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Synthesis, Characterization, and Catalytic Properties of Diphenyl- and Dichlorobutyltin Functionalities Grafted to Insoluble Polystyrene Beads by a $-(CH_2)_n-$ ($n = 4, 6$) Spacer

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Insoluble diorganotin functionalized polymers of the type $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{SnBuX_2})_t$, with $n = 4, 6$, X = Ph, Cl, and t being the degree of functionalization, were synthesized from Amberlite XE-305, an insoluble polystyrene ($\mathbf{P}{-}\mathrm{H}$) cross-linked with divinylbenzene. The synthesis conditions used gave rise to functionalization degrees varying from 25% to 30%. The tin-functionalized polystyrenes were characterized by elemental analysis, IR, and Raman as well as solid-state ^{117}Sn and ^{13}C NMR spectroscopy. Methodological and chemical features related to the determination of the functionalization degree have been investigated in detail. The catalytic activity of the Amberlite-grafted tin functionalities in transesterification reactions was studied.

Introduction

Tin derivatives are used as homogeneous catalysts in esterification[1−3] and transesterification reactions.[4−8] Removing tin traces from reaction mixtures can be challenging when industrial processes are considered, because of their toxicity.[9−11] This problem can be bypassed by anchoring organotin moieties to an insoluble macromolecular support.[12−17] After the application, the undesired metal moiety is removed from the desired substances by simple filtration of the grafting support. Cross-linked polystyrenes were widely used for such purposes.[18,19] Analysis tools for quantitative and qualitative characterization of tin functionalities grafted to insoluble supports are not numerous (elemental analysis, IR and Raman spectroscopy, solid-state ^{13}C and ^{117}Sn MAS NMR[20,21]).

Previous papers have mainly reported on organic synthesis applications of trialkyltins anchored to insoluble polystyrenes;[12−17,20−21] one focused on solid-state ^{117}Sn NMR characterizations of such systems,[21] based on comparisons with data on analogous compounds in solution,[22,23] while another explored their catalytic properties in lactonization reactions of α,ω-hydroxyal-

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kanoic acids.[20] This paper reports on novel dialkyltins grafted to insoluble cross-linked polystyrenes of the type $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{SnBuX_2})_t$, with $\mathbf{P} = -[\mathrm{CH_2CH}(p\text{-}\mathrm{C_6H_4})]-$, $n = 4, 6$, $\mathrm{X} = \mathrm{Ph, Cl}$, and t being the degree of functionalization. We focus on (i) the use of a quantitative method to obtain reliable data on the type, purity, and degree of the organotin functionality grafted to the insoluble carrier and (ii) catalytic activity in a reversible transesterification reaction using ethyl acetate and simple alcohols. Attention is paid to the recyclability of the catalysts and to the question of what extent grafting affects the catalytic activity of the diorganotins, the macromolecular support potentially being a sterically demanding factor. The performances of the grafted dialkyltins and their solution analogues $\mathrm{Bu_2SnPh_2}$ and $\mathrm{Bu_2SnCl_2}$, used as early model catalysts in transesterifications,[7] are compared.

