# Alkylchlorotins Grafted to Cross-Linked Polystyrene Beads by a $-(CH_2)_n-$ Spacer ($n=4$, 6, 11): Selective, Clean and Recyclable Catalysts for Transesterification Reactions

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**Abstract:** Insoluble polystyrene grafted compounds of the type $(P-H)_{(1-t)}\{P-(CH_2)_nSnBu_pCl_{3-p}\}_t$, $(P-H)_{(1-t)}\{P-(CH_2)_nSnBuO\}_t$ and $(P-H)_{(1-t)}[\{P-(CH_2)_nSnBuCl\}_2O]_{t/2}$, in which (P–H) is a cross-linked polystyrene; $n=4$, 6, and 11; $p=0$ and 1; and $t$ the degree of functionalisation, were synthesised from Amberlite XE-305, a polystyrene cross-linked with divinylbenzene. The compounds were characterised by using elemental analysis, and IR, Raman, solid-state $^{117}Sn$ NMR, and $^{1}H$ and $^{119}Sn$ high-resolution MAS NMR spectroscopy. The influence of the spacer length and the tin functionality on the catalytic activity of these compounds, as well as their recycling ability, was assessed in the transesterification reaction of ethyl acetate with various alcohols. These studies showed significant differences in the activity of the catalysts interpreted in terms of changes in the mobility of the catalytic centres. Some of the supported catalysts could be recycled at least seven times without noticeable loss of activity. The residual tin content in the reaction products was found to be as low as 3 ppm.

**Keywords:** NMR spectroscopy · supported catalysts · tin leaching · tin · transesterification

## Introduction

Mineral acids or alkalis used as catalysts for transesterification reactions in numerous applications are not always suitable for industrial purposes. As an alternative, the use of organotin compounds as catalysts allows the transesterification reaction to take place in almost neutral conditions, thus increasing the synthetic potential of these reactions. As early as 1969, Pereyre and co-workers reported that tri-*n*-butyltin methoxide and ethoxide act as transesterification catalysts.[1] In 1979, Poller et al.[2] investigated the relative catalytic activity of 18 organotin compounds in the transesterification reaction of propyl acetate with methanol. Otera and co-workers reported several studies on transesterifications with various organotin compounds, among which distannoxane compounds play an important role.[3–8] It was also recently disclosed that these compounds can act as pure Lewis acids and be recovered unchanged after completion of the reaction.[9,10] All these transesterifications proceed in homogeneous medium, in which the toxicity of tin remains a serious drawback for the industrial use of molecular organotin compounds, since removing traces of tin can be very tedious. The latter issue may be alleviated by grafting the organotin moieties to an insoluble macromolecular support, allowing removal of the undesired metal moiety from the desired substances by simple filtration of the grafting support. Macindoe et al. prepared a polystyrene supported butyltin(IV) di-

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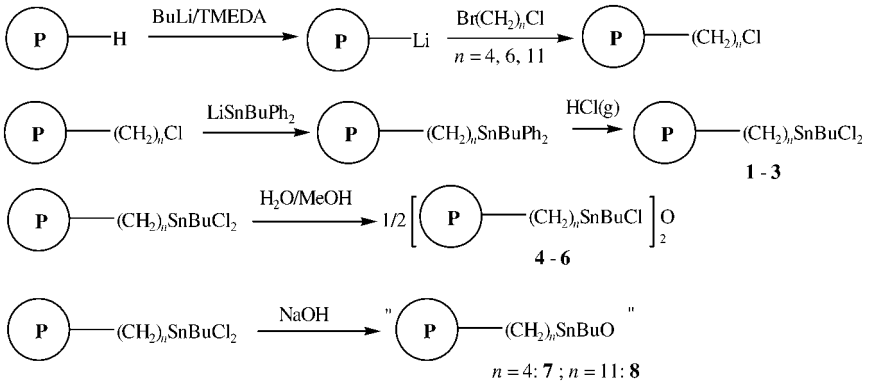
chloride that was successfully used as a catalyst in the acetylation reaction of sucrose.[11] Benzoylation of a glucopyranoside was performed by Whitfield with a distannoxane supported on a 5% cross-linked resin as a catalyst.[12] Copolymer-bound organotin oxides, prepared by Hunter as a mixture of stannol and distannoxane, have been shown to catalyse the lactonisation of hydroxycarboxylic acids.[13] The use of biphasic fluorous transesterification, in which the distannoxanes containing polyfluorinated alkyl chains can be recovered by decantation after reaction, is an alternative way to get rid of undesirable tin residues in the products.[14–16]

