Interface Synthesis, Characterization and Catalytic Properties of Dialkyldichlorotin and Tetraalkyl Distannoxane Functionalities Grafted to Insoluble Polystyrene Beads by a Hexamethylene Spacer

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Insoluble polystyrene-grafted compounds of the type $[(P–H)_{(1-t)}\{P–(CH_2)_6SnBuCl_2\}_t]$ and $[(P–H)_{(1-t)}(\{P–(CH_2)_6SnBuX\}_2O)_{t/2}]$, where (P–H) represents a cross-linked polystyrene, X is Cl, OH or $OOCCH_3$, and *t* is the degree of functionalization, were synthesized from Amberlite XE-305, a polystyrene cross-linked with divinylbenzene. The compounds were characterized by elemental analysis, IR and Raman spectroscopy, solid-state ^{13}C and ^{117}Sn NMR spectroscopy and, where appropriate, by ^{119}Sn hr-MAS NMR spectroscopy. The influence of the variable *t* and tin functionality on the catalytic activity of these compounds was assessed in the transesterification reaction of ethyl acetate with octanol. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

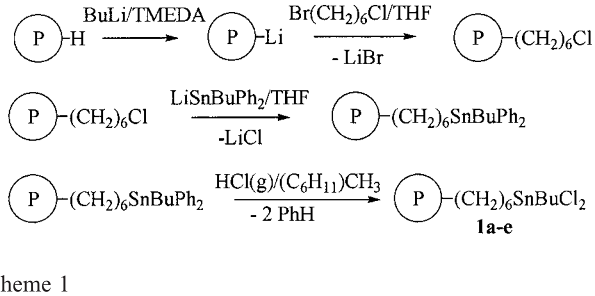
Introduction

While organotin compounds enjoy widespread use as versatile reagents or catalysts in a large variety of organic transformations,[1,2] their application is sometimes limited by their toxicity.[3,4] This adverse feature is further aggravated by the generally difficult quantitative removal of organotin reagents and their by-products from the reaction mixture,[5] often making them unsuitable for the synthesis of biological or pharmaceutical derivatives.[3,6] These concerns can be alleviated by grafting the organotin reagent onto a solid support, thereby creating so-called "clean" organotin reagents, which can be removed completely from reaction products by simple filtration. In a previous paper we reported on the synthesis[7] and characterization[7,8] of $[(P-H)_{(1-t)}\{P-(CH_2)_nSnBuX_2\}_t]$ ($n = 4, 6$; X = Ph, Cl; *t* (degree of functionalization) = 0.25−0.30]. The catalytic activity of these compounds in the transesterification reaction of ethyl acetate with simple alcohols such as octanol appeared reasonably good.[7] The work presented here describes the synthesis of analogues with a lower degree of functionalization, with the aim of evaluating the effect of *t* on the catalytic activity of these compounds. Furthermore, based on the work of Otera and co-workers,[9] which proposes the use of distannoxanes $[XR_2SnOSnR_2Y]_2$ (R = Bu, Me; X = Cl, NCS; Y = OH, Cl, NCS) as efficient catalysts in transesterification reactions, distannoxanes grafted to insoluble polystyrene, of the type $[(P-H)_{(1-t)}(\{P-(CH_2)_6SnBuX\}_2O)_{t/2}]$ (X = Cl, OH, $OOCCH_3$) were synthesized from the dialkyldichlorotin precursors. Their characterization and catalytic activity are also discussed.

Results and Discussion

Synthesis and Characterization

A series of five dialkyldichlorotin compounds $[(P-H)_{(1-t)}\{P-(CH_2)_6SnBuCl_2\}_t]$ (**1a−e**) with *t* varying between 0.03 and 0.31 was synthesized[7,8] according to Scheme 1.



Scheme 1

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Different degrees of functionalization were obtained by controlled variation of the amount of BuLi in the first lithiation step, resulting in five $(P{-}H)_{(1-t)}(P{-}Li)_t$ precursor compounds. The dependence of *t* on the BuLi/P−H molar ratio in this step is illustrated in Figure 1.

