteration, ^{1}H HR-MAS spectra of the material obtained after the 10th catalytic run were recorded (Figure 3, top and middle) and compared with a standard solution ^{1}H NMR spectrum of PCL (Figure 4). This reveals that the additional *-labeled HR-MAS resonances of Figure 3 result from residual PCL present within the material pores after the catalytic runs.

The diffusion filtered[49] spectrum (Figure 3, top) displays only resonances from PCL grafted to the material, while the standard one (Figure 3, middle) displays *all* PCL resonances, from grafted as well as translationally free PCL remnants. Taking the aromatic resonances of the polystyrene matrix in the 6.0−7.5 ppm range as a signal amplitude reference, comparison of both HR-MAS spectra (Figure 3, top and middle) indicates that even though a significant part of PCL molecules are free in solution, the fraction of PCL chains remaining grafted to the material is far from negligible (Figure 3, top). Nevertheless, since these grafted PCL resonances remain also rather sharp (Figure 3, top), it can be concluded that the grafted PCL chains also have a high degree of conformational mobility. On the other hand, comparing the diffusion filtered[49] HR-MAS spectra of fresh, nonused catalyst (Figure 3, bottom) and those of the catalyst after the 10th run (Figure 3, top) reveals a significant loss of
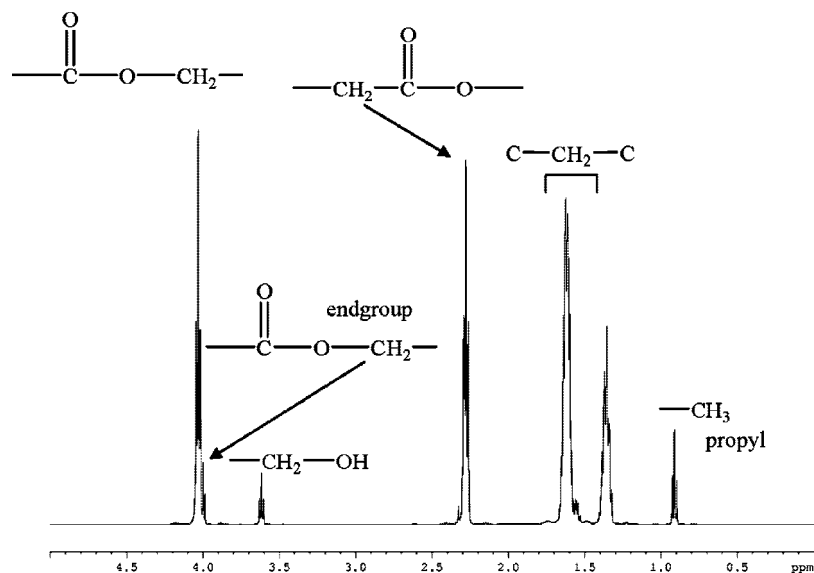
Figure 4. ^{1}H NMR spectrum (CDCl$_3$) of the crude reaction product, as obtained by ROP of CL initiated by *n*-propanol in the presence of grafted C11SnCl$_3$ catalyst in toluene at 100 °C after 2 h (run 2, Table 1). The absence of any resonance from the monomer indicates quantitative monomer-to-polymer conversion.

Table 1. Conversion, Yield, Degree of Polymerization (DP), Number-Average Molar Masses, As Assessed Both *in Situ* by NMR and after Polymer Isolation by SEC, and Polydispersity Index of Synthesized PCL in Successive Runs of ROP of CL Initiated by 10 mol % *n*-PrOH and Catalyzed by 0.5 mol % C11SnCl$_3$ with Respect to CL in Toluene at 100 °C for a Reaction Time of 2 h ([CL]$_0$ = 6.28 mol L^{-1})

	conversion			$M_{n,exp}$[b]		
run	NMR [%]	yield [%]	DP int. data[a]	NMR	SEC[c]	M_w/M_n[d]
1	98	68	8.8	1060	1110	1.9
2	100	71	10.4	1260	1060	1.5
3	100	72	13.5	1600	1300	1.7
4	100	79	8.0	970	1220	1.7
5	99	72	9.4	1130	980	1.7
6	100	78	7.8	950	910	1.6
7	100	74	8.2	1000	1130	1.6
8	100	74	8.2	1000	1040	1.8
9	100	84	7.8	950	840	1.6
10	100	80	8.2	1000	1080	1.7