Experimental Section

Synthesis. The starting material $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_4\mathrm{Cl})_t$ (**1**) was prepared using a known procedure,[15] from the polymer $\mathbf{P}{-}\mathrm{H}$ (Amberlite XE−305 Catalog No. 15721, Polysciences, Inc.; diameter 300−700 μm) converted to $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}\mathrm{Li})_t$ by lithiation with BuLi in hexane, followed by reaction with $\mathrm{Br(CH_2)_4Cl}$. Polymer **1** contains 2.14 mmol of CCl functionality/g of material, as determined by elemental analysis. Anal. Found: H, 7.62; C, 84.31; Cl, 7.58; Br, <100 ppm. The procedure was the same for $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_6\mathrm{Cl})_t$ (**2**) with $\mathrm{Br(CH_2)_6Cl}$. Polymer **2** contains 2.04 mmol of CCl/g. Anal. Found: H, 8.41; C, 84.00; Cl, 7.24; Br, <100 ppm. The polymers $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_4\mathrm{SnBuPh_2})_t$ (**3**) and $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_6\mathrm{SnBuPh_2})_t$ (**4**) were synthesized by extending the method previously used for $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{SnBu_2Ph})_t$ ($n = 4, 6$).[15] The target polymer **3** contains 1.39 mmol of Sn/g. Anal. Found: H, 7.24; C, 76.65; Sn, 16.49; Cl, 0.74. The target polymer **4** contains 1.18 mmol of Sn/g. Anal. Found: H, 7.64; C, 78.09; Sn, 14.00; Cl, 0.99. The polymer $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_4\mathrm{SnBuCl_2})_t$ (**5**) was prepared as follows. A 4 g amount of **3** was mixed with 30 mL of distilled methanol in a Schlenk tube. At room temperature and in darkness, 10 mL of a 2 M HCl/MeOH solution was slowly added. The reaction mixture was heated at 65 °C for 24 h. The target polymer **5** washed 8 times with 30 mL of methanol and dried at 60 °C under vacuum contained 1.39 mmol of Sn and 2.69 mmol of Cl/g of polymer, indicating a deficit of chlorine of 3.4% with respect to tin for the expected $\mathrm{SnCl_2}$ functionality. Anal. Found: H, 6.75; C, 65.51; Sn, 16.48, Cl, 9.53. The target polymer **6**, $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_6\mathrm{SnBuCl_2})_t$, prepared similarly, contains 1.30 mmol of Sn and 2.43 mmol of Cl, indicating a chlorine deficit of 7%. Anal. Found: H, 7.18; C, 67.60; Sn, 15.39; Cl, 8.63. The molecular tin precursor $\mathrm{Ph_2BuSnLi}$ was prepared as described previously[15] from $\mathrm{Ph_3SnCl}$ (Aldrich).

Catalysis Experiments on Transesterification Reactions. Ethyl acetate, used both as starting ester and solvent, and starting high-boiling alcohol (1-octanol (Aldrich), cyclohexanol (UCB), 3-ethyl-3-pentanol (Fluka)) were engaged in the molar ratio 7/1. The mixture of typically 34 mg of ethyl acetate (385 mmol), 55 mmol of alcohol, and insoluble Amberlite-supported catalyst (1 or 0.1 mol %) was refluxed (80 °C) for 24 or 48 h. The catalyst was filtered off and washed with $\mathrm{CHCl_3}$, THF, and ethanol. Ethyl acetate was distilled off from the reaction mixture. The ratio initial alcohol/obtained ester was determined by integration (±1%) of the respective $\mathrm{CH_2O}$ $^1\mathrm{H}$ resonances.

Scheme 1

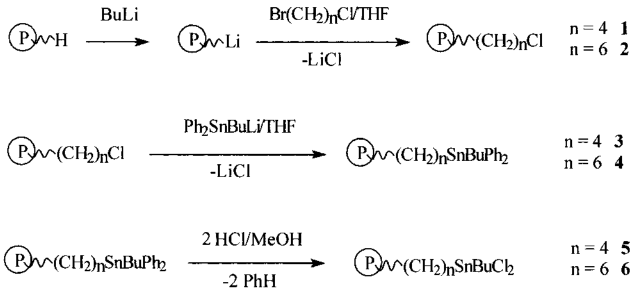

Table 1. Values of the Functionalization Degree t as Determined from Elemental Analysis, Mass Data and ^{13}C MAS NMR Spectra[a]

		t		
label	compd	elemental anal.[b]	calcd using wt[c]	from ^{13}C MAS NMR[c]
1	$\mathrm{P{-}(CH_2)_4Cl}$	0.289 ± 0.013	0.31	0.30
2	$\mathrm{P{-}(CH_2)_6Cl}$	0.308 ± 0.011	0.28	0.31
3	$\mathrm{P{-}(CH_2)_4SnBuPh_2}$	0.299 ± 0.009	0.25	
4	$\mathrm{P{-}(CH_2)_6SnBuPh_2}$	0.250 ± 0.008	0.26	
5	$\mathrm{P{-}(CH_2)_4SnBuCl_2}$	0.251 ± 0.002		
6	$\mathrm{P{-}(CH_2)_6SnBuCl_2}$	0.246 ± 0.006		

