# A Polystyrene-Supported Tin Trichloride Catalyst with a C11-Spacer. Catalysis Monitoring Using High-Resolution Magic Angle Spinning NMR

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The cross-linked polystyrene grafted organotin $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_{11}\text{-}SnCl_3]_t$, in which [**P**-H] represents the monomeric unit of the nonfunctionalized polymer and *t* is the functionalization degree, has been synthesized and characterized by 1D and 2D $^1$H, $^{13}$C, and $^{119}$Sn high-resolution magic angle spinning (HRMAS) NMR spectroscopy, elemental analysis, and IR spectrometry. Its catalytic activity was assessed in the transesterification model reaction between ethyl acetate and *n*-octanol. The catalyst displays an average conversion degree of 76% after 2 h and can be recycled at least nine times. The experimental concentration profiles were fitted to a mechanistic model, from which a turnover frequency in the range of $10^{-2}$ s$^{-1}$ was calculated. Residual tin contents on the order of 5 ppm in the reaction products were assessed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES). The combined use of $^1$H, $^{13}$C, and $^{119}$Sn HRMAS NMR and modulated DSC enables one to assess the chemical integrity of the catalyst upon recycling. Detailed analysis of $^{119}$Sn HRMAS NMR spectra under various chemical conditions mimicking the reaction mixtures allows gaining a better insight into the catalysis mechanism.

## Introduction

While monoorganotin compounds enjoy widespread applications as synergists for PVC stabilization,[1–4] in glass coatings,[2] or as homogeneous catalysts in transesterification reactions,[2,5] their effectiveness is overshadowed by pertinent metal toxicity concerns[6] and by drawbacks related to often tedious quantitative removal of their residues from reaction mixtures. An alternative strategy consists of anchoring the monoorganotin reagent onto a solid support, allowing the catalyst to be easily separated from the desired reaction product by simple filtration of the insoluble carrier onto which it is grafted. The forecasted deliverables of such systems include improved catalyst recyclability and reduced metal presence in the final reaction products, which should address environmental and toxicity issues raised by nonsupported organotins.

In previous investigations, we reported on the synthesis, characterization, and catalytic properties of organotins grafted onto cross-linked polystyrene of the type $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_n\text{-}SnBuX_2]_t$ [7–12] and $[\mathbf{P}\text{-H}]_{(1-t)}\{[\mathbf{P}\text{-}(CH_2)_n\text{-}SnBuY]_2O\}_{t/2}$ ($n = 4$, 6, 11),[7,9,12] where [**P**-H] represents the monomeric unit of the nonfunctionalized polystyrene, cross-linked by divinylbenzene, X = Ph, Cl, $OOCCH_3$, Y = Cl, OH, $OOCCH_3$, and *t* is the functionalization degree. The polystyrene-grafted organotin trichloride, $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-}(CH_2)_4\text{-}SnCl_3]_t$, synthesized more recently,[9] displayed the best catalytic performances ever observed for organotin grafts. This grafted tin trichloride with C4-spacer was synthesized by reaction of the corresponding grafted tricyclohexyltin moiety with $SnCl_4$ in dry toluene,[9] according to the Kocheshkov reaction, involving redistributions of alkyl and halogen substituents between organostannanes and tin

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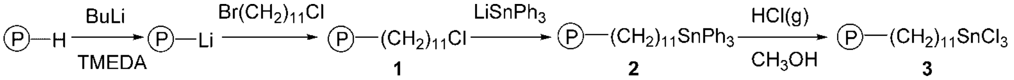
**Scheme 1. Synthetic Scheme of the Grafted Tin Trichloride with the C11-Spacer**



$$\text{Ⓟ}\text{-H} \xrightarrow[\text{TMEDA}]{\text{BuLi}} \text{Ⓟ}\text{-Li} \xrightarrow{\text{Br(CH}_2)_{11}\text{Cl}} \underset{\mathbf{1}}{\text{Ⓟ}\text{-(CH}_2)_{11}\text{Cl}} \xrightarrow{\text{LiSnPh}_3} \underset{\mathbf{2}}{\text{Ⓟ}\text{-(CH}_2)_{11}\text{SnPh}_3} \xrightarrow[\text{CH}_3\text{OH}]{\text{HCl(g)}} \underset{\mathbf{3}}{\text{Ⓟ}\text{-(CH}_2)_{11}\text{SnCl}_3}$$

halides.[13] Alternative synthesis methods of nongrafted monoalkyltin trichlorides, such as reactions of dialkyltin dihalides with $SnCl_4$ at 120–130 °C, under $POCl_3/P_2O_5$ catalysis,[14] in polar media,[15,16] using $SnCl_2$ with an unsaturated acyl chloride,[17] or involving a transition-metal-catalyzed process with redistributions between organotins and tin halides,[18] either do not proceed under mild enough conditions, require catalysts, or display limited yields and selectivities, making them inappropriate for solid-phase synthesis aiming at high functional purity of the target grafted organotin.

The present report analyzes a number of unexplored issues on the grafted $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnCl}_3]_t$ catalyst. First, the influence of using a much longer C11-spacer rather than the previously studied C4 one for this catalyst is emphasized. This is not just a matter of introducing a new variant, since in the synthesis of poly($\epsilon$-caprolactone), a grafted dialkyltin dichloride provided polymers with lower polydispersity and its recyclability was significantly better with the C11-spacer than with the C6-spacer, the carrier beads remaining intact with the former but bursting with the latter.[11,19] In other reactions, the C11-catalyst displayed better catalytic activities than the C6 one, emphasizing overall better performances when significantly longer spacers are used.[9] Second, in the few reactions investigated so far, the C4-grafted monoalkyltin trichloride is by far more active as a catalyst than the C4-grafted dialkyltin dichloride[9] so that thoroughly studying the C11-grafted monoalkyltin trichloride appeared worthwhile. This holds even more considering that the C4-grafted monoalkyltin trichloride featured an ill-defined degree of hydration,[9] leaving unclear whether this was the consequence of the followed synthetic route and its consecutive reaction workup. The present work explores whether an alternative synthetic route addresses this issue. Whereas for the C4-grafted monoalkyltin trichloride,[11] $^{1}H$ and $^{119}Sn$ high-resolution magic angle spinning (HRMAS) NMR were not used for the structural characterization and the assessment of the functional purity of the organotin graft, directly, *in situ* at the interface, using this technique should allow detailed monitoring of the synthesis and catalytic processes of the catalyst with the C11-spacer, $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnCl}_3]_t$, in particular with regard to the assessment of its functional purity and of the hydration issue. Its catalytic activity and recycling ability are assessed using again the model transesterification of ethyl acetate with *n*-octanol, in order to make possible comparisons with previous grafted catalysts. Attention is likewise paid to trace analysis of tin residues in the reaction products, evidencing strong influence of the reaction conditions, as well as to mathematical modeling of the catalyzed transesterification.