[a] Int. data represent ^{1}H NMR spectrum integration data. [b] $M_{n,exp}$ is the experimental number-average molar mass; estimated experimental errors for determination by NMR: ±100; by SEC: ±150. [c] SEC = size exclusion chromatography. [d] M_w is weight-average molar mass, and M_w/M_n represents the polydispersity index.

amplitude in the resonances of the C11 spacer in the aliphatic 1.0–2.5 ppm chemical shift range, in spite of the presence of overlapping PCL resonances in this range. This suggests loss of conformational mobility for the C11 spacer, unlike the grafted PCL chains, after the 10 catalytic runs.

Therefore, we tentatively suggest that the interface cross-linking arises from bridging of two tin moieties by intermolecular coordination expansion through the two oxygen atoms of a terminal carboxyl group of a pendant PCL chain used as a bidentate ligand coordinating the two tin atoms. This proposal is compatible with the noisy [117]Sn solid state pattern extending from −270 to −500 ppm, as mentioned above, with the loss of conformational mobility of the C11 spacer, and with the undisputable high conformational mobility of the grafted PCL chain. This view is, last but not least, in agreement with the well-known bridging capacity of carboxylate ligands between

tin atoms in organotin-functionalized polystyrenes.[61,62] Such carboxylates bridging two tin atoms display characteristic C=O and C−O stretching bands in the 1550–1560 and 1410–1425 cm^{-1} ranges,[61,62] which we do observe at 1553 and 1417 cm^{-1} in the grafted C11SnCl$_3$ catalyst after the 10th run, but which are absent in the IR spectra of both nonused catalyst and pure isolated PCL. On the other hand, the characteristic ester bands of pure isolated PCL at 1723 and 1246 cm^{-1} are in excellent agreement with those of grafted PCL at 1735 and 1235 cm^{-1} observed in the C11SnCl3 catalyst after the 10th catalytic run. This view also conforms to the suggestion formulated recently[49] for a similar catalyst interface modification involving possibly an acetate moiety in the model transesterification reaction of ethyl acetate by *n*-octanol.

In spite of all these chemical changes at the interface, already after the first run, the organotin catalyst could be reused in 10 consecutive ROP runs without any observable loss of catalytic activity, at least when a reaction time of 2 h is allowed. This is not so surprising since a pendant PCL chain, with its terminal CH$_2$OH moiety (evidenced by a minor resonance around 3.6 ppm in the ^{1}H NMR spectra of Figures 3 and 4), left behind by the previous catalytic run, appears as a convenient alternative and/or competitive initiator to *n*-propanol for the ROP of CL in the subsequent run, even though diffusive access hampering of the reagents to the tin atom caused by excessively accumulating interface cross-linking can also be a limiting factor (see below).

Characteristics of the Poly(ϵ-caprolactone). The conversion degree of CL monomer and the degree of polymerization (i.e., the average number of repeat units in the polymer chain) were assessed by integration of the appropriate ^{1}H resonances of the liquid reaction mixture obtained after each catalytic run (Figure 4).

The conversion degree can be calculated from the relative integrated areas of the CH$_2$−O−CO proton resonances of the PCL repeat units at δ = 4.1 ppm and the corresponding ones