[a] $\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{X}$ stands for $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{X})_t$. [b] Values from nonlinear least-squares analysis of elemental data (Experimental Section). [c] Estimations to ±0.03.

IR and Raman Spectra. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer (MIR beam) from 200 mg dry KBr pellets with ca. 5 mg of substance. The Raman spectra were recorded on a Perkin-Elmer 2000 near-IR FT-Raman spectrometer using a Raman_dpy2 beam with 310 mW of power. Polystyrene bands (cm^{-1}):[24,25] aromatic C−H stretchings, 3025, 3059, and 3082; aliphatic C−H stretchings, 2849 and 2921; weak overtone bands, 1719, 1802, 1871, and 1942 (monosubstituted aromatic rings); aromatic C−C stretchings: 1452, 1493, 1583, and 1601; weak in-plane aromatic C−H bending bands, 1028 and 1069; out-of-plane C−H aromatic bending bands, 696 and 756 (monosubstituted aromatic rings). Other bands (cm^{-1}): $\delta_{\mathrm{oop}}(\mathrm{C{-}C})_{\mathrm{di}}$ (out-of-plane C−C bending in disubstituted aromatics), 791 (**1**, **2**), 795 (**3**, **4**), and 791 (**5**, **6**); $\delta_{\mathrm{oop}}(\mathrm{C{=}C})_{\mathrm{ring}}$ (**3**, **4**), 1472 (w) and 1570 (w); $\delta_{\mathrm{oop}}(\mathrm{C{-}C})_{\mathrm{mono}}$ (**3**, **4**), 727 (w); $\nu(\mathrm{C{-}Cl})$ (**1**, **2**), 651 (w). Bands characteristic for Sn−X (cm^{-1}): $\nu(\mathrm{Sn{-}Ph})$ (**3**, **4**), 1073 (m); $\nu_{\mathrm{sym}}(\mathrm{Sn{-}Bu})^*$, 506 (w) (**3**, **4**) and 511 (w) (**5**, **6**); $\nu_{\mathrm{asym}}(\mathrm{Sn{-}Bu})^*$, 597 (w) (**3**, **4**) and 596 (w) (**5**, **6**); $\nu_{\mathrm{rock}}(\mathrm{Sn{-}Ph})^*$ (**3**, **4**), 656 (w); $\nu(\mathrm{Sn{-}Cl})^*$ (**5**, **6**), 343 (w) (an asterisk indicates that the band came from Raman spectra).

Solid-State NMR Data. All MAS spectra were recorded on a Bruker DRX250 spectrometer, operating at 62.90 and 89.15 MHz for ^{13}C and ^{117}Sn nuclei, respectively, using procedures described previously.[21,26] The solid-state ^{13}C and ^{117}Sn MAS NMR spectra were deconvoluted by total-line-shape (TLS) fitting[27,28] of the experimental spectra using PERCH (*pe*ak resea*rch*)[29] software. ^{13}C and ^{117}Sn solution data in $\mathrm{CDCl_3}$ for the model compounds $\mathrm{Bu_2SnPh_2}$ and $\mathrm{Bu_2SnCl_2}$ are available in the Supporting Information.

Determination of the Functionalization Degree. The functionalization degree t of the polymer $(\mathbf{P}{-}\mathrm{H})_{1-t}(\mathbf{P}{-}(\mathrm{CH_2})_n\mathrm{SnBuX_2})_t$ was determined from experimentally obtained elemental mass fractions using a mathematical nonlinear least-squares procedure[30−32] presented in the Supporting Information.