## Results and Discussion

**Synthesis and Characterization.** The general reaction scheme for the synthesis of the polystyrene-grafted alkyltin trichloride is given in Scheme 1.

The alkyl chloride grafted onto the cross-linked polystyrene was prepared starting from commercial Amberlite XE-305, using a procedure previously described in detail.[7–10,20] The stannylated graft $[\mathbf{P}\text{-H}]_{(1-t)}[\mathbf{P}\text{-(CH}_2)_{11}\text{-SnPh}_3]_t$ was synthesized by extending the method used earlier for the $SnBuPh_2$ analogue.[20] Triphenyltin lithium was prepared by lithiation of commercially available triphenyltin hydride and was subsequently allowed to react with the grafted undecyl chloride, yielding the desired grafted undecyltriphenyltin. Subsequently, the grafted target C11-tin trichloride was obtained by reaction of the triphenyltin moiety with an HCl/MeOH solution for 72 h under reflux. Long reaction times are required in order to ensure complete substitution of the third, less reactive phenyl group for a chlorine atom on the tin atom.

The grafted polystyrenes were fully characterized by elemental analysis, IR spectroscopy, and 1D and 2D HRMAS NMR spectroscopy.[8,9,11,21,22] The use of bipolar pulsed field gradient longitudinal eddy current delay (BPP-LED) diffusion-filtered 1D $^{1}H$ HRMAS NMR spectroscopy (diffusion-filtered HRMAS NMR) suppresses resonances from uninformative translationally mobile species from solvent molecules or nongrafted species, editing thus only, directly *in situ*, at the heterogeneous solid–liquid interface, grafted, rotationally mobile moieties.[8,21]

The terminal chloromethylene moiety of the C11-chain in precursor graft **1** provides a well-isolated characteristic $^{1}H$ resonance around 3.5 ppm (Figure 1, top panel, arrow) in the diffusion-filtered $^{1}H$ HRMAS spectrum. The triphenyltin group of **2** gives rise to two characteristic *ortho* and *meta/para* proton resonances for the phenyl groups, the $CH_2Cl$ signal of **1** having disappeared (Figure 1, middle panel). Due to the phenyl resonances vanishing in the next step, it can be concluded that a complete conversion to functionally pure grafts has been achieved in all reaction steps, at least within NMR detection limits (Figure 1, bottom panel).

The $^{119}Sn$ HRMAS spectra (Figure 2) of organotin grafts **2** and **3** display a single resonance around −100 and 3 ppm, respectively, characteristic for alkyltriphenyl- and trichlorotins.[23–27] Given the reasonable sensitivity of $^{119}Sn$ HRMAS NMR,[8] the absence, within detection limits, of weak resonances in the spectra of **2** and **3** evidence both the full degree of reaction completion and a satisfactory functional tin purity.

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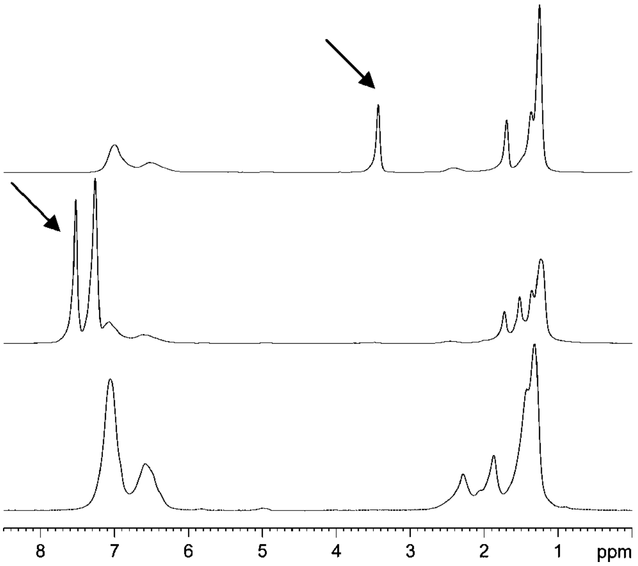

**Figure 1.** Diffusion-filtered $^1$H HRMAS NMR spectra of precursor graft **1** (top) and organotin grafts **2** (middle) and **3** (bottom).

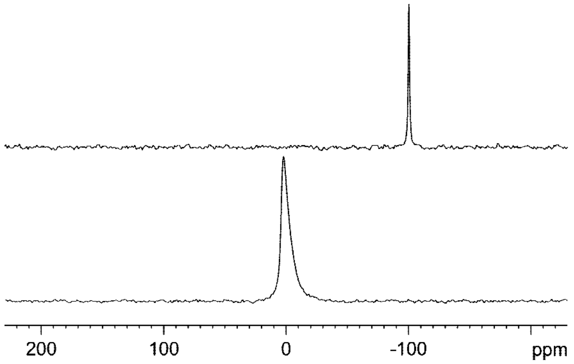

**Figure 2.** $^{119}$Sn HRMAS NMR spectra of the grafted C11-SnPh$_3$ (**2**) (top) and C11-SnCl$_3$ (**3**) (bottom) in CDCl$_3$.

The analysis of the resonances of the methylene groups in the spacer, subject to strong overlapping, was addressed using 1D $^1$H and $^{13}$C, along with 2D $^1$H−$^1$H TOCSY and $^1$H−$^{13}$C HSQC HRMAS NMR spectra, providing nearly complete $^1$H and $^{13}$C resonance assignments, as well as unresolved $^nJ(^{119/117}\mathrm{Sn},^1\mathrm{H})$ and $^nJ(^{119/117}\mathrm{Sn},^{13}\mathrm{C})$ coupling constants. Figure 3 shows an expansion of the aliphatic range of the α-CH$_2$ cross-peak of **3** in the 2D $^1$H−$^{13}$C HSQC spectrum at 700 MHz proton resonance frequency, displaying the characteristic E-COSY-like satellites, allowing the determination of the passive $^1J(^{119/117}\mathrm{Sn},^{13}\mathrm{C})$ and $^2J(^{119/117}\mathrm{Sn},^1\mathrm{H})$ coupling constants and their opposite signs, as deduced from the negative slope of the diagonal relating the two satellite cross-peaks.[11,23] The chemical shifts and coupling constants obtained in this way for the organotin grafts **2** and **3** (Tables 1 and 2) unambiguously indicate a four-coordinate tin atom, as expected from the properties of the grafts and the solvent conditions used.

