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Scope and Limitations of the Use of Grafted Undecyltin Trichloride As a Catalyst for Transesterifications: Effect of Tin Loading on Catalytic Activity, Recyclability, and Leaching

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The effect of the tin loading (functionalization degree t) on the catalytic activity and recyclability is investigated for a polystyrene-grafted undecyltin trichloride catalyst, **P-C11-SnCl$_3$**, in transesterification reactions involving either a primary or a secondary alcohol. For the latter, the achieved conversion degree in the first run is about 20% lower than with the primary alcohol. In subsequent runs, the reaction rates are strongly influenced by the tin loading of the catalyst. Unlike *low-loaded* **P-C11-SnCl$_3$** catalysts ($t \approx 0.10$), *high-loaded* catalysts ($t \approx 0.20$) display a simultaneous T_g increase (from 53 °C to 107 °C after 5 runs) and conversion decrease (from 52% to 15%) upon increasing number of runs, ascribed to reduced mobility of the organotin moieties resulting from undesired cross-linking at the reaction interface. Confirmation for the fact that, in this case, the catalytic performance is dominated by conformational mobility issues is found in the comparison between transesterifications involving either primary or secondary alcohols. Whereas a T_g increase is not associated with a reduced conversion degree for primary alcohols, a clear decrease in conversion is observed for secondary alcohols, illustrating that steric issues are especially pronounced in a *low-mobility* (*high-loaded*) system and are of no importance in *high-mobility* (*low-loaded*) systems. This also affects the leaching resistance of the compounds, the *high-loaded* catalysts displaying substantially higher tin leaching (311 ± 278 ppm) than the *low-loaded* ones (10 ± 8 ppm).

Introduction

Among the large variety of organotin compounds enjoying widespread use in a vast range of industrial applications, mono- or dialkyltin compounds[1−7] as well as tetraalkyldistannoxane derivatives[8−11] are generally recognized as highly efficient catalysts for transesterification reactions under mild and neutral conditions. A scientifically rewarding strategy to overcome the toxicity-related limitations to the industrial exploitation of such organotin catalysts involves their immobilization onto an insoluble support. As such, so-called "clean" organotin reagents, which can be easily removed from the final reaction product by simple filtration, are being developed.

Within this scope, our research group has contributed to the development and optimization of efficient cross-linked polystyrene-supported organotin catalysts and has explored their application potential as sustainable, recyclable, and environmentally benign transesterification catalysts.[12−18] We recently reported on the catalytic features of an undecyltin trichloride grafted onto cross-linked polystyrene, **P-C11-SnCl$_3$**.[16] Use of

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the latter catalyst in the model transesterification of ethyl acetate and 1-octanol resulted in average conversion half-lives of less than half an hour throughout at least 10 successive runs. Similar results were obtained for the ring-opening polymerization (ROP) of ε-caprolactone.[18] In addition, the catalyst displayed high leaching resistance, with leaching degrees averaging around 5 ppm of grafted tin per transesterification run of ethyl acetate and 1-octanol.[16]

On the other hand, combined use of HRMAS (high-resolution magic angle spinning) NMR spectroscopy and modulated temperature DSC measurements in the glass transition region of the catalyst demonstrated that its catalytic application results in chemical modifications that are accompanied by conformational mobility restrictions.[16,18] Upon successive transesterification runs, the tin functionalities at the spacer end lose their local rotational mobility due to increased organotin cross-linking at the solid−liquid interface, preventing the catalyst moieties from being visible by ^{119}Sn HRMAS NMR spectroscopy.[16,18] This increase in local rigidity was confirmed by a significant increase in the glass transition temperature, T_g, of the catalyst.[16,18]

These observations prompted us to investigate whether reducing the degree of functionalization, i.e., "diluting" the catalytic organotin sites at the solid−liquid interface, would prevent such cross-linking phenomenon between neighboring tin atoms, simply because their mutual distance would be too large to enable bridging. Earlier work on rhodium hydrogenation catalysts immobilized onto inorganic supports reported the benefits of reducing the surface coverage.[19,20] We observed an optimum degree of functionalization for a catalyst of the type **P-C6-SnBuCl$_2$**.[21] The aim of the present work is to investigate the impact of a reduced degree of functionalization on the catalytic activity, recyclability, and leaching resistance of the polystyrene-grafted organotin trichloride **P-C11-SnCl$_3$** in transesterification reactions involving either primary or secondary alcohols.