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Table 2. Conversion and Yield of Synthesized PCL, Number-Average Molar Masses, As Assessed Both *in Situ* by NMR and after Polymer Isolation by SEC, and Polydispersity Index, in Subsequent Runs of ROP of CL Initiated by 10 mol % *n*-PrOH and Catalyzed by 0.5 mol % C11SnCl₃ with Respect to CL in Toluene at 100 °C for a Reaction Time of 15 min ([CL]₀ = 6.28 mol L⁻¹)ᵃ

	run										
	1	2	3	4	5	6	7	8	9	10	11
conversion [%]	98	97	95	96	95	95	89	82	81	74	99
yield [%]	79	75	74	74	75	75	69	62	61	57	76
DP	9.0	8.6	8.5	8.4	7.1ᵇ	8.3	7.8	6.9	6.5	6.2	8.8
$M_{n,exp}$ᶜ NMR	1090	1040	1030	1020	870ᵇ	1000	960	840	800	760	1060
SEC	1280	1050	1090	1150	1160	1000	950	760	1020	1120	700
M_w/M_n	2.2	1.6	1.6	1.7	1.7	1.6	1.5	1.6	1.7	1.4	1.9

ᵃ Symbol significance, see Table 1. ᵇ Numerical value considered less accurate because of the presence of an impurity resonance overlapping with the CH₂OH resonance of PCL. ᶜ See footnotes *b* and *c* in Table 1.

in the monomer at $\delta = 4.2$ ppm. As there is no proton resonance visible at 4.2 ppm in almost every run (except for runs 1 and 5, less than 1% integrated area), it is clear that the conversion is complete within 2 h of reaction (see Table 1).

When compared to the previous data on CL polymerization under similar conditions with the [**P**-H]$_{(1-t)}$[**P**-(CH₂)$_n$SnBuCl₂]$_t$ (n = 6 or 11) catalyst,[14] it can be stated that the reaction rate is much higher; hence the C11SnCl₃ catalyst is much more efficient. Moreover, this quantitative conversion was persistently observed within 2 h throughout all subsequent polymerization runs. In addition to the values for the conversion degree calculated from the ¹H NMR spectrum, the yield of isolated, purified PCL is determined gravimetrically by weighing the dried isolated oligomers after purification by three selective precipitation–dissolution cycles using heptane as nonsolvent (Table 1). The yield of isolated polymer, averaging 75 ± 5% (N = 10), is systematically lower than the respective conversion degree determined on the crude reaction mixture, showing that the isolation procedure is subject to mass losses into the filtrates, most likely due to the more soluble oligomers with a lower number of repeat units. The expected number-average molar mass value of the synthesized PCL amounts to $M_{n,exp} = 1201$ g/mol, as calculated from the initial monomer-to-alcohol molar ratio of 10 under the assumption of a living coordination–insertion mechanism initiated by *n*-PrOH and with all the initiator converted and included in the polymer chain ($M_{n,th} = ([CL]_0/[n\text{-}PrOH]_0 \times MW_{CL}) + MW_{n\text{-}PrOH}$). Except for run 3, where an abnormally high experimental $M_{n,exp}$ of 1600 was obtained for unknown reasons, the agreement between the expected and experimentally determined molar masses is satisfactory, for those determined by both NMR and SEC.

The degree of polymerization of PCL (DP in Table 1) was determined from the integrated areas (I) of the CH₂−O−CO proton resonance of its repeat units ($\delta = 4.1$ ppm) and from the end-group proton resonances, more specifically from the CH₂−OH proton resonances ($\delta = 3.6$ ppm). The obtained DP appears to be slightly lower than the expected value of 10 in a living polymer mechanism, averaging around 8, except for runs 2 and 5, where it is close to 10, and again for the deviating run 3, where it is abnormally high. The latter can possibly be explained by transesterification of two or more oligomers. The $M_{n,exp}$ values have been determined by both size exclusion chromatography (SEC) with reference to polystyrene standards in combination with the Mark–Houwink–Sakaruda relationship[14,63–65] (see Experimental Section) and quantitative ¹H NMR spectroscopy in CDCl₃. In the latter approach, the

experimental number-average molar mass is simply acquired by the sum of the molar mass of the CL monomer multiplied by the calculated degree of polymerization (DP), to which the molar mass of the initiator (*n*-PrOH) is added ($M_{n,exp(NMR)} = (DP \times MW_{CL}) + MW_{n\text{-}PrOH}$). It should be realized, however, that the data obtained from the integrated areas of the NMR signal are subject to a significant variability. This results from the fact that the degree of polymerization is obtained from the polymer-to-initiator resonance ratio, which is in itself subject to a theoretical dynamic range of 10, therefore assigning a rather high relative uncertainty to resonance areas of the initiator.