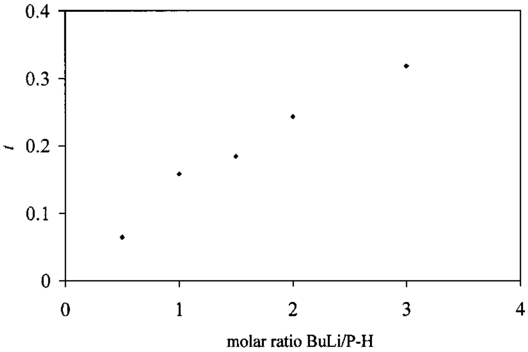
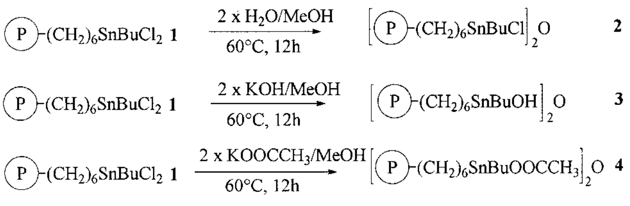


Figure 1. The experimental degree of functionalization (*t*) as a function of the molar ratio BuLi/P−H in the first reaction step of Scheme 1

The substitution of the phenyl groups by chlorine in the last step of the reaction in Scheme 1, previously performed by reaction with HCl in methanol, suffered from sluggish reactivity leading to polymers with a slight but significant chlorine deficit.[7] In the present synthesis route, pure HCl gas is bubbled for 15 minutes through a suspension of beads of $[(P{-}H)_{(1-t)}\{P{-}(CH_2)_6SnBuPh_2\}_t]$ in methylcyclohexane at −80 °C. Using this new route, a better control over the desired substitution reaction was obtained, since less than 2% of grafted R_3SnCl side-functionality was obtained instead of 6−7 % by the HCl/CH_3OH method, as assessed by solid state ^{117}Sn MAS NMR spectroscopy and elemental analysis. Moreover, any possible inconvenience arising from moisture can be better avoided with the latter synthesis route. The determination of *t* of all precursor compounds and of **1a−e** (**1a**, $t = 0.03$; **1b**, $t = 0.10$; **1c**, $t = 0.12$; **1d**, $t = 0.21$; **1e**, $t = 0.31$) was performed, as described previously,[7] from experimentally obtained elemental mass fractions of all elements involved, using a mathematical non-linear least-squares procedure, minimizing the impact of the elements leading to larger uncertainty margins.

Since distannoxanes, with general formula $YR_2Sn{-}O{-}SnR_2Y$, have also proved to be efficient transesterification catalysts,[9] we were interested in the conversion of compounds **1a−e** into compounds of the type $[(P{-}H)_{(1-t)}(\{P{-}(CH_2)_6SnBuX\}_2O)_{t/2}]$ with X = Cl, OH, $OOCCH_3$. The synthetic procedures leading to the different Sn−O−Sn-bridged compounds are given in Scheme 2. The reactions were performed twice successively, in order to achieve full conversion as far as possible. IR and Raman spectroscopy were used to monitor the reactions: in the Raman spectra the evolution of the ν(Sn−Cl) band was monitored, while in the IR spectra the appearance of new bands characteristic of the different Sn−O−Sn-bridged compounds can be observed. The purity of the compounds in Scheme 2 was determined by elemental analysis, solid state ^{117}Sn MAS NMR spectroscopy and, where appropriate, by ^{119}Sn hr-MAS NMR spectroscopy. The latter technique is a high resolution liquid NMR technique that is used to obtain NMR spectra of tin-containing grafts dipped in solution, in situ at the solid−liquid interface, provided sufficient local rotational mobility can be achieved on the grafts through matrix pore swelling by the solvent.[8]



Scheme 2

Whereas the reaction with H_2O and KOH was complete for the compounds with high *t* value (0.31, compounds **2e** and **3e**), incomplete conversion was observed for the compounds with lower *t* value (0.03−0.21, compounds **2a−d**, **3a−d**). This was shown by the presence of residual ν(Sn−Cl) bands in the Raman spectra of **3a−d** and the detection of residual amounts of chlorine for **3a−d** or too high amounts for **2a−d** by elemental analysis; the conversion degree appears to be dependent on *t*, as illustrated in Figure 2 and 3.