Results and Discussion

Transesterification of Ethyl Acetate with a Primary Alcohol. In a first stage, the effect of reducing the functionalization degree t from 20% to 10% on the catalytic activity of **[P-H]$_{1-t}$[P-C11-SnCl$_3$]$_t$** is assessed in the model transesterification of ethyl acetate with the primary alcohol 1-octanol. Ten successive catalysis experiments were performed with 1 mol % of grafted tin with respect to the initial molar amount of alcohol, using ethyl acetate in 4-fold excess. In order to allow proper comparison, the reaction time is kept constant at 2 h for all runs. Overall, a slightly better and more reproducible average catalytic performance is noted using catalyst **P-C11-SnCl$_3$** with a lower functionalization degree of 0.10, since 84 ± 4% of conversion in 2 h is observed, which compares favorably to the average conversion of 76 ± 10% obtained for a higher t-value of 0.20.[16] The complete series of 10 catalytic runs with the low-t catalyst results in a slightly lower average tin leaching degree (Table 1) of 3.7 ± 1.7 ppm, which compares favorably to the average of 5 ± 3 ppm for eight out of 10 runs using the high-t catalyst[16] (peaking values at 16 and 35 ppm for two runs).

Table 1. Tin Leaching into the Reaction Mixture for 10 Subsequent Runs of Catalyst P-C11-SnCl$_3$ with t = 0.10 in the Transesterification of Ethyl Acetate with 1-Octanol

	run											
	1	2	3	4	5	6	7	8	9	10	av	SD
ppm Sn	7.5	4.5	4.3	3.2	2.6	2.1	1.9	4.7	3.5	2.7	3.7	1.7

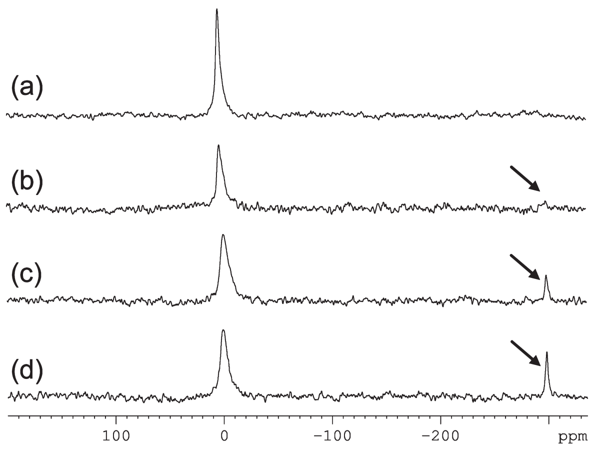

Figure 1. ^{119}Sn HRMAS NMR spectra (a) of pure, nonused **P-C11-SnCl$_3$** catalyst with t = 0.10; (b) after the first run; (c) after the fifth run; (d) after the 10th run in the transesterification of ethyl acetate with 1-octanol.

After each transesterification run, the chemical state of the organotin catalyst is monitored with ^{119}Sn HRMAS NMR. In contrast with the high-t catalyst,[16] the ^{119}Sn HRMAS spectra of the low-t catalyst do not display the dramatic S/N ratio decrease with increasing number of transesterification runs (Figure 1). Furthermore, whereas the high-t catalyst experienced a T_g increase of about 40 °C after 10 runs, a much less pronounced increase in T_g is measured for the low-t material, i.e., from 94.4 °C for freshly synthesized catalyst up to 97.7 °C after the 10th run. Moreover, the ^{119}Sn HRMAS spectra show the generation of an additional minor ^{119}Sn resonance at ca. −300 ppm (Figure 1, arrow), the amplitude of which increases with the number of successive transesterifications (integrating for about 17% after the 10th recycle (Figure 1, d)).