An additional interesting observation is the systematic decrease of the integrated resonance of the CH₃ end-group ($\delta = 0.9$ ppm) of the propoxy group, originating from the propanol initiator, with respect to the signal of the CH₂−OH protons ($\delta = 3.6$ ppm) as the number of catalytic runs increases. This indicates that the initiation of the polymerization undergoes increasing competition by remnant ring-opened CL and/or water in the material pores as the catalyst is recycled. In the opposite case the ratio of CH₃ to CH₂−OH resonance integrals should remain constant at 3/2, while it actually displays this value only for the first couple of runs, to steadily decrease from run to run in the subsequent ones until an end value of 1.22 is attained. As a consequence, this fact adds to the uncertainty of the $M_{n,exp}$ values determined from NMR, as they are directly related to the DP values. Nevertheless NMR and SEC provide $M_{n,exp}$ values in reasonable mutual agreement. Size exclusion chromatography reveals molar mass distributions with polydispersity indices (M_w/M_n) ranging from 1.6 to 1.9 (Table 1). These values are of the same order of magnitude as with previously reported grafted C11BuSnCl₂ catalyst, showing that with C11SnCl₃, as well, a remarkably narrower distribution is achieved than for C6BuSnCl₂ under similar conditions.[14] Nevertheless, it can be concluded that the reaction does not take place under ideal living polymerization conditions and is probably partially hampered by diffusion issues within the catalyst pores.

Short-Term Catalytic Runs. In order to obtain insight into the reaction progress within the predetermined 2 h, an aliquot of the reaction mixture is taken every 10 min. From ¹H spectra it can be concluded that already after 10 min a conversion of 96% is achieved using the C11SnCl₃ catalyst. This finding, revealing extremely high catalytic efficiency, prompted us to perform another series of 10 recycling experiments with a reaction time of only 15 min per run. After each experiment the catalyst is briefly washed with distilled toluene and immediately reused in a subsequent run. The conversions and yields of isolated PCL obtained under such short reaction time conditions are summarized in Table 2.

During the first six runs, the monomer-to-polymer conversion during 15 min reaction time remains constant within experimental error. However, the observed decreasing trend for the

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monomer conversions from the seventh run onward can be explained by the gradual increase of polymer remnants inside the pores of the beads after each run, likely to hamper eventually diffusive access of fresh monomer and initiator to the grafted tin atom; see above. After Soxhlet extraction with dichloromethane, the catalyst is reused in an 11th run and a conversion of 99% is again obtained, showing the slight catalytic activity reduction caused by interface alteration to be reversible upon thorough removal of PCL remnants by washing. The yields of isolated polymer after three precipitation–dissolution cycles follow the same decreasing trend as for the conversion degrees upon increasing number of runs, yet again are systematically lower because of mass losses into the filtrate (Table 2). The experimental number-average molar mass of the obtained PCL determined by quantitative ^{1}H NMR spectroscopy in CDCl$_3$ are systematically lower than the theoretically expected number-average molar masses due to the fact that the obtained degrees of polymerization are smaller than the theoretically expected 10 (Table 2). The M_n's determined by size exclusion chromatography are in satisfactory agreement with the theoretically expected ones, except for runs 8 and 11, which for unknown reasons are somewhat lower. Size exclusion chromatography also reveals polydispersity indices ranging from 1.4 to 2.2, as was the case for the polymerization runs lasting 2 h (compare results in Table 2 with those collected in Table 1).