The synthesis, characterisation and catalytic activity of various compounds obeying the formula $(P{-}H)_{(1-t)}\{P{-}(CH_2)_nSnBuX_2\}_t$, in which (P–H) a cross-linked polystyrene, $n=4$ and 6, X = Ph and Cl (**1** and **2**), and $t$ is a variable degree of functionalisation, have been reported.[17–19] The present paper reports on the synthesis and characterisation of an additional compound in this series ($n=11$, X = Cl: **3**) and of grafted organotin compounds of the type $(P{-}H)_{(1-t)}[\{P{-}(CH_2)_nSnBuCl\}_2O]_{t/2}$ ($n=4$: **4**; $n=6$: **5**; $n=11$: **6**), $(P{-}H)_{(1-t)}\{P{-}(CH_2)_nSnBuO\}_t$ ($n=4$: **7**; $n=11$: **8**), in partially hydrated or hydroxylated form, and $(P{-}H)_{(1-t)}\{P{-}(CH_2)_nSnCl_3\}_t$ ($n=4$: **9**), as well as on their catalytic activity. The compounds under investigation offer potential applications in catalysis of transesterifications under environment friendly as well as favourable recycling ability conditions. Important issues in this context are 1) whether and to what extent grafting affects the catalytic activity of the derivatives, the macromolecular support being potentially a sterically demanding factor; 2) the residual amount of tin derivatives in the reaction products, which was not reported, to the best of our knowledge, for other supported or fluorous[14–16] organotin catalysts and 3) the recycling ability of the supported catalysts, which is important to reduce the process cost, especially for industrial applications. A comparative study of the activity and recycling ability of various catalytically active moieties, grafted onto the solid support by spacers differing in their number of methylene groups, and an assessment of tin contamination of the reaction media are presented. The potential of these supported catalysts was investigated in the acetylation of various alcohols with ethyl acetate.

## Results and Discussion

**Synthesis and characterisation**: The general reaction scheme for the synthesis of polystyrene-grafted dialkyldichlorotin compounds and the corresponding distannoxanes and oxides starting from the cross-linked polystyrene beads, as described in detail elsewhere, is given in Scheme 1.[17–19]

Complete characterisation of compounds **1**–**3** and their




Scheme 1.

precursors was accomplished by elemental analysis, and IR and high-resolution MAS (HR-MAS) NMR spectroscopy.[18] The last technique especially proved extremely useful, allowing a control of the absence of the $-CH_2Cl$ functionality in the $^1H$ HR-MAS NMR spectra, and assessing the tin functionality in the $^{119}Sn$ HR-MAS spectra (see Figure 1).

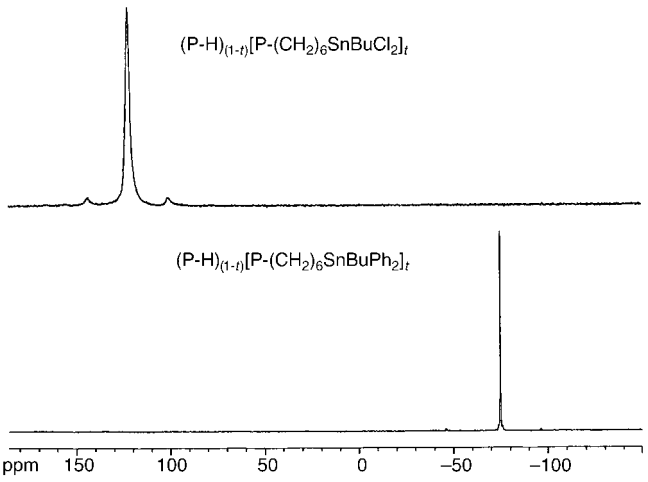



Figure 1. $^{119}Sn$ HR-MAS spectra of $(P{-}H)_{(1-t)}[P{-}(CH_2)_6SnBuPh_2]_t$ and $(P{-}H)_{(1-t)}[P{-}(CH_2)_6SnBuCl_2]_t$. The two small signals, flanking the major resonance, in the spectrum of the $-SnCl_2$ compound are residual spinning side bands.

The conversion to the desired chlorodistannoxanes **4**–**6**, is obtained by reaction of **1**–**3** with water in gently refluxing methanol. The presence of the O-Sn-O functionality cannot be demonstrated by the HR-MAS technique, since local rotational mobility of the graft, a condition necessary for the graft to be observable, was prevented by the additional cross-linking induced by the distannoxane O-Sn-O bridges. $^{117}Sn$ CP-MAS spectra were used instead together with elemental analysis data, and IR and Raman spectroscopy, to characterise the grafted chlorodistannoxanes. As an alterna-

tive, treatment of **1** with one equivalent of 4 N NaOH in THF for six hours led to **4** with a chlorine/tin ratio of 0.97, in good agreement with the functionality formula of the target chlorodistannoxane.