The functionalization degree *t* of all grafts was determined from elemental analysis data using a previously described nonlinear least-squares procedure.[7] The elemental analysis results for grafts **1**–**3** are given in Table 3 along with the corresponding calculated data for potential desired and undesired target grafts.[9]

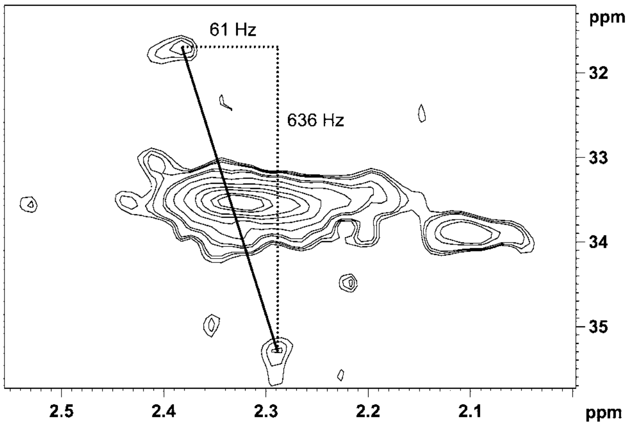

**Figure 3.** Expansion in the aliphatic range of the α-CH$_2$ cross-peak of **3** in the 2D $^1$H−$^{13}$C HSQC spectrum at 700 MHz proton resonance in CDCl$_3$ displaying the characteristic E-COSY-like satellites from the passive $^1J(^{119/117}\mathrm{Sn},^{13}\mathrm{C})$ (vertical axis) and $^2J(^{119/117}\mathrm{Sn},^1\mathrm{H})$ (horizontal axis) coupling constants and their opposite signs.

**Table 1. Assignment of the $^1$H, $^{13}$C, and $^{119}$Sn Resonances of the Polystyrene Supported Organotin Grafts 2 and 3 and Their Precursor 1**[a]

| | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| spacer | $^1$H | $^{13}$C | $^1$H | $^{13}$C | $^1$H | $^{13}$C |
| 1-(CH$_2$) | 3.48 | 45.0 | 1.33 | 11.3 | 2.31 | 33.7 |
| 2-(CH$_2$) | 1.75 | 32.6 | 1.54 | 26.8 | 1.91 | 24.9 |
| 3-(CH$_2$) | 1.41 | 26.9 | 1.18 | 34.4 | 1.49 | 32.5 |
| 4-(CH$_2$) | 1.32 | 28.9 | 1.05 | 29.3 | 1.37 | 28.9 |
| 5, 6, 7, 8, 9-(CH$_2$) | 1.32 | 29.6 | 1.05 | 29.7 | 1.32 | 29.6 |
| 10-(CH$_2$) | 1.51 | 31.6 | n.i. | 31.8 | 1.49 | 31.6 |
| 11-(CH$_2$) | 2.48 | 36.0 | 2.40 | 36.0 | n.i. | 35.7 |
| $^{119}$Sn | | | −100 | | +3 | |
| phenyl | | | | | | |
| (CH)$_o$ | | | 7.33 | 137.2 | | |
| (CH)$_m$ | | | 7.06 | 128.6 | | |
| (CH)$_p$ | | | 7.06 | 129.0 | | |
| C$_{ipso}$ | | | | 139.3 | | |

[a] Chemical shifts in ppm with reference to TMS for $^1$H and $^{13}$C spectra, and to tetramethyltin for $^{119}$Sn spectra; n.i.: not identified.

For organotin graft **2**, the value of the functionalization degree is slightly lower than the value of its precursor **1**, likely related to an underestimation of the experimental Sn mass fraction, a usual drawback related to incomplete combustion of Sn to SnO$_2$ in elemental analysis; the experimental mass fractions of C and H are in satisfactory agreement with the calculated values. There is no indication in the $^1$H and $^{119}$Sn HRMAS NMR spectra of **2** that these deviations might be due to the presence of grafted impurities, as mentioned above, unlike earlier observations for grafted tin dichlorides.[7]

For organotin graft **3**, the overall agreement between calculated and experimental data is fair, since the functionality degree obtained for **3** is close to the *t*-value of its precursor **2**. Although the experimental values for chlorine and tin differ somewhat from the calculated ones, the differences remain acceptable for these elements. A Karl Fischer analysis indicated the presence of 1.68 wt % of water in organotin graft **3**. Including this information in alternative empirical formulations for **3** as either **P**-(CH$_2$)$_{11}$SnCl$_3$·H$_2$O or **P**-(CH$_2$)$_{11}$SnCl$_2$OH resulted, however, in calculated values that displayed higher deviations on the carbon mass fractions with respect to the experimental data for the first formulation and on all mass fractions for the second one. While the presence of water traces is indisputable, the single $^{119}$Sn HRMAS resonance for **3** indicates high organotin functional purity. Its increased line-width when compared to the triphenyltin graft may be due, at least in part, to exchange

**Table 2. $^1J(^{119/117}Sn,^{13}C)$ and $^2J(^{119/117}Sn,^1H)$ Coupling Constants (in Hz) of the Polystyrene-Supported Organotin Grafts 2 and 3**

| | 2 | | 3 | |
|---|---|---|---|---|
| | $^nJ(^{119/117}Sn,^1H)$ | $^nJ(^{119/117}Sn,^{13}C)$ | $^nJ(^{119/117}Sn,^1H)$ | $^nJ(^{119/117}Sn,^{13}C)$ |
| 1-($CH_2$) | 50 $^2J^{a,b}$ | 395; 376 $^1J^c$ | 61 $^2J^{a,b}$ | 636 $^1J^{a,b}$ |
| 2-($CH_2$) | 99 $^3J^{a,b}$ | n.i. $^2J$ | 224 $^3J^{a,b}$ | 45 $^2J^{a,b}$ |
| 3-($CH_2$) | n.i. $^4J$ | 60 $^3J$ | n.i. $^4J$ | n.i. $^3J$ |
| $(CH)_o$ | 44 $^3J$ | 35 $^2J$ | | |
| $(CH)_m$ | n.i. $^4J$ | 47 $^3J$ | | |
| $C_{ipso}$ | | 479; 458 $^1J^c$ | | |

[a] Values obtained from the 2D $^1H-^{13}C$ HSQC spectrum. [b] Average $^nJ(^{119/117}Sn,^{13}C)$ coupling constant because of broad resonance; n.i.: not identified. [c] Resolved $^1J(^{119}Sn,^{13}C)$ and $^1J(^{117}Sn,^{13}C)$ coupling constants obtained from the 1D $^{13}C$ spectrum.

**Table 3. Experimental Elemental Analysis Data for the Organotin Grafts 2 and 3 and Their Precursor 1 and the Resulting Functionalization Degree *t* (calculated elemental analysis data are obtained starting from the functionalization degree of the immediate precursor)**

| graft | $t$ | % C | % H | % Sn | % Cl | |
|---|---|---|---|---|---|---|
| **1** | 0.252 | 85.36 | 9.09 | | 5.75 | expt |
| | 0.245 | 85.41 | 8.81 | | 5.78 | calcd[a] |
| **2** | 0.231 | 79.82 | 7.75 | 11.46 | | expt |
| | 0.252 | 79.60 | 7.45 | 12.95 | | calcd[b] |
| **3** | 0.221 | 66.45 | 6.91 | 13.60 | 10.78 | expt |
| | 0.231 | 66.10 | 6.76 | 14.31 | 12.83 | calcd[c] |
| **P**-$(CH_2)_{11}$-$SnCl_3.H_2O$ | 0.231 | 64.69 | 6.62 | 14.01 | 12.55 | |
| **P**-$(CH_2)_{11}$-$SnCl_2OH$ | 0.231 | 67.60 | 7.04 | 8.75 | 14.64 | |

[a] Calculated on the basis of $t = 0.245$ as determined gravimetrically. [b] Calculated on the basis of $t = 0.252$ of precursor graft **1**. [c] Calculated on the basis of $t = 0.231$ of organotin graft **2**.