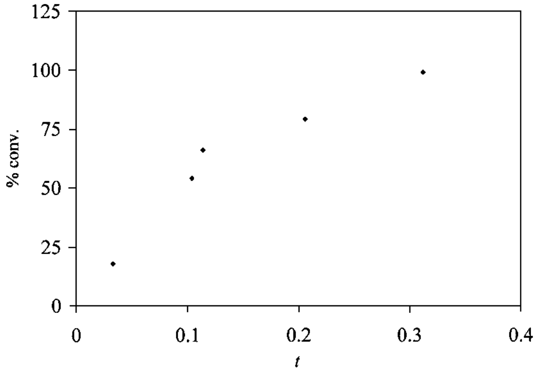


Figure 2. Percentage conversion of **1** into **2** as a function of *t*

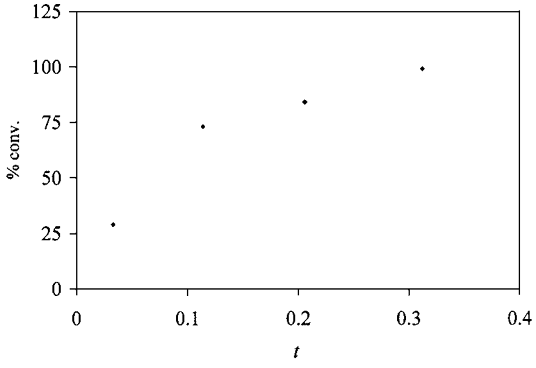


Figure 3. Percentage conversion of **1** into **3** as a function of *t*

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The explanation for this observation is to be found in the lack of sufficient neighbouring grafted functionalities, which are necessary to generate Sn−O−Sn cross-links, in the compounds with low functionality.

Further evidence for residual $-SnCl_2$ functionalities was found in the ^{119}Sn hr-MAS spectra of **2a−d** and **3a−d**, which still show resonances for this functionality. This technique, which is used to obtain high resolution liquid-like ^{119}Sn NMR spectra of solvent-swollen beads of $[(P-H)_{(1-t)}\{P-(CH_2)_6S\mathit{n}BuCl_2\}_t]$,[8] in which the tin functionality acquires local rotational mobility, was disappointingly uninformative for **2e** and **3e**, where complete conversion was obtained. In fact, no ^{119}Sn NMR resonance could be generated, probably due to the rigidity of the distannoxane moiety by the additionally introduced Sn−O−Sn cross-linking, preventing sufficient rotational mobility necessary for this technique to be successful.

When reacting **1e** with CH_3COOK in methanol, it was unclear beforehand whether grafted tin compounds of the distannoxane type, $[P-(CH_2)_6SnBuOOCCH_3]_2O$, or of the tin dicarboxylate type, $P-(CH_2)_6SnBu[OOCCH_3]_2$, with both chlorides substituted by acetate, would be obtained, since the synthesis of a compound similar to the latter has already been described in the literature, although in this case the tin moiety is grafted directly to the phenyl rings of an insoluble polystyrene matrix.[10] Therefore, the theoretical mass fractions were calculated for both models using the functionalization degree of the precursor **1e**. When these calculated values were compared to those determined by elemental analysis, the mass fractions, especially the ones for carbon and tin calculated for the Sn−O−Sn model, fitted the experimental values better (see Table 1). Moreover, the positions of the ν(C=O) bands in the IR spectrum of **4e** differ from those of the model dicarboxylate compound $Bu_2Sn(OOCCH_3)_2$, while other characteristic bands of the latter are not found. This favours the proposal that the obtained compound is indeed of the distannoxane type, as is the case for those obtained by reaction of **1** with H_2O or KOH.

Table 1. Comparison of the experimental mass fractions of compound **4e** with the theoretical ones using different models

Model	γ_C (%)	γ_H (%)	γ_{Sn} (%)
Experimental mass fractions	68.80	7.54	18.50
$[P-(CH_2)_6SnBuOOCCH_3]_2O$	68.52	7.43	17.99
$P-(CH_2)_6SnBu[OOCCH_3]_2$	66.98	7.32	16.70

Catalytic Activity

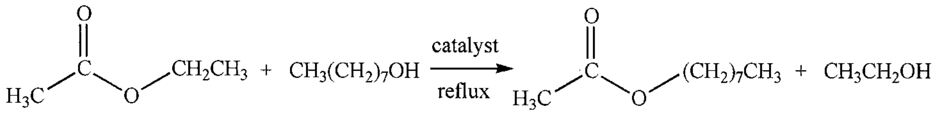
In order to evaluate the catalytic activity of the grafted organotins in **1−4**, the reaction between ethyl acetate and octanol (Scheme 3) was investigated. The degree of conversion was calculated from the ratio of initial alcohol to obtained ester by integration of the respective CH_2O ^{1}H NMR resonances. The results are summarized in Table 2.