Tin Leaching in the Ring-Opening Polymerization. Avoiding tin contamination of the synthesized polymer, or at least minimizing it as much as possible, is of prime importance. In order to investigate tin leaching into the reaction product, PCL is digested with concentrated nitric acid and quantitatively analyzed by ICP/AES. For each of the 10 consecutive runs with reaction times of 2 h, an average tin content of 50 ± 5 ppm is detected in the reaction mixture, corresponding to an average loss of $0.8 \pm 0.1\%$ with respect to the amount of tin used for the run. The dependence of reaction time on the leached tin amount is highlighted by the significantly lower leaching values of 17 ± 10 ppm for polymerization times of only 15 min, in which case the average loss is reduced to $0.2 \pm 0.2\%$. Although higher than for the model transesterifications, where they amounted to ca. 5 ppm,[49] the leached tin amounts in PCL after 15 min of reaction correspond to only 0.2% of the tin amount present under standard homogeneous catalysis conditions, to be compared with 0.4% loss in the previous study involving the C4 analogue in the transesterification of ethyl acetate with *n*-octanol.[47] The higher tin contamination in the ROP experiments with the C11SnCl$_3$ catalyst after 15 min of reaction (17 ± 10 ppm, $N = 10$, see above), when compared to transesterification of ethyl acetate by *n*-octanol (5 ± 3 ppm, $N = 8$),[49] is most probably due to the higher temperature in the former (100 °C) than in the latter (78 °C).

For comparison, the amount of residual tin contaminant present in PCL isolated and purified under strictly identical conditions after 2 h of ROP reaction with 0.5 mol % of BuSnCl$_3$ in solution rather than with grafted C11SnCl$_3$ turned out to be as high as 3400 ppm, to be compared to the 50 ppm found above for the grafted catalyst. Thus, the benefits of using the grafted catalyst are undisputable, in view of not only its better catalytic activity but also, more significantly, the dramatically lower tin pollution in the final reaction product. Hence, the limited tin leaching from the grafted catalyst appears harmless, since the grafted tin trichloride catalyst does not show any decrease in catalytic activity after 2 h and does not provide any change in control over the polymerization rate and the polymer polydis-

persity, which do not vary significantly with the number of catalytic runs.

In order to confirm that the polymerization is undeniably catalyzed by the grafted organotin, and not by leaching tin, a reaction run is performed after filtering off the solid support with its C11SnCl$_3$ graft, only 5 min after the reaction start in a first experiment and 9 min in a second one. The respective conversions of 11% and 91% observed after 5 and 9 min of contact time with the grafted insoluble material did not further increase after removal of the catalyst. Hence no additional PCL was generated by further keeping the reaction mixture at 100 °C for another 2 h without grafted material, clearly evidencing that the polymerization is catalyzed only by the grafted organotin species.

Conclusion

The catalytic activity and recyclability of undecyltin trichloride grafted onto cross-linked polystyrene was shown to be highly effective in the ROP of ϵ-caprolactone, with quantitative conversions obtained within 2 h. In addition, the catalyst was recyclable at least nine times without any loss of activity, despite a chemical modification occurring at the liquid–solid interface in the course of subsequent catalytic runs. This modification was shown to involve a loss in local rotational mobility of the graft, as demonstrated by ^{119}Sn HR-MAS experiments as well as by thermal analysis in the glass transition region of the insoluble polystyrene carrier. Even though the chemical modification appeared to be only partially reversible, it was shown to remain essentially harmless to the catalytic activity. Upon drastically shortening the reaction times from 2 h to 15 min, a slight decrease of the CL conversion rate became apparent from the seventh run onward as a direct consequence of the chemical alteration of the interface. However, the initial catalytic activity was fully restored after thorough extraction of the reaction residue. Leaching of tin traces into the reaction products did not appear to harm the catalytic activity. Moreover it remained very low with respect to the tin amounts remaining in reaction mixtures under homogeneous catalysis conditions, averaging a mere 0.2% of grafted tin per run for short reaction times. Considering this fundamental advantage associated with the use of grafted species, along with the high catalytic activity provided by the tin trichloride in the PCL oligomer synthesis, this work indisputably demonstrates the wide potential provided by this class of recyclable tin-based catalysts.

Experimental Section

Synthesis. The synthesis (Scheme 1) and characterization of the grafted C11SnCl$_3$ catalyst were described recently.[49] Samples from the same catalyst batch were used in the present study.