It is known that molecular, nongrafted dialkyltindichlorides, $R_2SnCl_2$, can be converted into polymeric, insoluble dialkyltin oxides, obeying formally the formula $R_2SnO$, by reaction with a large excess of concentrated aqueous sodium or potassium hydroxide. To assess to which extent both chlorine atoms of a grafted analogue of the type $\mathbf{P}(CH_2)_nBuSnCl_2$ can also be removed toward grafted dialkyltin oxide analogues, we performed the reaction on **1** and **3** with ten equivalents of 4 N NaOH under reflux for 24 h with the goal to obtain the corresponding $\mathbf{P}(CH_2)_nBuSnO$ oxides **7** and **8** (Scheme 1).

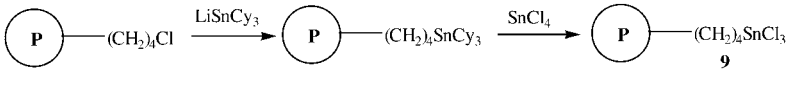
Table 1. Comparison of the experimental elemental analysis data for the grafted dialkyltin oxides **7** and **8** and the resulting functionalisation degree *t*. The elemental analysis data was calculated on the basis of the functionalisation degree of its immediate precursor for different possible target compounds.

| Compound | *t* | % C | % H | % Sn | % Cl | % O | found or calcd |
|---|---|---|---|---|---|---|---|
| **7** | | 70.59 | 7.36 | 16.00 | 0.12 | 3.31 | found |
| $\mathbf{P}(CH_2)_4BuSnO$ | 0.274[a] | | | | | | |
| $\mathbf{P}(CH_2)_4BuSn(OH)_2$ | 0.243[a] | | | | | | |
| $\mathbf{P}[(CH_2)_4BuSn(OH)]_2O$ | 0.258[a] | | | | | | |
| $\mathbf{P}(CH_2)_4BuSnO$ | 0.246[b] | 72.59 | 7.30 | 17.72 | 0 | 2.39 | calcd |
| $\mathbf{P}(CH_2)_4BuSn(OH)_2$ | 0.246[b] | 70.69 | 7.40 | 17.26 | 0 | 4.65 | calcd |
| $\mathbf{P}[(CH_2)_4BuSn(OH)]_2O$ | 0.246[b] | 71.63 | 7.35 | 17.49 | 0 | 3.54 | calcd |
| **8** | | 71.59 | 8.46 | 11.35 | 3.41 | 2.76 | found |
| $\mathbf{P}(CH_2)_{11}BuSnO$ | 0.287[a] | | | | | | |
| $\mathbf{P}(CH_2)_{11}BuSn(OH)_2$ | 0.250[a] | | | | | | |
| $\mathbf{P}[(CH_2)_{11}BuSn(OH)]_2O$ | 0.268[a] | | | | | | |
| $\mathbf{P}(CH_2)_{11}BuSnO$ | 0.230[b] | 74.94 | 8.18 | 14.87 | 0 | 2.01 | calcd |
| $\mathbf{P}(CH_2)_{11}BuSn(OH)_2$ | 0.230[b] | 73.28 | 8.25 | 14.55 | 0 | 3.92 | calcd |
| $\mathbf{P}[(CH_2)_{11}BuSn(OH)]_2O$ | 0.230[b] | 74.10 | 8.22 | 14.71 | 0 | 2.97 | calcd |

[a] The value of *t* refers to the functionalisation degree calculated from the experimental mass fractions of the target compound; the functionalisation degrees *t* were calculated by using homemade software based on the mathematical MATLAB package, as explained elsewhere.[17] [b] The value of *t* refers to the functionalisation degree expected on the basis of the *t* value of the precursor.