For the compounds $[(P-H)_{(1-t)}\{P-(CH_2)_6SnBuCl_2\}_t]$ with variable functionalization degree, two types of experiments were performed. Entries 1−4 (type A) were carried out with a constant mass of catalyst (367 mg, corresponding to 1 mol % of **1e**), and consequently a variable molar amount of tin sites. Entries 5−7 (type B) describe reactions with 1 mol % of catalyst (% Sn with respect to octanol). In the first series reasonably good results were obtained for all compounds, with a maximum conversion obtained for $t = 0.21$, which appears to be the optimal functionalization degree for the catalytic activity (see Table 2). In the second series a slight decrease in conversion was observed with increasing t. Both data sets are in agreement with a better accessibility of the reagents to the catalytic centre at a moderate degree of functionalization, emphasizing the need to find the optimum compromise between having a sufficient number of catalytic sites and avoiding side-chain entanglement due to a too high degree of functionalization.

As far as the distannoxanes are concerned, the catalytic activity is reported for the functionally pure compounds **2e**, **3e** and **4e** only. Although a decreased molecular mobility of the grafted tin functionality is to be expected due to the introduction of Sn−O−Sn bridges, good conversion degrees, comparable (or slightly higher) to those of the precursor compound **1e**, were obtained when using these compounds as catalysts in the transesterification reaction of ethyl acetate with octanol (Table 2; entries 8−11).

The chemical stability of the catalysts under reaction was assessed by solid state ^{117}Sn CP-MAS NMR spectroscopy, at least within the signal-to-noise conditions under which the spectra were obtained. The spectra of compounds **1e** and **2e**, after their use as a catalyst, are reasonably superimposable on the spectra of the same compounds before catalysis. The isotropic chemical shift is found at the same position and no evidence for significant generation of new functionalities can be seen. By way of an example, Figure 4 shows the ^{117}CP-MAS spectrum of **2e** prior to and after a transesterification experiment for 48 hours.

In contrast, the grafted HOSn−O−SnOH (**3e**) and $CH_3COOSn-O-SnOOCCH_3$ (**4e**) compounds are chemically modified during the reaction. Only very ill-defined noisy spectra of these compounds could be obtained, under



$$H_3C-C(=O)-O-CH_2CH_3 + CH_3(CH_2)_7OH \xrightarrow[\text{reflux}]{\text{catalyst}} H_3C-C(=O)-O-(CH_2)_7CH_3 + CH_3CH_2OH$$

Scheme 3

Table 2. Catalytic activities of dialkyltin- and distannoxane-functionalized polystyrenes in the transesterification of ethyl acetate with octanol

Entry	Catalyst	Type[a]	*t*	Conv. after 24 h (%)	Conv. after 48 h (%)
1	**1b**	A	0.10	58	87
2	**1c**	A	0.12	65	88
3	**1d**	A	0.21	89	94
4	**1e**	A	0.31	74	89
5	**1c**	B	0.12	84	95
6	**1d**	B	0.21	80	94
7	**1e**	B	0.31	74	89
8	**2e**	B	0.31	78	96
9	**3e**	B	0.31	72	94
10	**4e**	B	0.31	54	90
11	**4e** (re-used)	B	0.31	58	87

[a] A: 367 mg of catalyst, corresponding to 1 mol % Sn with respect to octanol for **1e**, was used; B: 1 mol % Sn (variable mass) with respect to octanol.