Polymerization Procedure of ϵ-Caprolactone. ϵ-Caprolactone (CL, Fluka, $\geq$ 99%), toluene (Aldrich, 99%), and *n*-propanol (Aldrich, 99.5+%) were dried over calcium hydride (CaH$_2$) and distilled before reaction. Prior to any ROP experiment, the C11SnCl$_3$ catalyst was dried at 60 °C under reduced pressure for 15 h. In the first catalytic run, 200 mg of catalyst material (0.220 mmol tin; 13.0 mass % tin)[49] was introduced into a preliminarily flamed and nitrogen-purged round-bottom flask equipped with a three-way stopcock and a rubber septum. Subsequently, three successive vacuum/nitrogen purging cycles were applied in order to render the round-bottom flask completely moisture free. After azeotropic removal of its head fraction by distillation, 2 mL of dry toluene and 4.66 mL of CL (43.95 mmol) were injected into the flask. The reaction medium was heated to 100 °C before adding 330 μL of *n*-propanol (4.395 mmol). After a ROP reaction time of 2 h under

mechanical low-speed shaking, the reaction was quenched by immersing the reaction mixture flask into cold tap water. An aliquot of about 50 μL was taken from the reaction mixture to determine the degree of conversion, the polymerization degree, and molar mass parameters using quantitative liquid ^{1}H NMR. Next, because of the too high viscosity of the slurry obtained, the mixture was diluted with 25 mL of dry toluene in order to make smooth filtration of the material possible. The grafted catalyst was then washed five times with 5 mL of dry toluene and dried under vacuum at 60 °C. After 24 h of drying, 20 mg of catalyst was used to perform HR-MAS NMR experiments to investigate its status, the remaining aliquot being reused in a subsequent polymerization experiment. The PCL was precipitated three times by adding dropwise a 7-fold excess of *n*-heptane to the liquid reaction mixture. The precipitate was filtered and dried under reduced pressure at 60 °C until constant weight in order to determine the yield of polymer.

In order to assess the reaction progress within the 2 h of reaction time, a polymerization run was started under identical conditions, and every 10 min an aliquot of about 50 μL was withdrawn for analysis by means of liquid ^{1}H NMR spectroscopy. In the second series of recycling experiments, the reaction was carried out under identical reaction conditions but was stopped after 15 min.

Size Exclusion Chromatography (SEC). Size exclusion chromatography was performed in THF at 35 °C 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 concentration = 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 molar masses ranging from 500 to 10^6 Da). Molar masses were calculated by reference to a polystyrene standard calibration curve using the Mark–Houwink−Sakaruda 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}, $a_{PCL} = 0.600$).

Modulated Temperature Differential Scanning Calorimetry (MTDSC). MTDSC experiments were performed on a helium-purged (25 mL/min) TA Instruments Q1000 DSC equipped with Tzero Technology and MDSC option. Subambient cooling was achieved using a RCS cooling accessory. Temperature calibration was performed using an indium standard. The samples were measured at a heating rate of 2.5 °C/min with an imposed temperature modulation of ±0.5 °C/60 s. The glass transition temperatures were determined by the peak position in the derivative of the heat capacity signal.

NMR Spectroscopic Data. The ^{1}H, ^{13}C, and ^{119}Sn HR-MAS NMR spectra were recorded on a Bruker Avance II 500 instrument operating at 500.13, 125.77, and 186.50 MHz, respectively, with a dedicated Bruker ^{1}H/^{13}C/^{119}Sn HR-MAS probe equipped with z-gradient coils; the sample was prepared by adding a sample of C11SnCl$_3$ (20 mg) to a HR-MAS rotor (80 μL). Swelling of the resin was achieved by adding CDCl$_3$ directly to the rotor. The magic angle spinning rate was 4 kHz. (CH$_3$)$_4$Sn was used as an external reference, after calibration to $\Xi = 37.290665$ MHz for ^{119}Sn NMR measurements.[66]

Samples used for the determination of the ratio initial alcohol/ obtained ester were prepared by dissolving about 10 mg of mixture into CDCl$_3$ (0.5 mL). In the ROP experiments, the quantitative ^{1}H NMR spectra were recorded on a Bruker Avance II 500 instrument, using a relaxation delay of 10 s, sufficient to achieve fully relaxed FID sampling conditions.

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