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Table 2. ^{117}Sn and ^{13}C Chemical Shifts (ppm) from Solid-State MAS NMR Spectra for the Functionalized Polymers 1−6[a]

compd	$\delta(^{117}Sn)$	$\delta(^{13}C$ aliph)	$\delta(^{13}C$ arom)
P$-(CH_2)_n$Cl (**1**, **2**)		40 (C1),[d] 45 (C2),[d] 40−28 (C3),[d] 45 (C4)	146 (α), 128 (β)
P$-(CH_2)_n$SnBuPh$_2$ (**3**, **4**)	−70, −42[b]	10−11 (C5), 14 (C6)	144−146 (α), 128 (β), 137 (χ)
P$-(CH_2)_n$SnBuCl$_2$ (**5**, **6**)	125, 150[c]	14−15 (C6)	146 (α), 128 (β)

[a] See Chart 1 for compound and atom labeling. [b] Secondary tin functionality, ca. 2% as estimated from simulations of solid-state ^{117}Sn MAS NMR spectra (see Experimental Section). [c] Secondary tin functionality, ca. 3−6%. [d] The same resonances are found for the other compounds **3**−**6**.

Results and Discussion

The insoluble diorganotin-functionalized target polystyrenes were synthesized as shown in Scheme 1, where **P**−Z stands for $(\mathbf{P}-H)_{1-t}(\mathbf{P}-Z)_t$ and Z is substituting the *para* position of the styrene phenyl group.

The tetra- or hexamethylene spacer aims at ensuring sufficient molecular mobility to the tin functionality in order to improve reagent accessibility and weakened reactivity due to the grafting. Moreover, the tin atom is bound to an aliphatic rather than aromatic carbon atom, so as to achieve stronger grafting of the organotin to the polymeric support. The degree of functionalizations *t* of all the materials was computed from elemental analysis data using a nonlinear least-squares analysis of the overdetermined system of equations, giving *t* as a function of element mass fractions[30−32] (see the Supporting Information and Table 1).

The sluggish reactivity of such systems necessitated the use of a large excess of HCl in methanol for the conversion of compounds **3** and **4** to **5** and **6**, respectively. This did not lead to a Cl/Sn ratio higher than 2 and even provided a slight default of chlorine in **5** and **6** with respect to the expected 2/1 ratio. The functionalities are identified from IR and Raman spectra, showing the expected functionality bands[33−35] (Experimental Section).

Table 2 displays the ^{13}C and ^{117}Sn MAS NMR data of derivatives **1**−**6**, using the atom labeling of Chart 1. The phenyl and butyl as well as the polystyrene aliphatic backbone ^{13}C signals were assigned by analogy with solution ^{13}C spectra of the Bu_2SnPh_2 and Bu_2SnCl_2 analogues (Supporting Information) and from a ^{13}C DEPT NMR spectrum of soluble polystyrene in $CDCl_3$. The solid-state isotropic ^{117}Sn chemical shifts from MAS spectra of **3**−**6** characterize the grafted target as well as minor side-reaction tin functionalities. In all cases the tin atom is four-coordinate.[22,23]

The single main ^{117}Sn MAS resonance of **3**−**6** has no anisotropy pattern, at least when the sample is spun above 10 kHz for **5** and **6**. For **3** and **4**, the minor ^{117}Sn resonance with ca. 2% relative intensity is characteristic for R_3SnPh compounds (R = Bu and/or grafted $-(CH_2)_n$ chain), while for **5** and **6**, it amounts to ca. 3−6% and is characteristic for R_3SnCl moieties. A typical spectrum is shown together with simulations and deconvolutions in Figure 1 for compound **5**.