In the case of compound **7**, by using the functionalisation degree $t=0.246$ experimentally found for its precursor $\mathbf{P}(CH_2)_4BuSnCl_2$, the elemental data reveal a composition which reflects satisfactorily the desired target formula $\mathbf{P}(CH_2)_4BuSnO$ (see Table 1), with a basically negligible amount of residual chlorine remaining being left (0.1 %). However, alternative formulae, reflecting either hydration of the grafted oxide, such as $\mathbf{P}(CH_2)_4BuSnO\cdot H_2O$, which can be viewed formally as $\mathbf{P}(CH_2)_4BuSn(OH)_2$, or formation of the grafted dihydroxy distannoxane, $\mathbf{P}[(CH_2)_4SnBu(OH)]_2O$, reasonably match the elemental analysis as well, and display slightly better agreement between experimental and calculated mass fractions and/or functionalisation degrees. For similar reasons as for the grafted chlorodistannoxanes $\mathbf{P}[(CH_2)_4SnBuCl]_2O$ **4**–**6**, no direct evidence can be provided to either proposal by HR-MAS $^{119}Sn$ NMR. It is therefore more reasonable to view the compound eventually obtained as a mixture in unknown ratios of the target compound **7**, and its hydrated $\mathbf{P}(CH_2)_4BuSn(OH)_2$ and/or hydroxylated dihydroxy distannoxane $\mathbf{P}[(CH_2)_4SnBu(OH)]_2O$ adducts. Even though characteristic OH bands are observed around 3500 $cm^{-1}$, the IR spectrum fails to identify formally Sn–OH type moieties. Similar conclusions hold for target compound **8**, even though more residual chlorine was observed, typically 3 %, reflecting the presence of unconverted grafted tin dichloride, intermediate dichlorodistannoxane, and/or mixed hydroxychlorodistannoxane,
which resulted in poorer agreements between experimental and calculated mass fractions for C and Sn, mainly. The reasons for this difference in behaviour between target systems **7** and **8**, which differ only in the length of their polymethylene spacer ($n=4$ for **7**, $n=11$ for **8**) remains unclear at the moment, but could be due to spacer intermingling being more likely with $n=11$ than with $n=4$. Nevertheless, the data remain in fair agreement with the grafted $\mathbf{P}(CH_2)_nBuSnO$ compound, or its hydrated $\mathbf{P}(CH_2)_nBuSn(OH)_2$ and $\mathbf{P}[(CH_2)_nSnBu(OH)]_2O$ dihydroxy distannoxane variants. Indeed, considering that theoretically, upon ideal reaction course without any undesired grafted side-functionality formation, the functionalisation degrees of the target compound and its precursor should be strictly identical (this is of course experimentally unrealistic), the agreement between the experimental and calculated mass fractions are more than fair, especially for the case $n=4$. Therefore, one should keep in mind that ideal agreement for all mass fractions and the functionalisation degree *t* would imply a 100 % clean conversion from the grafted precursor to only a single-grafted target functionality, which, in practice, can at most only be approached. Moreover, once generated, grafted side-functionalities cannot be removed. Finally for both $n=4$ and 11, the best agreement for the mass fractions of oxygen between experimental and calculated figures is obtained for the dihydroxy distannoxane $\mathbf{P}[(CH_2)_nSnBu(OH)]_2O$ adducts.

The supported tin trichloride was prepared according to Scheme 2. Tricyclohexylstannyllithium,[20] prepared from a stoichiometric amount of tricyclohexyltin hydride and lithium diisopropylamide (LDA), was treated with the grafted alkyl chloride in order to introduce the tricyclohexyltin group at the end of the tetramethylene chain. Subsequently,




**9**

Scheme 2.

treatment of the tricyclohexyltin functionalised polystyrene with one equivalent of tin tetrachloride for 48 h in the dark afforded the corresponding target compound meant to be the grafted tin trichloride **9**. Table 2 gives the elemental analysis data for compound **9**, as well as calculated data for different possible target compounds.

Table 2. Comparison of the experimental elemental analysis data and the resulting functionalisation degree $t$ for **9**. The elemental analysis data was calculated for different possible target compounds, on the basis of the functionalisation degree of its immediate precursor.

| Compound | $t$ | % C | % H | % Sn | % Cl | found or calcd |
|---|---|---|---|---|---|---|
| **9** | | 58.86 | 5.97 | 16.15 | 14.85 | found |
| $\mathbf{P}(CH_2)_4BuSnCl_3$ | 0.288[a] | | | | | |
| $\mathbf{P}(CH_2)_4BuSnCl_2OH$ | 0.321[a] | | | | | |
| $\mathbf{P}(CH_2)_4BuSnCl_3.H_2O$ | 0.269[a] | | | | | |
| $\mathbf{P}(CH_2)_4BuSnCl_3.2H_2O$ | 0.252[a] | | | | | |
| $\mathbf{P}(CH_2)_4BuSnCl_3$ | 0.235[b] | 63.20 | 5.72 | 16.39 | 14.69 | calcd |
| $\mathbf{P}(CH_2)_4BuSnCl_2OH$ | 0.235[b] | 64.82 | 8.01 | 16.84 | 10.06 | calcd |
| $\mathbf{P}(CH_2)_4BuSnCl_3.H_2O$ | 0.235[b] | 61.67 | 5.85 | 15.99 | 14.33 | calcd |
| $\mathbf{P}(CH_2)_4BuSnCl_3.2H_2O$ | 0.235[b] | 60.17 | 5.98 | 15.63 | 14.01 | calcd |