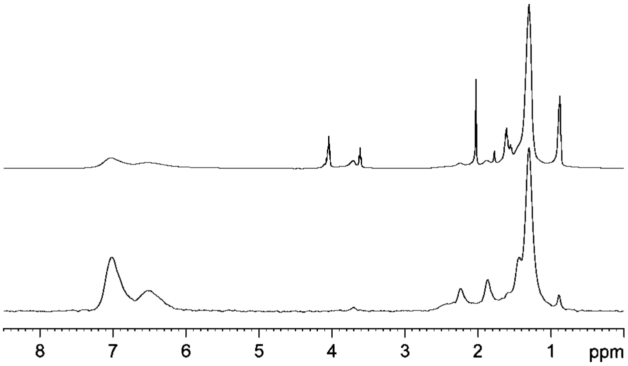

**Figure 4.** $^1H$ HRMAS NMR spectrum of C11-$SnCl_3$ in the presence of its reaction mixture (ethyl acetate, *n*-octanol, octyl acetate, and ethanol) (top) and the corresponding DOSY-filtered $^1H$ HRMAS NMR spectrum (bottom).

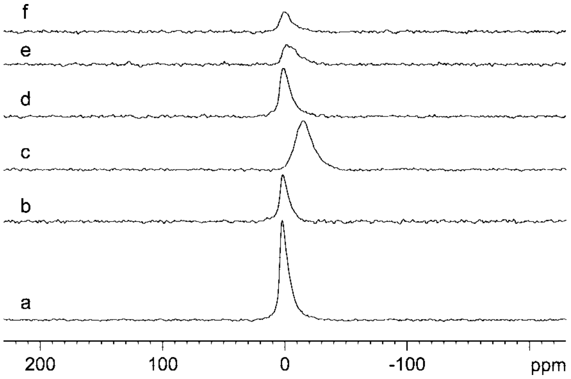

**Figure 5.** $^{119}Sn$ HRMAS NMR spectra in $CDCl_3$ of pure, nonused C11-$SnCl_3$ catalyst (**3**) (a); after the first run (b); after the second run (c); after the third run (d); after the 10th run (e); after the 10th run followed by thorough Soxhlet extraction of the material with $CH_2Cl_2$ (f).

coalescence originating from an association–dissociation equilibrium between the four-coordinate $SnCl_3$ moiety and its complex with the small amount of water observed.

**Catalytic Activity in a Model Transesterification.** The catalytic activity of **3** has been investigated in the transesterification of ethyl acetate with *n*-octanol:

$$CH_3COOEt + OctOH \rightarrow CH_3COOOct + EtOH \qquad (1)$$

This model reaction was selected in order to make comparisons possible with previous studies in which it was used to assess the activity of other grafted organotin catalysts.[7–9] In these previous studies, however, the thermodynamically reversible equilibrium reaction was driven to completion by using a 7-fold excess of starting ethyl acetate while distilling off the ethanol generated, which affects the reaction mixture volume and the normal, catalysis-controlled, time evolution of the reaction component concentrations. In order to ensure reproducible determinations of conversion degrees, usable for modeling purposes (see below), the reaction was performed with a stoichiometric 1:1 ratio of ester and alcohol. In this way, the half-life time toward chemical equilibrium could be used as a reliable quantitative indicator of the rate of conversion of the transesterification (see Experimental Section).

The resulting half-life times toward thermodynamic equilibrium, obtained for the 10 successive catalytic runs of recycled catalyst, averaged at 28 ± 3 min, indicating both a high catalytic activity and a good recyclability of the catalyst under the transesterification conditions used, as well as a constant activity from run to run. For comparison, a single run performed with the soluble nongrafted catalyst $BuSnCl_3$ provided a half-life time of 36 min, confirming the good performance of the grafted catalyst, being competitive with the soluble one. After each transesterification run and prior to being reused in a subsequent reaction, the chemical state of the grafted catalyst was monitored by $^1H$ and $^{119}Sn$ HRMAS NMR (Figures 4 and 5).[8,21] Figure 4 (top) shows a standard $^1H$ HRMAS NMR spectrum of **3** in its reaction mixture, i.e., the equilibrium mixture of ethyl acetate, *n*-octanol, ethanol, and octyl acetate. Due to the spectrum dynamic range, the resonances of the grafted catalyst, which are also broader, are hardly visible above the noise level of the reaction component resonances.

When applying a diffusion filter (Figure 4, bottom), only the signals from the translationally immobile catalyst remain visible, those from translationally mobile species in the reaction mixture being suppressed. This diffusion-filtered spectrum shows some additional resonances when compared to that of the freshly synthesized catalyst, suggesting a chemical modification possibly involving the acetate residues of the esters (see below).

The $^{119}Sn$ chemical shift of the catalyst around 3 ppm after the first run is roughly unaltered by the reaction, and no additional resonances are visible (Figure 5).

Nevertheless, already after the first catalytic run, the $^{119}Sn$ resonance shows a stronger distortion at the low-frequency side,

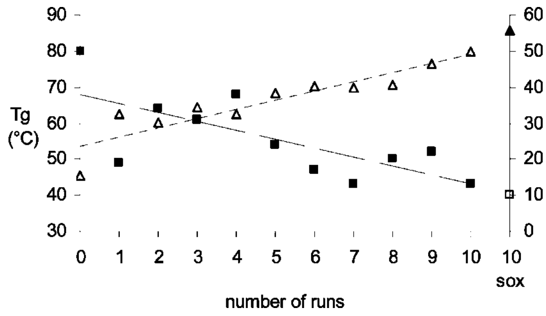

**Figure 6.** Glass transition temperature $T_g$ (△) and signal-to-noise ratio S/N (■) of the $^{119}$Sn HRMAS NMR spectra of the C11-SnCl$_3$ catalyst, as a function of the number of successive transesterification runs; subsequently to thorough Soxhlet of the sample after the tenth run (▲; □, on the right vertical axis). Short-dashed and long-dashed lines show the increasing $T_g$ and decreasing S/N trends upon increasing the number of catalytic runs.

when compared to the nonused catalyst, indicating that some residual reaction components are still present in the material pores after filtration and light washing (with ethyl acetate) and that they effectively interact with the tin atom of the grafted catalyst, explaining the low-frequency shoulder. Thus, the persistent presence of residual donors interacting with tin in the material pores, even after washing, is unavoidable given the high Lewis acidity of monoorganotin trichlorides. Even for nonused catalyst, the $^{119}$Sn HRMAS resonance shows some shape dissymmetry likely related to small traces of water acting as an exchanging Lewis base but certainly not due to incorrect phase correction. Moreover, the signal-to-noise ratio measured under identical FID acquisition conditions has decreased by a factor 2.5 after the first run, which is not accounted for by tin leaching alone since the latter amounts at only 2.6% after a contact time of 24 h with the reaction mixture. Although considered with care because of the difficulty of achieving identical conditions of bead stacking and interface heterogeneity in the sample preparation from one run to another, the overall trend of S/N decrease with the number of catalytic runs is indisputable (Figure 6).