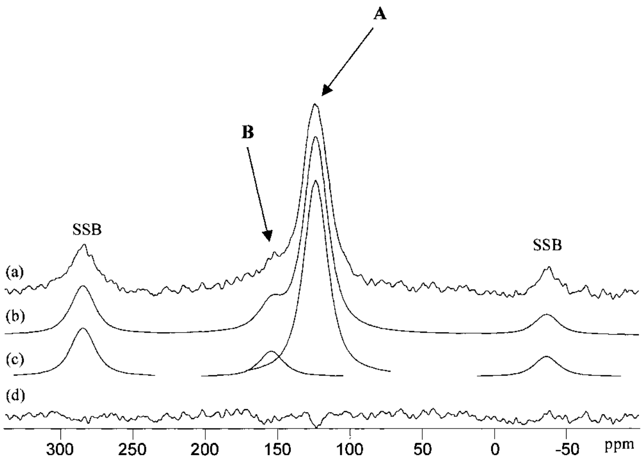
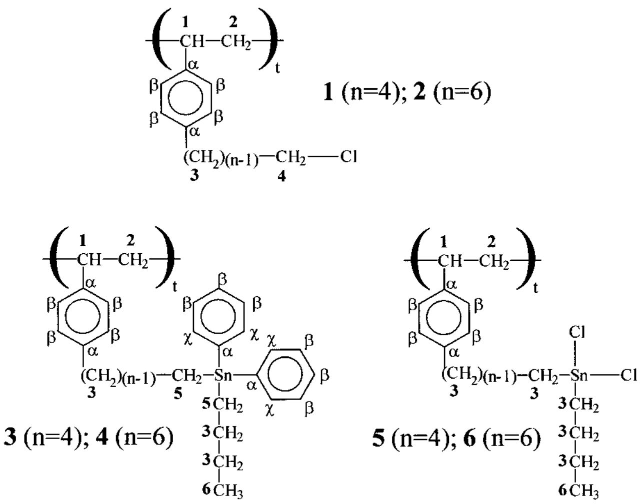


Figure 1. Solid-state ^{117}Sn MAS NMR spectra of compound **5** (rotation speed of the sample 14 kHz; SSB = spinning side band): (A) expected resonance of the target R_2SnCl_2 functionality (125 ppm); (B) resonance of the R_3SnCl side functionality (150 ppm); (a) experimental spectrum; (b) simulated spectrum; (c) deconvolution peaks; (d) difference between experimental and simulated spectra.

Chart 1



The elemental analysis results for compounds **3** and **4** reveal the presence of traces of chlorine (0.5−1 mass %), indicating small amounts of unreacted terminal CH_2Cl moieties from **1** and **2**. For compounds **5** and **6**, a Cl/Sn ratio slightly below 2 is in line with the presence of the small R_3SnCl resonance in the ^{117}Sn MAS spectra. The minor R_3SnPh type grafting in **3** and **4** can be tentatively ascribed to a lithium−phenyl exchange between $Ph_2BuSnLi$ and a $\mathbf{P}-(CH_2)_4SnBuPh_2$ moiety which results in the generation of Ph_3BuSn (as identified by ^{117}Sn solution NMR of the reaction mixture) and grafted $\mathbf{P}-(CH_2)_4SnBuPhLi$. The latter then reacts with still unreacted $\mathbf{P}-(CH_2)_n$Cl functionality, accompanied