On the basis of the latter ^{119}Sn chemical shift, and in line with results previously obtained for **P-C11-SnBuCl$_2$**—its catalytic use resulting in the observation of a grafted side-functionality of the type **P-C11-SnBu(OOCCH$_3$)$_2$** resonating at −203 ppm[17]—the current side-functionality at −300 ppm likely indicates an increasing modification of the catalyst into a functionality of the type **P-C11-Sn(OOCCH$_3$)$_3$** or **P-C11-SnCl(OOCCH$_3$)$_2$**. In view of its visibility in ^{119}Sn HRMAS NMR, this modified fraction clearly involves rotationally mobile organotin grafts, an observation that is in strong contrast with results obtained for the high-t catalyst.[16] In the latter case, the modified catalyst functionalities did not provide a ^{119}Sn HRMAS resonance and caused the observation of only an additional broad, ill-defined anisotropy pattern around −300 ppm in the ^{117}Sn solid-state NMR spectra.[16] Considering the resemblance in this low-frequency ^{119}Sn chemical shift behavior, we suggest that both modified fractions are of similar nature, however with the rotationally immobilized ones existing in an aggregated state, favored at higher organotin concentrations.

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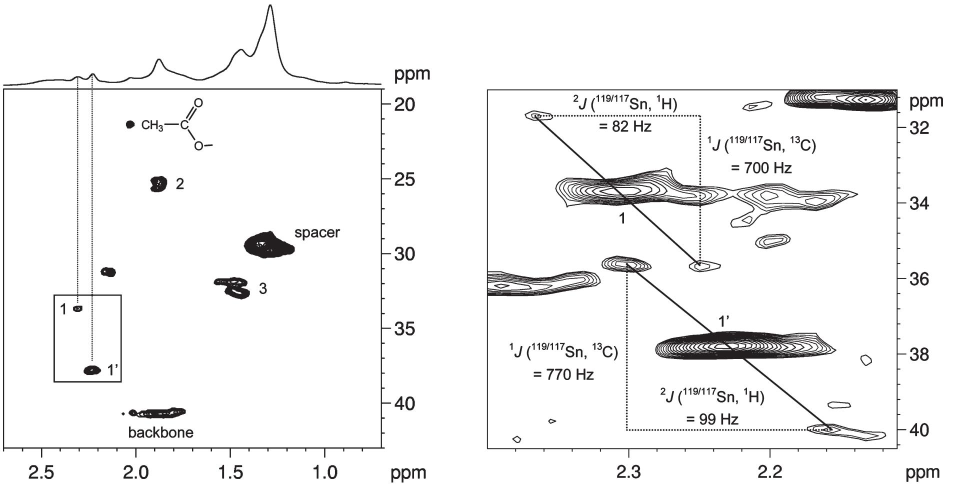

Figure 2. 2D HSQC HRMAS NMR spectrum expansion of the low-t catalyst after 10 catalytic runs (left), with an inset at lower intensity level of the cross-peaks **1** and **1′** (right).

	% conversion			
run	**$t = 0.10$**	**$t = 0.10$**	**$t = 0.17$**	**$t = 0.21$**
	(1)	**(2)**		
1	85	66	55	52
2	83	66	48	53
3	84	59	35	33
4	88	62	41	18
5	75	64	37	15
av	**83**	**63**	**43**	**34**
SD	**5**	**3**	**8**	**18**

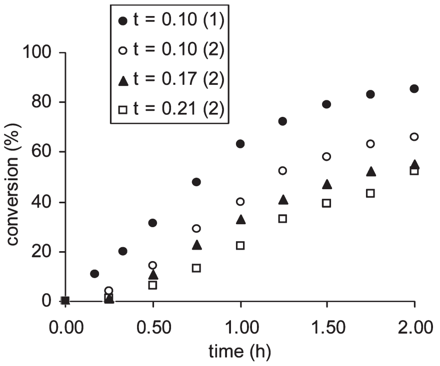

Figure 3. Conversion degrees obtained in consecutive runs after a reaction time of 2 h in the transesterification of ethyl acetate and 1-octanol (1) or ethyl acetate and cyclohexanol (2), using catalyst **P-C11-SnCl$_3$** with different degrees of functionalization t (left). The graph (right) shows the corresponding time evolution of the conversion in the course of the first run, within a reaction duration of 2 h.