An increase of the glass transition temperature $T_g$ of the material, as determined by modulated DSC, from 45.4 °C for nonused catalyst to 62.5 °C after a single catalytic run, sheds some light on the origin of the strongly decreasing signal-to-noise ratio of the $^{119}$Sn HRMAS resonance. Grafting the conformationally flexible C11-spacer, whatever the terminal functionality, dramatically decreases the $T_g$ (**1**, $T_g = 17.9$ °C; **2**, $T_g = 28.8$ °C) with respect to nonfunctionalized cross-linked polystyrene (Amberlite XE-305, $T_g = 115.2$ °C). In this view, taking **1** as a reference to show the plasticizing effect of a grafted C11 side-chain on the cross-linked polystyrene, any increase of $T_g$ with respect to **1** can be considered as resulting from a local reincrease of the rigidity at the interface, hence evidencing a loss of local rotational mobility of the functionality at the end of the C11-spacer. Substituting the Cl atom of **1** for the SnPh$_3$ moiety of **2** increases $T_g$ by ca. 11 °C, reflecting a slight loss of local rotational mobility. Substituting the SnPh$_3$ moiety of **2** for the SnCl$_3$ one of **3** results apparently in a somewhat higher loss of rotational mobility, as suggested by the $T_g$ increase by another 16 °C. This can be ascribed to weak donor–acceptor interactions involving chlorine and tin atoms of neighboring C11-chains in the dry state of the material, resulting from the high Lewis acidity of the tin atom in the tin trichloride. That, after a single catalytic run, the $T_g$ increases by again another 17 °C is evidence in favor of an additional loss of local rotational mobility of the organotin function at the interface. Figure 6 shows a general trend toward higher $T_g$ values upon increasing the number of catalytic runs—up to 10—using recycled catalyst.

These observations suggest some additional cross-linking due to a chemical modification of the organotin functionality, which probably involves the acetate residue of the esters and the tin atoms, in agreement with the well-established bridging capacity of carboxylate ligands between tin atoms in polystyrenes.[28,29] In view of this additional organotin cross-linking at the interface, the loss of signal-to-noise ratio in the $^{119}$Sn HRMAS resonance of the catalyst after one catalytic run is readily explained, since rotationally immobilized chemical moieties become HRMAS NMR invisible.[8,21] This is in agreement with the absence of any detectable $^{119}$Sn HRMAS resonance in grafted distannoxanes synthesized purposely, the additional Sn−O−Sn bridging causing also loss of local rotational mobility at the interface.[9] Hence, the necessary condition for HRMAS resonances to be visible is no longer fulfilled for that fraction of organotin moieties that underwent the additional functional cross-linking, also strongly supported by the modulated DSC measurements. This interpretation is confirmed by the additional anisotropy pattern that appears at low frequency in the solid-state $^{117}$Sn MAS NMR spectrum of the catalyst in the dry solid state after the catalytic runs, even though the latter is noisy, broad, and ill-defined.

After the second run, the $^{119}$Sn resonance of the catalyst shifted to −16 ppm with a line-width increase with respect to the first catalytic run (Figure 5). This low-frequency shift is reversible and is caused by residual amounts of reaction product weakly interacting with tin atoms and being trapped inside the bead pores as a consequence of too superficial sample washing in the catalyst recycling procedure. This is harmless, since slightly more thorough washing after each subsequent catalytic run gives again a $^{119}$Sn HRMAS resonance with the same chemical shift and comparable shoulder characteristics at its low-frequency side (Figure 5), as after the first run.

The overall increasing trend of $T_g$ upon increasing number of runs (Figure 6, short-dashed line) fairly parallels the overall decreasing trend in the signal-to-noise ratio of the $^{119}$Sn HRMAS resonance (Figure 6, long-dashed line). These trends suggest that cross-linking involving tin atoms continues upon successive transesterification runs, hampering the conformational mobility of an increasing fraction of the organotin moieties at the C11-spacer end, consequently resulting in the disappearance of their $^{119}$Sn HRMAS signal and an overall decrease in the signal-to-noise ratio for the $^{119}$Sn resonance of the unaltered SnCl$_3$ fraction that still remains observable. After 10 runs, the $T_g$ of the catalyst increases up to 80 °C, in parallel with a $^{119}$Sn signal-to-noise ratio decrease to about one-fifth of its original value. Upon thorough Soxhlet extraction of the catalyst after the 10th run, an additional $T_g$ increase by about 6 °C is measured, probably due to the removal of residual amounts of plasticizing reaction product trapped inside the bead pores. Accordingly, the line-width of the $^{119}$Sn resonance returns to nearly its initial value.

Interestingly, this chemical modification of the organotin upon catalytic use appears harmless to the catalytic activity. Thus, conversion half-life times remained basically unchanged in up to nine subsequent runs (ca. 0.5 h on average), demonstrating

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(28) Angiolini, L.; Biesemans, M.; Caretti, D.; Salatelli, E.; Willem, R. *Polymer* **2000**, *41*, 3913.

(29) Dalil, H.; Biesemans, M.; Willem, R.; Angiolini, L.; Salatelli, E.; Caretti, D.; Chaniotakis, N. A.; Perdikaki, K. *Helv. Chim. Acta* **2002**, *85*, 852.

the excellent recyclability of the grafted organotin trichloride catalyst. When comparing the performance of the supported tin trichloride **3** to that of the molecular butyltin trichloride in homogeneous solution, the grafted system showed slightly higher catalytic activity under comparable conditions. Considering furthermore the much easier recycling of the grafted catalyst when compared to its nongrafted analogue in solution, the benefits of grafted organotin catalysts are unambiguously demonstrated.

**Tin Leaching in the Model Transesterification.** Tin leaching into the reaction mixture is a major concern in the use of grafted organotin catalysts. As using them is precisely meant to avoid or at least minimize tin contamination of the synthesized reaction products, it is important to address this issue prior to considering any industrial application. Residual tin contents in all transesterification reaction products were measured by inductively coupled plasma/atomic emission spectroscopy.