[a] See footnote [a] in Table 1. [b] Functionalisation degree found experimentally for the precursor $\mathbf{P}(CH_2)_4SnCy_3$ and henceforth expected for the target **9** (see Experimental Section).

The agreement between calculated and experimental data, especially at the level of the functionalisation degree is poorest for the grafted $SnCl_2OH$ compound; this allows us to exclude safely any extended hydrolysis of the grafted tin trichloride. However, the data are in better agreement with the grafted tin trichloride moiety being coordinated by one or two additional water molecules. In particular for the composition $\mathbf{P}(CH_2)_4SnCl_3{\cdot}2\,H_2O$, the calculated mass fractions match the experimental ones very satisfactorily. This proposal is in good agreement with the high Lewis acid character of tin in monoorganotin trichlorides, with the tin atom tending to expand its coordination sphere.

**Catalytic activity**: The acetylation of various alcohols by ethyl acetate [Eq. (1)] was investigated. Reactions were performed with a sevenfold excess of ethyl acetate at reflux for 24 and 48 h, with catalysts **5** and **6**, and, for comparison, a few experiments with **2** and **3**. During the reaction, about 20% of solvent together with the formed ethanol was distilled off as an azeotropic mixture in order to drive the reaction to completion. The reaction mixtures were analysed by $^1$H NMR spectroscopy after distillation of the excess of ethyl acetate.

$$CH_3COOCH_2CH_3 + ROH \rightarrow CH_3COOR + CH_3CH_2OH \quad (1)$$

The results are summarised in Table 3, from which it can be concluded that the catalyst with the undecamethylene spacer, $(P{-}H)_{(1-t)}[\{P{-}(CH_2)_{11}SnBuCl\}_2O]_{t/2}$ (**6**), is generally slightly more active than its hexamethylene analogue **5**, demonstrating that the spacer length influences the conversion degree in the transesterification reactions under study (see entries 1 and 4). The selectivity of both catalysts is, however, comparable; competition between a primary alcohol and phenol or tertiary alcohol results in the exclusive acetylation of the primary alcohol (entries 7–12), implying that both catalysts are totally inefficient toward tertiary alcohols and phenols. Furthermore, reactivity is influenced by steric factors, since the primary alcohol in 2-phenyl-1,2-propanediol is less reactive than the less hindered phenethyl alcohol (entries 9–12, to be compared with 1, 2, 4, and 5). Also, though not inactive, the catalysts are significantly less active toward the secondary alcohols cyclohexanol (entries 13–14) and 4-methyl-2-pentanol (entries 18–19), when compared to phenethyl alcohol (entries 1–2 and 4–5) and *n*-octanol (entries 15–17). These facts illustrate that the approach of bulky reagents to the grafted distannoxanes is hampered by steric factors, as was also demonstrated by Otera,[4] who stated that especially the bulkiness of the ester has an effect on the transesterification catalysed by distannoxanes. The grafting itself has also an influence, since we observed previously that grafted catalysts (with $n=4$ and 6) have lower activity than the corresponding soluble homogeneous catalyst.[17] This problem seems to be alleviated to some extent by introducing a longer spacer, since in most cases slightly higher conversions

Table 3. Assessment of the catalytic activity of grafted organotins in transesterification reactions with various alcohols and ethyl acetate in sevenfold excess.