In an attempt to confirm the formation of the organotin carboxylate moiety, a 2D ^{1}H$-^{13}$C HRMAS experiment (Figure 2) clearly reveals the existence of two α-CH$_2$ cross-peaks at (^{1}H, ^{13}C) chemical shifts of 2.31, 33.7 ppm and 2.23, 37.8 ppm, indeed confirming the presence of two types of organotin species, respectively denoted as **1** (remaining fraction of original catalyst **P-C11-SnCl$_3$**) and **1′** (modified fraction). An expansion of the 2D spectrum (Figure 2, right) displays their $^2J(^{119/117}\mathrm{Sn}, ^1\mathrm{H})$ and $^1J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ coupling constants, respectively 82 and 700 Hz for **1** and 99 and 770 Hz for **1′**.

In addition, Figure 2 (left) shows a key cross-peak at 2.03, 21.3 ppm, which can be assigned to an acetate moiety, in good agreement with the above statement on the formation of an organotin carboxylate moiety.

Transesterification of Ethyl Acetate with a Secondary Alcohol. In a second stage, the catalytic efficiency and recycling ability of grafted **P-C11-SnCl$_3$** are assessed in the transesterification of ethyl acetate with a more sterically hindered alcohol, i.e., cyclohexanol. For the sake of comparison with the above results, all experiments are likewise performed with 1 mol % of grafted tin with respect to the initial molar amount of alcohol, using ethyl acetate in 4-fold excess. For each of three **P-C11-SnCl$_3$** catalysts, differing only in their degrees of functionalization, five consecutive transesterification runs with a constant reaction time of 2 h are performed.

In the first run, the achieved conversion degree toward the ester is about 20% lower as compared to the reactions performed previously with the primary alcohol 1-octanol (Figure 3), for a given reaction time of 2 h. While, for this primary alcohol, no pronounced effect of the degree of functionalization on the catalytic activity and recyclability could be observed (see above and Figure 3), the performance of the **P-C11-SnCl$_3$** catalyst in transesterification involving a secondary alcohol is shown to be highly dependent on the tin loading. In a first run, the use of a low t-value of 0.10 leads to about 15% higher conversion after 2 h as compared to the reaction performed with catalyst having a higher t-value of 0.21 (Figure 3, graph).

Also the recycling ability of each of the catalysts considerably depends on their tin loading (Figure 3, left). While, overall, the low-t catalyst maintains its initial catalytic efficiency throughout five successive runs, an increasing drop in conversion is observed upon increasing tin loadings. This observation can be readily assigned to the occurrence of additional cross-linking of organotin functionalities at the interface, since this phenomenon is more likely for a high-t than for a low-t catalyst. This is confirmed by the ^{119}Sn HRMAS spectra of the catalysts after the different runs (Figure 4), displaying similar trends to those of the transesterification with 1-octanol (see above). Thus, application of the high-t catalyst in the transesterification with cyclohexanol likewise results in a severe loss of the ^{119}Sn