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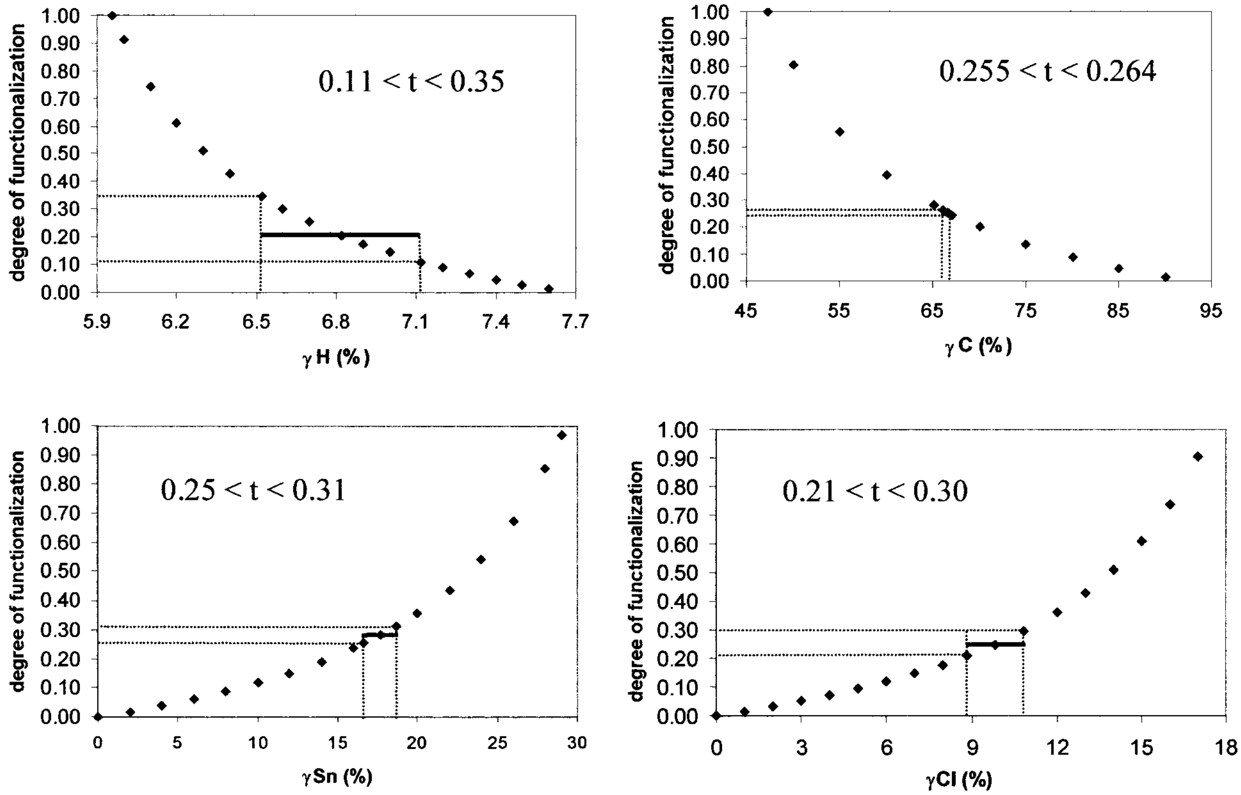


Figure 2. Charts of the degree of functionalization t as a function of the mass fraction for each element in $(\mathbf{P}-H)_{1-t}(\mathbf{P}-(CH_2)_4SnBuCl_2)_t$. Only the physically possible range of the graphs ($0 \leq t \leq 1$) is displayed; for the mass fractions from elemental analysis the uncertainty margins are given (H ±0.3%; C, ±0.5%; heteroelements, ±1%).

by elimination of LiCl, providing the double-grafted R_3SnPh side functionality. A similar stannylation reaction performed in solution with the starting model compound $Ph(CH_2)_4Cl$ supports this proposal, since small ^{117}Sn signals characteristic for R_3SnPh and $RSnPh_3$ were found in addition to the main resonance of R_2SnPh_2 (R = Bu and/or $Ph(CH_2)_4$) in the ^{117}Sn solution NMR spectrum of the reaction mixture. The presence of a grafted R_3SnPh side functionality naturally results in grafted R_3SnCl during the HCl/methanol conversion from $\mathbf{P}-(CH_2)_nSnBuPh_2$ to $\mathbf{P}-(CH_2)_nSnBuCl_2$, the relative amount of the latter being roughly compatible with the Cl/Sn deficit.