| Entry | Alcohol[a] | Catalyst[b] | Time [h] | Ester [mol%] |
|---|---|---|---|---|
| 1 | $Ph(CH_2)_2OH$ | **5** | 24 | 78 |
| 2 | | **5** | 48 | 100 |
| 3 | | **2** | 24 | 98 |
| 4 | | **6** | 24 | 94 |
| 5 | | **6** | 48 | 100 |
| 6 | | **3** | 24 | 92 |
| 7 | 3-OH-$Ph(CH_2)_2OH$ | **5** | 48[c] | 100 |
| 8 | | **5** | 24[c] | 93 |
| 9 | $PhC(CH_3)(OH)CH_2OH$ | **5** | 24[c] | 35 |
| 10 | | **5** | 48[c] | 49 |
| 11 | | **6** | 24[c] | 53 |
| 12 | | **6** | 48[c] | 67 |
| 13 | $C_6H_{11}OH$ | **5** | 48 | 41 |
| 14 | | **6** | 48 | 66 |
| 15 | $CH_3(CH_2)_7OH$ | **5** | 24 | 96 |
| 16 | | **5** | 48 | 99 |
| 17 | | **6** | 24 | 98 |
| 18 | $CH_3CH(OH)CH_2CH(CH_3)_2$ | **5** | 48 | 59 |
| 19 | | **6** | 48 | 62 |

[a] Molar ratio alcohol/ethyl acetate = 1:7. [b] Catalyst **5** = $(P{-}H)_{(1-t)}[\{P{-}(CH_2)_6SnBuCl\}_2O]_{t/2}$; **6** = $(P{-}H)_{(1-t)}[\{P{-}(CH_2)_{11}SnBuCl\}_2O]_{t/2}$; **2** = $(P{-}H)_{(1-t)}[P{-}(CH_2)_6SnBuCl_2]_t$; **3** = $(P{-}H)_{(1-t)}[P{-}(CH_2)_{11}SnBuCl_2]_t$; 2 mol% of Sn. [c] Primary alcohol is exclusively acetylated.

are obtained with the C11 spacer than with the C6 spacer. Taking into consideration that in grafted distannoxanes the reagents must enter the pores of the catalyst in order to reach the active sites and that the products must leave the catalyst after reaction, the bulkiness of reaction products might hinder to some extent this diffusion process. Additionally, in order to avoid damaging of the catalyst, all reactions were carried out without stirring, a factor that also can decrease the reaction velocity to some extent.

The precursor $(P{-}H)_{(1-t)}[P{-}(CH_2)_6SnBuCl_2]_t$ (**2**) showed, under the same reaction conditions, somewhat higher activity than the distannoxane $(P{-}H)_{(1-t)}[(P{-}(CH_2)_6SnBuCl)_2O]_{t/2}$ (**5**). The conversion to phenethyl acetate was 98 and 78%, respectively (entries 3 and 1). By contrast, both C11 catalysts $(P{-}H)_{(1-t)}[P{-}(CH_2)_{11}SnBuCl_2]_t$ (**3**) and $(P{-}H)_{(1-t)}[(P{-}(CH_2)_{11}SnBuCl)_2O]_{t/2}$ (**6**) have comparable conversion degrees of 92 and 94%, respectively (entries 6 and 4). Beads of **2** and **3**, isolated after reaction with phenethyl alcohol, were investigated by $^1H$ and $^{119}Sn$ HR-MAS NMR and IR spectroscopy. Although the HR-MAS NMR spectra were identical, within experimental error, before and after catalysis, the IR spectra showed a new absorption at 605–610 $cm^{-1}$, which indicates the presence of an Sn-O-Sn functionality. Beads of **5**, isolated after reaction with phenethyl alcohol, lack the absorption at 345 $cm^{-1}$ of the Sn–Cl vibration in the Raman spectrum. Despite these indications that the catalyst undergoes some changes, maybe induced by the presence of some amounts of residual water in the reagents, the catalytic activity remains unaltered in further runs, as was demonstrated in earlier work.[17]

Subsequently, the conditions of the transesterification were slightly modified in order to investigate in more detail the activity of catalysts **4**, **6**, **7**, **8** and **1**. A 1% amount of the catalyst was used to slow down the reaction and to enhance the differences between the catalysts, while *n*-octanol was chosen as the starting alcohol and the distillation of 20% of the solvent was omitted. The results are given in Table 4.

Table 4. Catalytic activity under modified conditions, as applied to the transesterification of *n*-octanol by an excess of ethyl acetate.

| Entry | Catalyst | Ester [mol%] |
|---|---|---|
| 20 | **4** | 14 |
| 21 | **6** | 22 |
| 22 | **7** | 23 |
| 23 | **8** | 27 |
| 24 | **1** | 41 |