In a first set of 10 consecutive experiments with recycled catalyst, the residual tin content was determined after removal of the tin-functionalized carrier. With ethyl acetate in 4-fold excess, the reaction reaches equilibrium in ca. 2 h, with a conversion degree averaging 76 ± 10%. For eight out of 10 catalytic runs, the residual tin content averaged 5 ± 3 ppm, reflecting a globally satisfactory low leaching degree. Only after the second and the third runs, did the values peak at 16 and 35 ppm, respectively, for unknown reasons.

The degree of tin leaching is extremely sensitive to the contact time between the catalyst and the refluxing reaction mixture. In the first run of another set of experiments using ethyl acetate and *n*-octanol in molar ratio 1:1 under reflux for 24 h, 220 ppm of residual tin was detected in the reaction mixture. Not surprisingly, in the second run, where the reaction was stopped after 2 h—with chemical equilibrium not yet achieved—the tin content amounted to only 16 ppm. In three subsequent runs of 6 h—in order to ensure full equilibrium conditions for modeling purposes—tin leaching averaged 103 ± 50 ppm.

Notwithstanding the detection of tin traces in the reaction product after every run, in amounts strongly dependent on reaction conditions and time, catalyst **3** did not show any measurable decrease in catalytic activity when used subsequently. In order to prove that the transesterification is not catalyzed by the leaching tin species, the reaction mixture was further refluxed without organotin graft after a reaction time of 40 min. Within experimental error, no additional conversion was observed within the next 24 h of reflux, undoubtedly confirming that the grafted organotin is indeed the active catalyst in the reaction, excluding any tin trace in solution being responsible for this.

**Mechanistic Aspects of the Grafted Catalysis in the Model Transesterification.** The catalysis mechanism, in particular the coordination of the tin atom of the catalyst *in situ* at the solid–liquid interface, was investigated using samples mimicking the transesterification conditions, exploiting the sensitivity of the $^{119}$Sn chemical shift (Figure 7) to interactions between the tin atom and a nucleophilic substrate.

The concentrations in ester and alcohol are identical to those used in the transesterification reaction, while the concentration in catalyst, expressed in tin molar equivalents, is 6 times higher for the model samples than for the reaction mixture, so as to achieve an acceptable $^{119}$Sn signal-to-noise ratio without unacceptably long spectrum recording times. The $^{119}$Sn HRMAS NMR spectrum in $CDCl_3$ of the pure, nonused catalyst shows a reasonably narrow resonance around 3 ppm (Figure 7a), consistent with the characteristic four-coordinate tin atom of nonused catalyst. The $^{119}$Sn chemical shift of the catalyst decreases to –69 ppm when ethyl acetate is added, indicating additional shielding of the $^{119}$Sn nucleus by coordination expansion of the tin atom with the nucleophilic ethyl acetate (Figure 7b). This broadened but still single averaged resonance is ascribed to an exchange equilibrium between four-coordinate tin in the grafted C11-$SnCl_3$ moiety and five- and/or six-coordinate tin of the latter species interacting with the nucleophilic ethyl acetate. This exchange appears moderately fast on the $^{119}$Sn NMR time scale, as inferred from the coalescence broadening. Although a minor influence of chemical shift anisotropy distortion may contribute to the dissymmetry of the line shapes, it is not believed that this is the only factor since such a dissymmetry does not occur in all spectra where donors are present and cause line broadening. The $^{119}$Sn chemical shift of the grafted C11-$SnCl_3$ in the presence of only *n*-octanol shifts to −197 ppm, indicating an even higher degree of shielding by *n*-octanol than by ethyl acetate. This suggests a stronger coordination for the alcohol toward tin than for the ester (Figure 7c). The further broadening of the single $^{119}$Sn resonance is readily explained by the fact that, while still indicating a moderately fast exchange regime in the same sense as in Figure 7b, the intrinsic $^{119}$Sn chemical shift difference between four-coordinate and five/six-coordinate tin upon interaction with *n*-octanol has further increased. Adding a mixture of both ethyl acetate and *n*-octanol in a molar ratio 1:1, mimicking the reaction conditions at the transesterification start, results as well in a $^{119}$Sn resonance at –196 ppm (Figure 7d), yet slightly narrower than with *n*-octanol alone (Figure 7c). This indicates slightly faster exchange kinetics at equilibrium between the different tin species, while shielding of the tin atom remains mainly determined by *n*-octanol, showing the dominant role of *n*-octanol in the equilibrium mixture of the different tin complexes. With a 1:1:1:1 mixture of ethyl acetate, *n*-octanol, *n*-octyl acetate, and ethanol, mimicking the actual transesterification equilibrium concentrations of the four reaction components at reaction end, the $^{119}$Sn chemical shift is found at –217 ppm, a value lower by another 20 ppm (Figure 7e). This additional $^{119}$Sn nucleus shielding suggests slightly stronger interactions of the mixture components with the tin atom in the solution mimicking the final reaction mixture than in the one mimicking the initial one.

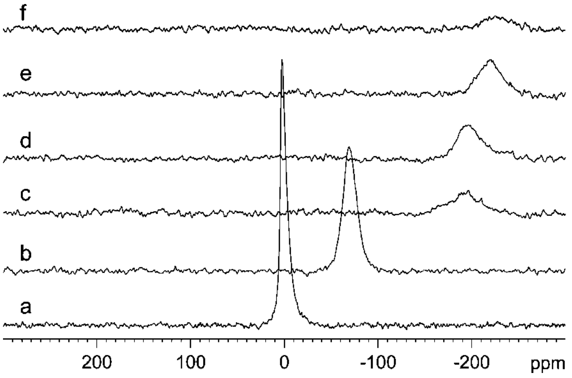

**Figure 7.** $^{119}$Sn HRMAS spectra in $CDCl_3$ of pure, nonused grafted C11-$SnCl_3$ catalyst without any added component (a); nonused catalyst in the presence of only ethyl acetate (b); the same, in the presence of only *n*-octanol (c); the same, in the presence of a 1:1 mixture of ethyl acetate and *n*-octanol (d); the same, in the presence of a 1:1:1:1 mixture of ethyl acetate, ethanol, *n*-octyl acetate, and *n*-octanol mimicking the equilibrium mixture (e); used catalyst, in contact with its own equilibrium mixture after five catalytic runs (f). In order to improve the signal-to-noise ratio, the quantity of tin was higher in all samples (a to f) than in the actual reaction mixture.

**Table 4. Experimental and Fitted Half-Life Times (in min) toward Chemical Equilibrium for Successive Runs in the Transesterification Reaction of Ethyl Acetate and *n*-Octanol with C11-SnCl$_3$ as a Catalyst**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | av | SD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $t_{1/2,\mathrm{exp}}$[a] | 30 | 24 | 32 | 30 | 26 | 28 | 27 | 32 | 27 | 26 | 28 | 3 |
| $t_{1/2,\mathrm{fit}}$ | 33 | 25 | 34 | 28 | 25 | 28 | 28 | 29 | 26 | 24 | 28 | 3 |

[a] Experimental half-life times were interpolated from the obtained experimental data, using the experimental points closest to half-life time with respect to chemical equilibrium.