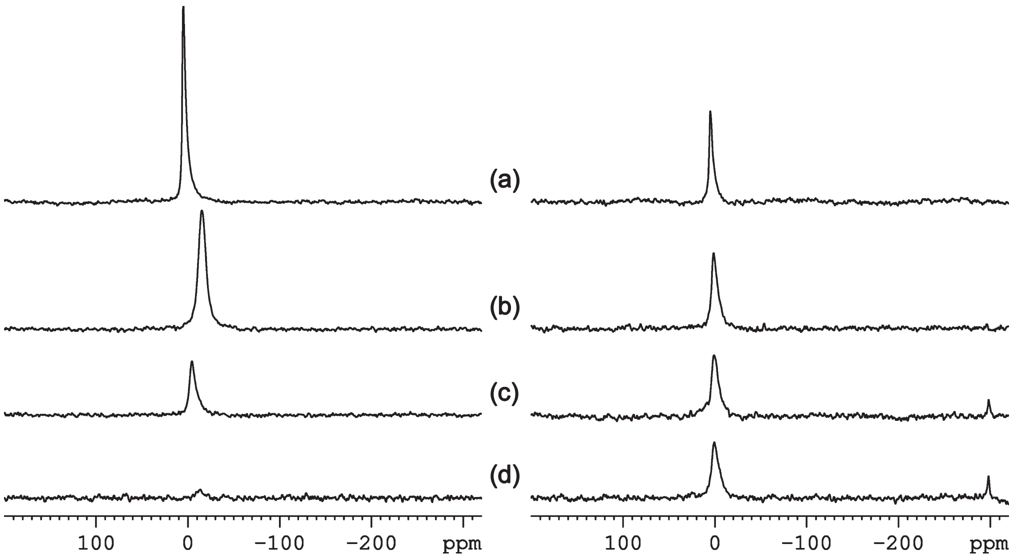

Figure 4. ^{119}Sn HRMAS NMR spectra (a) of pure, nonused **P-C11-SnCl$_3$** catalyst with t = 0.20 (left) and t = 0.10 (right); (b) after the first run; (c) after the third run; (d) after the fifth run in the transesterification of ethyl acetate with cyclohexanol.

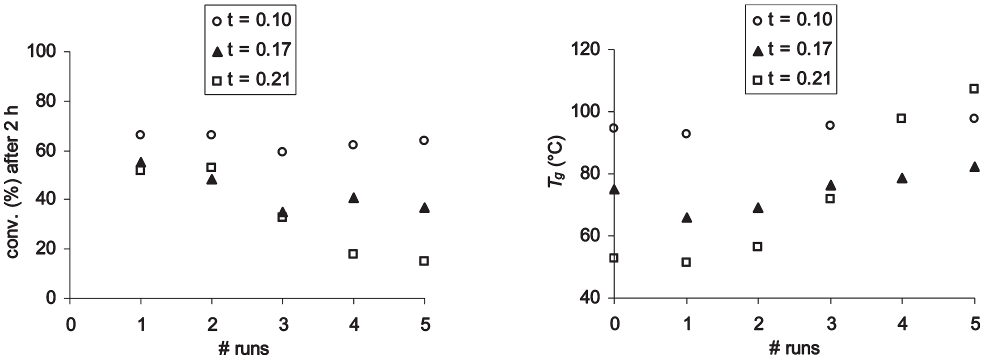

Figure 5. Conversion degrees (left) and glass transition temperatures T_g of **P-C11-SnCl$_3$** (right) obtained after successive transesterification runs of ethyl acetate and cyclohexanol with a reaction time of 2 h.

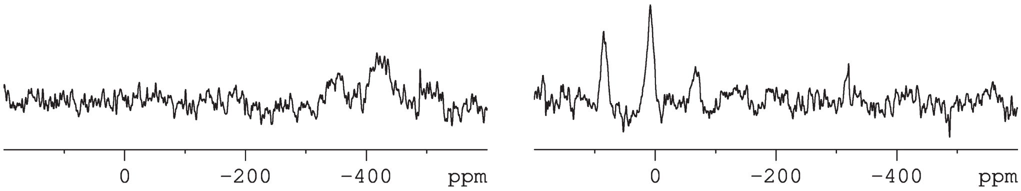

Figure 6. ^{117}Sn solid-state NMR spectra of **P-C11-SnCl$_3$** catalyst with t = 0.20 (left) and t = 0.10 (right) after the fifth run in the transesterification of ethyl acetate with cyclohexanol.

HRMAS resonance with increasing number of recycling experiments (Figure 4, left). On the contrary, for the low-*t* catalyst, no dramatic S/N decrease is observed, while an additional tin functionality around −300 ppm is generated (Figure 4, right).