As already evidenced in the case of the transesterification reaction with phenylethanol (entries 1, 3, in Table 3), the supported chlorodistannoxanes (entries 20 and 21 in Table 4) and oxides (entries 22 and 23) gave lower yields than the corresponding dichloride (entry 24) with the shorter ($n=4$) spacer. In homogeneous reactions chlorodistannoxanes and diorganotin oxides are more efficient than the corresponding dichlorides. The reverse effect recorded in this series of grafted organotins shows that the mobility of the catalytic group is a key factor to explain the differences in activity of the polymer-supported organotin catalysts. This can be explained by the distannoxane bridge between neighbouring tin atoms that restricts their mobility by introducing additional cross-linking at the surface of the polystyrene, which could lower the accessibility of the reagents. This restricted local molecular mobility is supported by the absence of any distannoxane $^{119}Sn$ resonance in the $^{119}Sn$ HR-MAS spectrum. The higher yields obtained within the same type of catalyst (entries 20 and 21/22 and 23) in the case of the polymer-supported tin with the longer chain strengthens this proposal, as longer and more flexible chains should increase the mobility and formation ability of coordination bonds between the tin atoms and transesterification reaction components.

A third set of experiments was finally performed in order to assess the recycling ability of the better catalysts in the series and to quantify the residual tin content in the esters generated. The same transesterification conditions were applied except that a 0.1% amount of catalyst was used for 8 h. Grafted catalyst performances were also compared to those of some homogeneous transesterification catalysts (see Table 5).

Table 5. Recycling ability and tin leaching assessment of selected catalysts.

| Entry | Catalyst | Ester [mol%] | Tin content of ester [ppm] |
|---|---|---|---|
| 25 | **1** | 6 | 3 |
| 26 | **3** | 15 | 3 |
| 27 | $Bu_2SnCl_2$ | 26 | 700[d] |
| 28 | **9** | 70[a] | |
| 29 | **9** | 64[b] | |
| 30 | **9** | 64[c] | 4[c] |
| 31 | $BuSn(OH)_2Cl$ | 92 | 700[d] |

[a] Yield of the first run. [b] Yield of the seventh run. [c] Average value of seven runs with the same catalyst. [d] Value calculated on the basis of homogeneous catalyst used in the experiment, and not removed from the reaction product.

As underlined above, the supported catalyst with the longer spacer **3** gave higher yields than the supported organotin compound with the shorter one **1** (entries 25–26), confirming the importance of the mobility of the catalytic centre for the efficiency of the transesterification reaction. When compared to soluble dibutyltin dichloride (entry 27), the activity of **3** (entry 26) was not negligible, as it was only 40% lower than the soluble one. However, the best result was obtained with **9** with a conversion degree as high as 70% (entry 28), being only 30% lower than the yield obtained with the structurally closer, industrially used catalyst, chlorobutyltin dihydroxide (entry 31). In order to demonstrate its ability to be recycled, the same beads of **9** were used in several successive transesterifications, the catalyst being recovered by filtration after each run, without any washing between the runs. A 64% yield of the transesterification was measured after seven runs (entry 29), with an average value over the seven runs of 64% (entry 30). These results thus demonstrate the high recycling ability of **9**.

The residual tin contents in the esters recovered from the transesterifications catalysed with **1**, **3** and **9** were measured by ICP/MS. They were very low, the values ranging from 3 to 4 ppm. This amount corresponds to a tin content of about 0.5 mg of tin per mole of octyl acetate, the tin content with a homogeneous catalyst left completely in the reaction products being 120 mg. This clearly shows a dramatic decrease by a factor of approximately 200 in the residual amount of tin found in the reaction product upon switching from a homogeneous catalyst to a grafted counterpart, unambiguously demonstrating the benefits of grafting organotin catalysts. In the latter case, residual tin in the reaction product is indeed only induced by the loss from the beads of 0.4% of grafted tin per run. The use of supported organotin catalysts is thus a pertinent solution to reduce the amount of organotins in esters obtained by catalytic transesterifications, without lowering to a dramatic extent the transesterification rate.

## Conclusion

All catalysts screened are reasonably active in the reactions under investigation. They are more active toward primary rather than secondary or bulky primary alcohols and not reactive toward tertiary alcohols or phenols, indicating that steric factors play an important role in the reaction mechanism. The length of the spacer also plays a significant role; whereas no significant difference in activity was found between spacer lengths 4 and 6,[17] elongation of the spacer to 11 methylene groups has a beneficial effect whatever the nature of the substituents on the tin atom. Among all catalysts tested, trichlorotin-substituted target polymers led to the best yields of ester, in the same range as the more efficient soluble ones. They could be recycled at least seven times without loss of activity. The residual amount of organotin in the prepared esters, expressed in tin mass, was as low as 3 ppm.