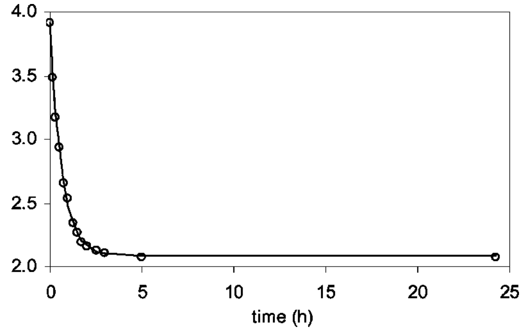

**Figure 8.** Experimental (○) and fitted (full line) concentrations of *n*-octanol ([A]) as a function of time during the first transesterification run with C11-SnCl$_3$ as a catalyst.

The $^{119}$Sn chemical shift found in this model mixture (Figure 7e) is very close to the one found for used catalyst in the presence of its actual equilibrium mixture (Figure 7f), showing the model mixture is mimicking satisfactorily well the chemical properties of the actual equilibrium, at least for tin coordination. In the latter, the broader and flatter resonance with lower signal-to-noise ratio is traced to the chemical cross-linking alteration of the grafted organotin after the series of catalytic runs, as explained above, resulting in exchange kinetics conditions that are different for the actual equilibrium mixture than for the model mixture. This interpretation is supported by the presence of residual reaction species from former runs in the pores of the catalyst, as outlined above. The systematic low-frequency $^{119}$Sn shift indicates a global coordination expansion of the tin atom of the grafted C11-SnCl$_3$ catalyst from pure, unaltered four-coordination to five- and/or six-coordination during the transesterification. The additional finding that this $^{119}$Sn signal is both single and broad indicates the exchanging tin species equilibrium to be averaged out on the $^{119}$Sn NMR time scale, and hence to be as fast as on the order of at least 40 kHz, given the huge $^{119}$Sn chemical shift difference of ca. 37 kHz (200 ppm) between least and most coordinated tin complexes.

In conclusion, the ester and alcohol are brought in close mutual vicinity thanks to their common coordination to tin, favoring nucleophilic attack of the alcohol oxygen onto the carbonyl carbon atom of the ester needed for the transesterification.

The above mechanistic study results are in agreement with a bimolecular reaction scheme for which a mathematical model allowed proper fitting of the experimental half-life time data. The details are presented in the Supporting Information. The experimental and fitted half-life times for the 10 successive catalytic runs of continuously recycled **3** display a good agreement. All data are gathered in Table 4 and illustrated for the first run in Figure 8.

Average values over 10 runs for $k_1$ and $k_2$ amounted to $(5.4 \pm 0.5) \times 10^{-5}$ and $(5.5 \pm 0.8) \times 10^{-5}$ L mol$^{-1}$ s$^{-1}$, respectively, resulting in an average equilibrium constant $K$ of $0.99 \pm 0.14$. As a result, the average turnover frequency (TOF)[30,31] (see Experimental Section) amounted to $(1.1 \pm 0.2) \times 10^{-2}$ s$^{-1}$. For comparison, the TOF obtained for the corresponding grafted undecylbutyltin dichloride was about 1 order of magnitude smaller.[12]

## Conclusion

A simple synthesis procedure provided a functionally pure monoalkyltin trichloride grafted onto cross-linked polystyrene. HRMAS NMR spectroscopy was used for monitoring the solid-phase synthetic procedures in the presence of the liquid phase, allowing convenient assessment of organotin functional purity, and for assessing chemical modifications and recyclability of the catalyst, enabling one to get insight into the mechanistic aspects of the catalytic process. The catalyst is recyclable at least nine times in the transesterification of ethyl acetate and *n*-octanol, without any sizable loss of its excellent catalytic activity under mild reaction conditions. It showed a slightly better catalytic performance than its soluble analogue *n*-butyltin trichloride. The easy recycling conditions of the grafted catalyst and the satisfactory tin leaching results, at least for short reaction times, demonstrate the benefits of grafting the catalyst. Starting from the mechanistic study results, a mathematical model allowed proper fitting of the experimental half-life time data. Finally, a chemical modification of the catalyst involving additional cross-linking was evidenced by the combined use of HRMAS NMR and DSC measurements in the glass transition region of the polystyrene carrier. This modification, however, does not affect the catalytic properties of the organotin graft.

Obviously, using HRMAS NMR enables one to set up a general approach for the follow-up, *in situ* at the solid–liquid interface, of both synthesis and catalytic processes of organometallic compounds grafted onto environmentally friendly insoluble solid supports.

## Experimental Section

**Materials.** Amberlite XE-305 was purchased from PolySciences Inc. and washed thoroughly prior to use, following procedures described previously.[32] Cyclohexane (Aldrich, 99%) was dried over sodium at room temperature and distilled immediately prior to reaction under a dry nitrogen atmosphere. Butyllithium (2.5 M in hexane), triphenyltin hydride, and 11-bromo-1-undecanol (98%) were purchased from Aldrich. Triphenyltin hydride was purified prior to use by column chromatography with petroleumether/benzene (4:1) as an eluent. Tetrahydrofuran (THF, Aldrich, 99+%) was dried over lithium aluminum hydride (LiAlH$_4$), distilled, and used immediately. Tetramethylethylenediamine (TMEDA, Aldrich, 99.5+%) and di-isopropylamine (DIA, Aldrich, 99%) were dried over calcium hydride (CaH$_2$), distilled, and immediately engaged into reaction. Ethyl acetate and *n*-octanol were distilled prior to all transesterification experiments.

**Synthesis.** Precursor graft **1** was synthesized according to a procedure previously reported for the synthesis of the grafted SnBuCl$_2$ analogue with the undecamethylene spacer.[9] In short, divinylbenzene cross-linked polystyrene Amberlite XE305 was used as the insoluble support **P**-H. An undecamethylene spacer with terminal chloride was grafted onto the preliminarily *para*-phenyllithiated cross-linked polystyrene. Organotin graft **2**, the Ph$_3$Sn analogue of **1**, was subsequently synthesized by a stannylation reaction with Ph$_3$SnLi, in which DIA (0.29 g, 2.82 mmol) and *n*-BuLi (2.82 mmol) were successively added to dry THF (5 mL)

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at 0 °C under dry nitrogen atmosphere. After 10 min, $Ph_3SnH$ (1.21 g, 3.45 mmol) was added and the mixture was stirred for 20 min. This solution was then added to **1** (1 g) in dry THF. The mixture was stirred for 4 h at room temperature. Subsequently, the beads were washed 2 times with 30 mL of dry THF and the stannylation reaction was repeated overnight. The obtained target organotin graft **2** was filtered off, washed with THF/$H_2O$ (2:1; 30 mL), THF (6 × 30 mL), and ethanol (2 × 30 mL), and finally dried under vacuum at 60 °C.