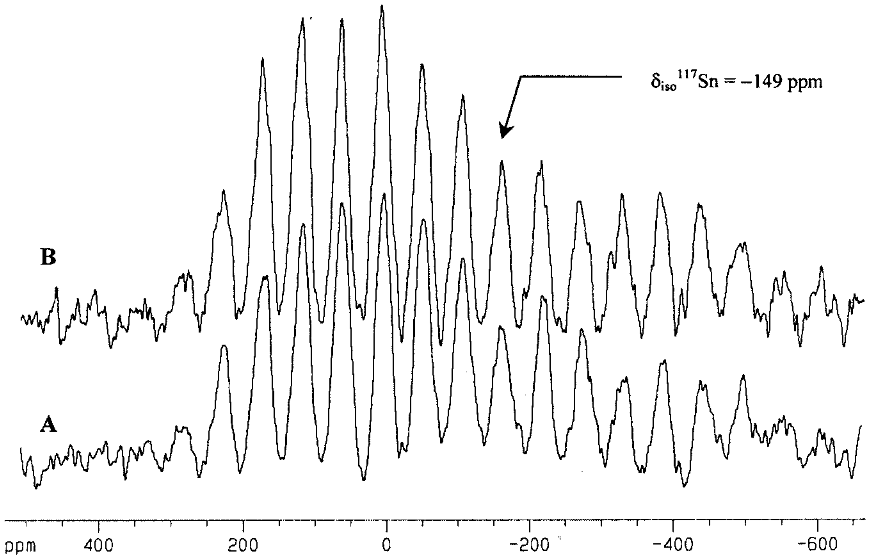


Figure 4. ^{117}Sn CP-MAS spectra of **2e** prior to (A) and after (B) a transesterification experiment

identical acquisition conditions as for the compound before its use as a catalyst, indicating that the organotin grafts are altered during the activation process. The identification of the distannoxane compounds was therefore impossible. Notwithstanding this observation, the catalyst was amenable to a second transesterification run to provide an identical conversion yield as in the first run within experimental error (entry 11 in Table 2). However, as they are chemically unstable, their potential as catalysts is less reliable than for **2e**, which appears to be both efficient and reasonably chemically stable, at least for the model reaction investigated during this work.

Conclusion

Dialkyldichlorotin-grafted polystyrene compounds were obtained with variable degree of functionalization. All compounds showed reasonable catalytic activity in the transesterification reaction of ethyl acetate with octanol. Evidence was found for the existence of an optimal degree of functionalization, interpreted as a compromise between having a sufficient number of catalytic sites and avoiding side-chain entanglement due to a too high degree of functionalization.

The dialkyldichlorotin-grafted polystyrenes were converted into three types of tetraalkyldistannoxanes by reaction with water, hydroxide or acetate. Complete conversion could only be obtained with a sufficiently high degree of functionalization. Their catalytic activity was similar to that of the dialkyldichlorostannanes.

Experimental Section

Synthesis of [(P−H)$_{(1-t)}${P−(CH$_2$)$_6$SnBuCl$_2$}$_t$] (1a−e): The polymers were synthesized as summarized in Scheme 1, following a procedure described previously,[7] modified in the last step to allow for a better control of possible side-reactions.[8] In all cases, a divinylbenzene cross-linked polystyrene, Amberlite XE305 (PolySciences Inc.), was used as the insoluble solid support P−H. In short, a hexamethylene spacer with terminal chloride was grafted onto the insoluble polystyrene P−H, preliminarily lithiated to different extents in the *para* position, by varying the amount of BuLi. In the next step a stannylation reaction with $Ph_2SnBuLi$ in THF substituted the chlorine atom for the $BuPh_2Sn$ group. The $BuCl_2Sn$ functionality in compound **1** was obtained by reaction with HCl gas at −78 °C in methylcyclohexane.[8] IR (cm^{-1}): $\nu_{(Sn-Cl)}$ 340 (m); $\nu_{sym(Sn-Bu)}$ 515 (w); $\nu_{asym(Sn-Bu)}$ 595 (w). $(C_8H_8)_{(1-t)}(C_{18}H_{28}Cl_2Sn)_t$ **1a** ($t = 0.033$): calcd. C 86.97, H 7.59, Cl 2.03, Sn 3.40; found C 86.96, H 7.78, Cl 3.07, Sn 2.63. **1b** ($t = 0.104$): calcd. C 78.42, H 7.34, Cl 5.33, Sn 8.92; found C 78.19, H 7.51, Cl 5.44, Sn 7.73. **1c** ($t = 0.117$): calcd. C 77.16, H 7.30, Cl 5.81, Sn 9.73; found C77.47, H 7.34, Cl 6.32, Sn 9.53. **1d** ($t = 0.206$): calcd. C 70.21, H 7.10, Cl 8.49, Sn 14.21; found C 70.34, H 7.19, Cl 7.86, Sn 14.46. **1e** ($t = 0.312$): calcd. C 64.50, H 6.93, Cl 10.68, Sn 17.88; found C 64.51, H 7.24, Cl 10.56, Sn 18.08. ^{119}Sn hr-MAS NMR: $\delta = 124$ ppm.