The evolution in glass transition temperature, from 52.8 °C for freshly synthesized high-*t* catalyst to a very broad T_g with a maximum around 107 °C after five catalytic runs, confirms the significant rigidity increase at the interface of this catalyst (Figure 5, right). As explained above, this cancels out all local rotational mobility of the C11-grafted organotin functionalities, consequently leading to the loss of the characteristic ^{119}Sn HRMAS resonance around 0 ppm. From Figure 5 (right) it is clear that this effect significantly diminishes for the low-*t* catalyst, displaying a T_g increase of only ca. 3 °C after five catalytic runs. This indicates that this low-*t* catalyst does not undergo any organotin cross-linking at the interface as a result of its reduced concentration of organotin sites.

The latter interpretations are supported by the solid-state ^{117}Sn NMR spectra of the high- and low-*t* catalyst after five recycling experiments (Figure 6, left and right, respectively). For the low-*t* catalyst the spectrum displays, next to the anisotropy pattern of the original SnCl$_3$ catalyst centered around 0 ppm, an additional though noisy resonance around −300 ppm, whereas for the high-*t* one only a very broad and noisy anisotropy pattern is observed at low frequency.

As suggested above, the observed chemical modification of the high-*t* catalyst likely involves an acetate moiety, which is consistent with the bridging capacity of carboxylate

Table 2. Tin Leaching into the Reaction Mixture for Five Consecutive Runs of 2 h in the Transesterification Reaction of Ethyl Acetate with Cyclohexanol, Using Catalyst P-C11-SnCl$_3$ with Different Functionalization degrees *t*

	leaching (ppm Sn)		
run	$t = 0.10$	$t = 0.17$	$t = 0.21$
1	24	31	22
2	7	10	39
3	6	18	670
4	9	19	445
5	5.5	57	381
av	10	27	311
SD	8	18	278

ligands between tin atoms in functionalized polystyrenes.[22,23] Such carboxylates bridging two tin atoms have shown to display characteristic C═O and C−O stretching bands in the 1550−1560 and 1410−1425 cm^{-1} ranges.[22,23] In this respect, the clear appearance of new bands at 1542 and around 1400 cm^{-1} (shoulder) in the IR spectrum of the high-*t* catalyst after five consecutive runs supports this interpretation. For the low *t*-value, no such intense bands are visible, in line with the above proposal that no acetate bridging is possible with low functionalization degree. Similar bands were observed after application of the catalyst to the ring-opening polymerization of ε-caprolactone as well.[18]

Figure 5 unambiguously correlates the performance of the catalyst (conversion, left) and the local rotational molecular mobility of its catalytic sites at the solid−liquid interface (T_g, right): the lower the amount of remaining flexible C11 chains with increasing number of runs, the higher the value of T_g and, thus, the more dramatic the reduction in conversion degree from run to run. Noteworthy, this conclusion only holds for the transesterifications performed with a secondary alcohol; the additional cross-linking with high-*t* catalysts is harmless for the catalyzed transesterification with a primary alcohol (see above), showing both restricted mobility of the catalytic organotin sites *and* the steric hindrance of the secondary alcohol to cause the catalyst to be poorly recyclable.

For comparison, performing a single run with the soluble nongrafted catalyst BuSnCl$_3$, under comparable reaction conditions, results in a conversion degree of only 43% after 2 h. Moreover, the high-*t* catalysts display a lower leaching resistance as compared with the low-*t* ones (Table 2). For the catalyst with a *t*-value of 0.21, reasonably low tin contents of 22 and 39 ppm were detected in the reaction product after the first and second runs, respectively. In the subsequent three runs, however, extremely high residual tin leaching values averaging at 499 ± 152 ppm were observed. Conversely, five consecutive runs of catalyst with lower *t*-values of 0.17 and 0.10 resulted in acceptable tin leaching contents, averaging at 27 ± 18 and 10 ± 8 ppm, respectively. The pronounced weaker leaching resistance of the high-loaded catalyst can be readily related to its above-mentioned chemical modification upon catalytic use. In this respect, it has been reported that nucleophilic coordination expansion at tin can cause changes in reaction selectivity, favoring aliphatic carbon−tin bond cleavage.[24] This assumption is supported by the stronger leaching resistance of the low-loaded catalysts, where this cross-linking by tin coordination expansion upon catalytic use does not take place, as shown above.