The degree of functionalization t, never exceeding 32 mol % for **1** and **2**, is apparently limited by the size of the polystyrene beads, the dimension of the pores inside the beads, and/or the steric demand resulting from the cross-linking. The parameter t could be be reliably determined only by a nonlinear least-squares analysis[30,31] of elemental mass fractions, since values obtained from ^{13}C NMR data suffer from overlapping for **3**−**6**, and those from weighing are subject to too small molar mass differences between the functionalities of **3**/**4** and **5**/**6**, respectively. Note, nevertheless, the fair agreement between values from elemental data, weighing, and/or semiquantitative solid-state ^{13}C MAS NMR data, where such comparisons are possible (Table 1). Since compounds **3** and **4** contain small amounts of side functionalities, it is much more difficult to get accurately their degree of functionalization, a single main functionality being assumed and preliminarily identified for its calculation. Therefore, the values of t for compounds **3**−**6** are to be considered more as indicative. Furthermore, a detailed analysis of the equations (eq 1 in the Supporting Information and similar ones for the other elements) giving the functionality degree t as a function of the mass fractions of all elements involved has been performed; it reveals that even when the functionality is pure, the values of t found from the overdetermined system of equations associated with the considered functionalized polymer can deviate dramatically from the actual ones. Figure 2 shows simulations of such functions for compound **5** for the mass fractions of C, H, Sn, and Cl around their expected values and illustrates that predetermined uncertainty margins on the mass fraction data can lead to very widespread uncertainty margins of the t values, depending on the element used. Thus, there is a large error bar on the value of t using the equation for the mass fraction of H, such that the slightest change therein, even within experimental error, gives an important change in the value of t. This justifies the use of the statistical nonlinear least-squares approach minimizing the impact of the elements leading to larger uncertainty margins.

Transesterification reactions have been performed in the presence of the insoluble organotin-grafted compounds **3**−**6** as potential catalysts. The reaction between ethyl acetate and octanol (Scheme 2) has been investigated.

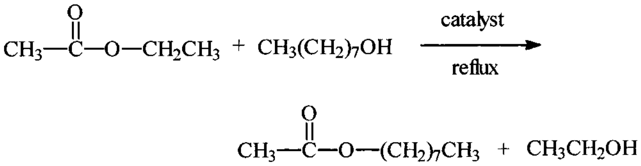
In the absence of catalyst, no reaction at all is observed. Table 3 reveals a moderate to reasonable catalytic activity for compounds **3**, **5**, and **6** in terms of reaction duration. The soluble molecular species Bu_2SnPh_2 and Bu_2SnCl_2 (experiments 1 and 2) have higher activity than the corresponding grafted systems $\mathbf{P}-(CH_2)_4$-$SnBuPh_2$ and $\mathbf{P}-(CH_2)_4SnBuCl_2$ (experiments 3 and 5),

Table 3. Catalytic Activities of Compounds 3, 5, and 6 in Transesterifications of Ethyl Acetate