**$[P\text{-}H]_{(1-t)}[P\text{-}(CH_2)_{11}Cl]_t$ (1).** Anal. (%) Calcd: H 8.81, C 85.41, Cl 5.78, obtained on the basis of $t = 0.245$, as determined by weighing. Found: H 9.09, C 85.36, Cl 5.75; $t = 0.252$. IR ($cm^{-1}$): $\nu(CCl)$ 651 (w). $^1H$ HRMAS NMR: $\delta$ 3.48 ppm ($-CH_2Cl$).

**$[P\text{-}H]_{(1-t)}[P\text{-}(CH_2)_{11}SnPh_3]_t$ (2).** Anal. (%) Calcd: H 7.45, C 79.60, Sn 12.95, on the basis of $t = 0.252$ found for **1**. Found: H 7.75, C 79.82, Sn 11.46, resulting in $t = 0.231$. IR ($cm^{-1}$): $\nu(Sn-Ph)$ 1074 (m), $\nu(Sn-C_{alif})_{sym}$ 510 (w), $\nu(Sn-C_{alif})_{asym}$ 594 (w), $\nu(Sn-C)_{rock}$ 656 (w), $\delta_{oop}(C-C)_{mono}$ 727 (w). $^{119}Sn$ HRMAS NMR: $\delta$ −100 ppm.

**$[P\text{-}H]_{(1-t)}[P\text{-}(CH_2)_{11}SnCl_3]_t$ (3).** A 1.5 g amount of **2**, immersed in absolute methanol, was treated with an excess of hydrochloric acid in absolute methanol (7 mL, 5 M). The mixture was stirred for 72 h at reflux temperature. Every 12 h, an additional amount of HCl/MeOH solution was added in order to ensure a sufficient inflow of HCl into the reaction mixture throughout the whole reaction time. Subsequently, the target organotin graft **3** was washed with methanol (6 × 20 mL) and methylene chloride (3 × 20 mL) and dried under vacuum at 60 °C. Anal. (%) Calcd with $t$ value of 0.231 of organotin graft **2**: H 6.76, C 66.10, Sn 14.31; Cl 12.83. Found: H 6.91, C 66.45, Sn 13.60, Cl 10.78; $t = 0.220$. IR ($cm^{-1}$): $\nu(Sn-Cl)$ 366 (m). $^{119}Sn$ HRMAS NMR: $\delta$ 3 ppm.

**Catalysis Experiments on a Transesterification Reaction.** In a first series of experiments, in which the reaction mixture was solely allowed to evolve to chemical equilibrium, ethyl acetate and *n*-octanol were used in a 1:1 molar ratio. A mixture of ethyl acetate (3.9 g, 44 mmol), *n*-octanol (5.8 g, 44 mmol), and **3** (1 mol% Sn with respect to *n*-octanol; 400 mg) was gently stirred and refluxed until chemical equilibrium was achieved. At equilibrium, the reaction mixture contains all four reaction components in identical molar fractions (25 mol %) within experimental error (max. 3 mol %). For monitoring the evolution of the molar fraction of the reaction components toward thermodynamic equilibrium, negligibly small aliquots of 50 $\mu$L of reaction mixture were regularly tapped and analyzed by $^1H$ NMR spectroscopy after evaporation of ethyl acetate and ethanol.

In a second series of experiments, aiming at determining the degree of tin leaching, the reaction was allowed to evolve toward completion. Ethyl acetate was used in a 4-fold excess, and the ethanol generated was distilled off. For run 1 the reaction time was 3 h and for all subsequent runs 2 h.

After each reaction run, the catalyst was filtered off and gently washed with ethyl acetate. The ethyl acetate and ethanol were distilled off from the mixture. The ratio of initial alcohol to obtained ester was determined by integration (±1%) of the respective $CH_2O$ $^1H$ NMR resonances.

Turnover rates were calculated as $v_0/N_s$, where $v_0$ is the initial reaction rate ($=k_1[A]_0[E]_0$) in mol $L^{-1}$ $min^{-1}$ and $N_s$ is the number of catalytic tin sites in moles as determined by elemental analysis.

**IR Spectroscopy.** IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer, equipped with a MIR source, a KBr beam splitter, and a DGTS detector, from 200 mg of dry KBr pellets with ca. 5 mg of substance.

**NMR Spectroscopic Data.** The $^1H$, $^{13}C$, and $^{119}Sn$ HRMAS NMR spectra were recorded on Bruker AMX500 and Avance II 500 instruments operating at 500.13, 125.77, and 186.50 MHz, respectively, with a dedicated Bruker $^1H/^{13}C/^{119}Sn$ HRMAS probe equipped with gradient coils; sample rotors were filled with ca. 20 mg of resin beads, swollen in approximately 80 $\mu$L of $CDCl_3$; magic angle spinning rate was 4 kHz. $(CH_3)_4Sn$ was used as external reference, after calibration to $\Xi = 37.290665$ MHz for $^{119}Sn$ NMR measurements.[33] The $^{119}Sn$ spectra were recorded under broadband $^1H$ decoupling during acquisition. The 2D $^1H-^{13}C$ HSQC spectra of **3** were acquired on a 700 MHz Bruker Avance II spectrometer equipped with a gradient $^1H/^{13}C/^{119}Sn$ HRMAS probe at 298 K, at a spinning rate of 4 kHz. Then 1024 and 256 complex points were acquired in the acquisition ($t_2$) dimension and the indirect ($t_1$) dimension, respectively. A total of 64 scans were used for each $t_1$ increment. Sine-shaped gradient pulses were used to select the appropriate coherence order pathway. The sample was prepared by adding **3** (20 mg) to a HRMAS rotor (80 $\mu$L). Swelling of the resin was achieved by adding $CDCl_3$ directly to the rotor.

Samples used for the determination of the ratio initial alcohol/obtained ester were prepared by dissolving about 10 mg of mixture in $CDCl_3$ (0.5 mL). Quantitative $^1H$ spectra were recorded on a Bruker DRX250 spectrometer operating at 250.13 MHz.

**Differential Scanning Calorimetry (DSC).** Modulated temperature differential scanning calorimetry (MTDSC) experiments were performed on a helium-purged (25 mL/min) TA Instruments 2920 DSC with MDSC option and a RCS cooling accessory. Temperature calibration was performed using an indium standard, whereas a poly(methyl methacrylate) standard was used for heat capacity calibration. The samples were measured at a heating rate of 2.5 °C/min and 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.

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**Supporting Information Available:** Calculation details on the mechanistic model used to fit the experimental concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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