Synthesis of $[(P-H)_{(1-t)}(\{P-(CH_2)_6SnBuCl\}_2O)_{t/2}]$ (2): Typically, 0.7 g of **1** was covered by MeOH (30 mL) and heated to 60 °C. Water (4 mL) was then added to the reaction mixture. The reaction mixture was stirred magnetically at 60 °C for 6 hours. The solution was removed with a capillary tube and then MeOH (30 mL) and water (4 mL) were again added successively to the polymer beads. The reaction mixture was kept at 60 °C for 18 hours. The obtained target polymer $[(P-H)_{(1-t)}(\{P-(CH_2)_6SnBuCl\}_2O)_{t/2}]$ (**2**) was washed 8 times with methanol (20 mL) and dried under vacuum at 60 °C. $(C_8H_8)_{(1-t)}(C_{18}H_{28}SnClO_{0.5})_t$ ($t = 0.31$): calcd. C 67.29, H 7.23, Cl 5.57, Sn 18.65; found C 66.98, H 7.32, Cl 6.13, Sn 18.30. IR (cm^{-1}): $\nu_{(Sn-Cl)}$ 337 (m); $\nu_{(Sn-O-Sn)}$ 602 (m); $\nu_{sym(SnBu)}$ 522(w); $\nu_{asym(SnBu)}$ 600 (w). ^{117}Sn MAS NMR: $\delta_{iso} = -149$ ppm.

Synthesis of $[(P-H)_{(1-t)}(\{P-(CH_2)_6SnBuOH\}_2O)_{t/2}]$ (3): The procedure was identical to that described for **2**, but instead of water a solution of KOH (229 mg, 4.08 mmol) in MeOH (20 mL) was added to the reaction mixture. $(C_8H_8)_{(1-t)}(C_{18}H_{29}SnO_{1.5})_t$ ($t = 0.31$): calcd. C 69.37, H 7.61, Cl 0, Sn 19.15; found C 69.62, H 7.74, Cl 0.33, Sn 19.05. IR (cm^{-1}): $\nu_{(OH)}$ 3650 (w); $\nu_{(Sn-O)}$ 448 (w); $\nu_{asym(Sn-O-Sn)}$ 581 (w); $\nu_{sym(SnBu)}$ 506 (w); $\nu_{asym(SnBu)}$ 601 (w). ^{117}Sn MAS NMR: $\delta_{iso} = -171$ ppm.

Synthesis of $[(P-H)_{(1-t)}(\{P-(CH_2)_6SnBuOOCCH_3\}_2O)_{t/2}]$ (4): The procedure was identical to that described for **2**, but instead of water a solution of CH_3COOK (400 mg, 4.08 mmol) in MeOH (20 mL) was added to the reaction mixture. $(C_8H_8)_{(1-t)}(C_{20}H_{31}SnO_{2.5})_t$ ($t = 0.31$): calcd. C 68.52, H 7.43, Cl 0, Sn 17.99; found C 68.80, H 7.54, Cl 0.40, Sn 18.50. IR (cm^{-1}): $\nu_{sym(CO)}$ 1319 (w); $\nu_{asym(CO)}$ 1630 (w); $\Delta\nu_{(CO)} = 311$; $\nu_{(Sn-O)}$ 481 (m); $\nu_{asym(Sn-O-Sn)}$ 608 (w); $\nu_{sym(SnBu)}$ 517 (w); $\nu_{asym(SnBu)}$ 598 (w). ^{117}Sn MAS NMR: $\delta_{iso} = -167$ ppm.

Catalysis Experiments on Transesterification Reactions: Ethyl acetate, used both as reactant ester and solvent, and 1-octanol (Aldrich) were used in a 7:1 molar ratio. A mixture of ethyl acetate (34.1 g, 388 mmol), octanol (7.2 g, 55 mmol) and insoluble Amberlite-supported catalyst (1 mol % Sn with respect to octanol; 367 mg for **1e**) was refluxed for 24 or 48 hours. The catalyst was filtered off and washed with $CHCl_3$, THF and ethanol. The ethyl acetate was distilled off from the reaction mixture. The ratio of initial alcohol to obtained ester was determined by integration (±1 %) of the respective CH_2O ^1H NMR resonances.

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 containing about 5 mg of substance. The Raman spectra were recorded on a Perkin−Elmer 2000 NIR FT-RAMAN spectrometer using a Raman dpy2 beam with 310 mW power.