expt	catalyst	amt of catalyst (tin mol %)	alcohol	reacn time (h)	conversn (%)
1	Bu_2SnPh_2	1	$CH_3(CH_2)_7OH$	24	98
2	Bu_2SnCl_2	1	$CH_3(CH_2)_7OH$	24	94
3	P$-(CH_2)_4SnBuPh_2$	1	$CH_3(CH_2)_7OH$	24	77
4	P$-(CH_2)_4SnBuPh_2$	1	$CH_3(CH_2)_7OH$	48	90
5	P$-(CH_2)_4SnBuCl_2$	1	$CH_3(CH_2)_7OH$	24	82
6a	P$-(CH_2)_4SnBuCl_2$, 1st run	1	$CH_3(CH_2)_7OH$	48	99
6b	P$-(CH_2)_4SnBuCl_2$, 2nd run	1	$CH_3(CH_2)_7OH$	48	98
7a	P$-(CH_2)_4SnBuCl_2$, 1st run	1	$CH_3(CH_2)_7OH$	48	96
7b	P$-(CH_2)_4SnBuCl_2$, 2nd run	1	$CH_3(CH_2)_7OH$	48	95
7c	P$-(CH_2)_4SnBuCl_2$, 3rd run	1	$CH_3(CH_2)_7OH$	48	96
7d	P$-(CH_2)_4SnBuCl_2$, 4th run	1	$CH_3(CH_2)_7OH$	48	90
7e	P$-(CH_2)_4SnBuCl_2$, 5th run	1	$CH_3(CH_2)_7OH$	48	92
8	P$-(CH_2)_4SnBuCl_2$	0.1	$CH_3(CH_2)_7OH$	24	55
9	P$-(CH_2)_4SnBuCl_2$	0.1	$CH_3(CH_2)_7OH$	48	86
10	P$-(CH_2)_6SnBuCl_2$	1	$CH_3(CH_2)_7OH$	24	81
11	P$-(CH_2)_4SnBuCl_2$	1	$C_6H_{11}OH$[a]	24	23
12	P$-(CH_2)_4SnBuCl_2$	1	$C_6H_{11}OH$[a]	48	33
13	P$-(CH_2)_4SnBuCl_2$	1	$(CH_3CH_2)_3COH$	24	0

[a] $C_6H_{11}OH$ = cyclohexanol.

Scheme 2



but not to a very large extent. When one considers the easy recycling of the grafted systems, the only slightly lower conversion of the latter for equal reaction durations is only a minor drawback. The R_2SnCl_2 and R_2SnPh_2 compounds are comparably (experiments 3 and 4 vs 5 and 6a) active, even though, after 48 h, conversion is quantitative or nearly so for **P**$-(CH_2)_4SnBuCl_2$ but not for **P**$-(CH_2)_4SnBuPh_2$. **P**$-(CH_2)_4SnBuCl_2$ appears recyclable, with the same catalytic efficiency in the second as in the first run. ^{117}Sn MAS spectra of this compound after and before reaction are identical (experiments 6a,b). A solution ^{117}Sn spectrum of the distillate and the evaporated reaction mixture after filtration of the catalyst did not reveal any presence of observable tin within the sensitivity limits of solution ^{117}Sn NMR. With another fresh sample, transesterification yields of 96, 95, 96, 90, and 92% were obtained in runs 1−5, respectively (experiments 7a−e), revealing a satisfactory lifetime of the catalyst and its easy recyclability. Reducing the catalyst amount by a factor of 10 reduces the conversion from 99 to 86% after 48 h of reaction (experiments 6a,b and 9). The length of the spacer has no influence (experiments 5 and 10). The **P**$-(CH_2)_4SnBuCl_2$ catalyst is much less active toward secondary than primary alcohols, conversion decreasing 2.5 to 3 times upon switching from octanol to cyclohexanol (experiments 6a,b vs 12 and 5 vs 11), and is totally unefficient toward the tertiary alcohol 3-ethyl-3-pentanol (experiment 13). Basic Amberlite showed no conversion at all, while **P**$-(CH_2)_4Cl$ showed unexpectedly 4% conversion. The latter is likely due to lithium introduced by BuLi during the conversion of **P**−H to **1**; thus, when **P**−H is treated with all reagents needed for its conversion to **1** minus BuLi, no reaction occurred. However, 1% LiCl did not result in any transesterification. Because of the very marginal activity of **P**$-(CH_2)_4Cl$ in comparison to the grafted dialkyltin compounds, there is no doubt that the influence of possible contaminants in **3**, **5**, and **6** is inconsequential.

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Supporting Information Available: Text giving solution NMR data of Bu_2SnCl_2 and Bu_2SnPh_2 and a full treatment, with example, of the nonlinear least-squares determination of the functionalization degree *t*. This material is available free of charge via the Internet at http://pubs.acs.org.

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