Conclusion

The present study addressed the influence of the functionalization degree of polystyrene-supported undecyltin trichloride on its catalytic activity and recyclability in transesterification reactions.

Reaction rates can sometimes be strongly influenced by the tin catalyst loading on the support. For highly loaded catalysts, a simultaneous T_g increase and conversion decrease with increasing number of runs originate both from reduced conformational mobility of the organotin moieties resulting from additional cross-linking by tin coordination expansion. Confirmation of the fact that the catalytic performance is dominated by mobility issues was found in the comparison between transesterifications involving either primary or secondary alcohols. In the case of primary alcohols, a T_g increase is not associated with a reduced conversion, whereas it is in the case of secondary alcohols, illustrating that steric issues are pronounced in a *low-mobility* system, whereas they are of subordinate importance in *high-mobility* systems.

When comparing the performances of the supported alkyltin trichloride and a soluble analogue, *n*-butyltin trichloride, the grafted system showed higher catalytic activity under comparable conditions, an effect even more pronounced in the case of reactions with secondary alcohols *and* low-*t* catalysts. Considering, furthermore, the satisfactory tin leaching results and the easy recycling conditions of the grafted catalyst as compared to its nongrafted analogue in solution, the benefits of grafting organotin catalysts are unambiguously confirmed.

Experimental Section

The synthesis and full characterization of **P-C11-SnCl$_3$** have been described in detail in a previous report.[16]

Catalysis Experiments. Ethyl acetate (Aldrich, 99.5+%), 1-octanol (Aldrich, 99+%), and cyclohexanol (Aldrich, 99%) were distilled prior to all transesterification experiments. Ethyl acetate and 1-octanol or cyclohexanol were used in a 4:1 molar ratio. A mixture of ethyl acetate (3.5 g, 40 mmol), alcohol (10 mmol), and supported catalyst (0.10 mmol Sn; 1 mol % Sn) was gently stirred with a magnetic stirrer at reflux temperature while the generated ethanol was distilled off to drive the reaction to completion. The reaction time was limited to 2 h. For monitoring the time evolution of the conversion during the transesterification, negligibly small aliquots of 50 μL of reaction mixture were regularly tapped and analyzed by solution ^{1}H NMR spectroscopy using CDCl$_3$ as a solvent, after evaporation of ethyl acetate and ethanol. The ratio of initial 1-octanol (cyclohexanol) to obtained 1-octyl acetate (cyclohexyl acetate) was determined by integration (±1%) of the respective CH$_2$O (CHO) ^{1}H NMR resonances. After each transesterification run, the catalyst was filtered off and gently washed with ethyl acetate.

NMR Spectroscopy. The ^{1}H, ^{13}C, and ^{119}Sn 1D and 2D HRMAS NMR spectra were recorded on a Bruker Avance II 500 instrument operating at 500.13, 125.77, and 186.50 MHz, respectively, or on a 700 MHz Bruker Avance II spectrometer operating at 700.13, 176.05, and 261.08 MHz, respectively, both with a dedicated Bruker ^{1}H/^{13}C/^{119}Sn HRMAS probe equipped

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with gradient coils. Sample rotors were filled with ca. 15 mg of resin beads, swollen in approximately 80 μL of $CDCl_3$; magic angle spinning rate was 4 kHz. ^{119}Sn NMR measurements were referenced to Ξ = 37.290665 MHz.[25] The ^{119}Sn spectra were recorded under broadband ^{1}H decoupling during acquisition. A diffusion LED sequence[26] was used to eliminate contributions from any mobile species from one-dimensional ^{1}H HRMAS spectra, using a 50 ms diffusion delay and 1.5 ms sine-shaped gradient pulses. 2D ^{1}H$-$^{13}C HSQC HRMAS spectra were recorded on the 700 MHz Bruker Avance II spectrometer. A total of 2048 and 512 complex points were acquired in the acquisition (t_2) and the evolution (t_1) time domains, respectively. A total of 32 or 64 scans were used for each t_1 increment.

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. 3 mg of sample.

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