NMR Spectroscopic Data: Samples used for the determination of the initial alcohol to obtained ester ratio were prepared by dissolving about 10 mg of mixture in 0.5 mL of $CDCl_3$. Quantitative ^1H NMR spectra were recorded on a Bruker AMX500 instrument. The ^{119}Sn hr-MAS spectra were recorded on the same instrument (186.50 MHz) with a specially dedicated Bruker $^1H/^{13}C/^{119}Sn$ hr-MAS probe equipped with gradient coils, by using full rotors containing approximately 20 mg of resin beads, swollen in approximately 100 µL of $CDCl_3$ and spinning at 4000 Hz around the magic angle. External referencing with $\Xi = 37.290665$ MHz was used. The solid state (CP)-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.[11,12] The solid state ^{117}Sn MAS NMR spectra were deconvoluted by total-lineshape (TLS) fitting[13,14] of the experimental spectra using the PERCH[15] software package.

Acknowledgments

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[1] [1a] A. G. Davies, in *Chemistry of Tin*, 2nd ed. (Ed.: P. J. Smith), Blackie, London, **1998**, pp. 265−289. [1b] A. G. Davies, *Organotin Chemistry*, VCH, Blackie, Weinheim, **1997.** [1c]O. A. Mascaretti, R. E. Furlan, *Aldrich Chim. Acta* **1997**, *30*, 55−68.

[2] B. Jousseaume, M. Pereyre, in *Chemistry of Tin*, 2nd ed. (Ed.: P. J. Smith), Blackie, London, **1998**, pp. 290−387.

[3] W. P. Neumann, M. Peterseim, *React. Polym.* **1993**, *20*, 189−205.

[4] [4a] M. Hoch, *Appl. Geochem.* **2001**, 719−743. [4b] Y. Arakawain, in *Chemistry of Tin*, 2nd ed. (Ed.: P. J. Smith), Blackie, London, **1998**, pp. 388−428. [4c] M. A. Champ, P. F. Seligman, *Organotin: Environmental Fate and Effects*, Chapman & Hall, London, **1996**.

[5] C. J. Salomon, G. O. Danelon, O. A. Mascaretti, *J. Org. Chem.* **2000**, *65*, 9220−9222 and references cited therein.

[6] B. Delmond, G. Dumartin, in *Solid-State Organometallic Chemistry: Methods and Applications* (Eds.: M. Gielen, R. Willem, B. Wrackmeyer), Wiley, Chichester, **1999**, pp. 445−471, and references cited therein.

[7] F. A. G. Mercier, M. Biesemans, R. Altmann, R. Willem, R. Pintelon, J. Schoukens, B. Delmond, G. Dumartin, *Organometallics* **2001**, *20*, 958−962.

[8] J. C. Martins, F. A. G. Mercier, A. Vandervelden, M. Biesemans, J.-M. Wieruszeski, E. Humpfer, R. Willem, G. Lippens, *Chem. Eur. J.* **2002**, *8*, 3431−3441.

[9] [9a] J. Otera, T. Yano, A. Kawabata, H. Nozaki, *Tetrahedron Lett.* **1986**, *27*, 2383−2386. [9b] J. Otera, S. Ioka, H. Nozaki, *J. Org. Chem.* **1989**, *54*, 4013−4014. [9c] J. Otera, N. Dan-Oh, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5307−5311. [9d] J. Otera, N. Dan-Oh, H. Nozaki, *J. Chem. Soc., Chem. Commun.* **1991**, 1742−1743. [9e] J. Otera, N. Dan-Oh, H. Nozaki, *Tetrahedron* **1993**, *49*, 3065−3074.

[10] W. M. Macindoe, A. Williams, R. Khan, *Carbohydr. Res.* **1996**, *283*, 17−25.

[11] G. Dumartin, J. Kharboutli, B. Delmond, M. Pereyre,

M. Biesemans, M. Gielen, R. Willem, *Organometallics* **1996**, *15*, 19–23.

[12] M. Biesemans, R. Willem, S. Damoun, P. Geerlings, M. Lahcini, P. Jaumier, B. Jousseaume, *Organometallics* **1996**, *15*, 2237–2245.

[13] R. Laatikainen, *J. Magn. Reson.* **1991**, *92*, 1–9.

[14] R. Laatikainen, M. Niemitz, U. Weber, J. Sundelin, T. Hassinen, J. Vepsäläinen, *J. Magn. Reson.* **1996**, *A120*, 1–10.

[15] PERCH Version 1/99; University of Kupio, Finland, **1999**.

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