## Experimental Section

**Synthesis**: The syntheses of **1**, **2**, **4** and **5** have already been reported.[17–19] The syntheses of **3** and **6** were performed according to the same procedure with $Br(CH_2)_{11}Cl$ being used in the first reaction step instead of $Br(CH_2)_6Cl$. $Br(CH_2)_{11}Cl$ was prepared from $Br(CH_2)_{11}OH$ (Aldrich) by reaction with $SOCl_2$, following an established literature procedure.[21] The ensuing reaction steps were completely analogous to those used for **4**.

**$(P-H)_{(1-t)}[P-(CH_2)_{11}Cl]_t$**: Elemental analysis calcd (%) for $t=0.29$: H 8.96, C 84.47, Cl 6.57; found: H 8.93, C 84.34, Cl 5.97; IR: $\tilde{\nu}=651\ cm^{-1}$ (w; CCl); $^1H$ HR-MAS NMR: $\delta=3.49$ ppm ($-CH_2Cl$)

**$(P-H)_{(1-t)}[P-(CH_2)_{11}SnBuPh_2]_t$**: Elemental analysis calcd (%) for $t=$ 0.26: H 8.07, C 78.48, Sn 13.45; found: H 7.87, C 78.27, Sn 12.61, Cl $<0.2$; IR: $\tilde{\nu}=1074$ (m, Sn–Ph), 727 (w, C–$C_{mono}$), 656 (w, Sn–$C_{rock}$), 594 (w, Sn–$Bu_{asym}$), 510 $cm^{-1}$ (w, Sn–$Bu_{sym}$); $^{119}Sn$ HR-MAS NMR: $\delta=$ $-71$ ppm.

**$(P-H)_{(1-t)}[P-(CH_2)_{11}SnBuCl_2]_t$ (3)**: Elemental analysis calcd (%) for $t=$ 0.26: H 7.65, C 68.64, Sn 14.84, Cl 8.87; found: H 7.71, C 68.49, Sn 13.77, Cl 8.72; Raman: $\tilde{\nu}=596$ (w, Sn–$Bu_{asym}$), 520 (w, Sn–$Bu_{sym}$), 347 $cm^{-1}$ (m, Sn–Cl); $^{119}Sn$ HR-MAS NMR: $\delta=126$ ppm.

**$(P-H)_{(1-t)}[\{P-(CH_2)_{11}SnBuCl\}_2O]_{t/2}$ (6)**: Elemental analysis calcd (%) for $t=0.26$: H 7.92, C 71.11, Sn 15.35, Cl 4.59; found: H 7.90, C 70.82, Sn 14.59, Cl 6.23; Raman: $\tilde{\nu}=597$ (w, Sn–$Bu_{asym}$), 517 (w, Sn–$Bu_{sym}$), 345 $cm^{-1}$ (m, Sn–Cl); IR: $\tilde{\nu}=603\ cm^{-1}$ (m, Sn-O-Sn).

**$(P-H)_{(1-t)}[P-(CH_2)_4SnBuO]_t$ (7)**: An aqueous solution of sodium hydroxide (0.1 mL, 4 M) was added to a suspension of **1** (400 mg) in dry THF (20 mL) at 65 °C. After 6 h, polymer **7** was filtered off and washed successively with a mixture THF/$H_2O$ (50/50), THF and then ethanol. Elemental analysis (%) found: H 7.36, C 70.59, Sn 16.00, O 3.10, Cl 0.12; see Table 1.

**$(P-H)_{(1-t)}[P-(CH_2)_{11}SnBuO]_t$ (8)**: This compound was prepared by a similar procedure to that for **7**. Elemental analysis (%) found: H 8.46, C 71.59, Sn 11.35, O 2.76, Cl 3.41; see Table 1.

**$(P-H)_{(1-t)}[P-(CH_2)_4SnCl_3]_t$ (9)**: Diisopropylamine (1.39 g, 13.6 mmol) and *n*BuLi (13.6 mmol) were successively added to dry THF (10 mL) at 0 °C. After 15 min, $Cy_3SnH$ (5 g, 13.6 mmol) was added slowly and the mixture was stirred for 30 min. This solution of $Cy_3SnLi$ was slowly added to $(P-H)_{(1-t)}[P-(CH_2)_4Cl]_t$ (3 g) suspended in dry THF (20 mL). The mixture was stirred for 15 h at room temperature. After filtration, $(P-H)_{(1-t)}[P-(CH_2)_4SnCy_3]_t$ was washed with THF/$H_2O$ (50/50; 40 mL), THF (6×40 mL) and ethanol (2×20 mL). Elemental analysis calcd (%) for $t=0.23$: H 8.60, C 77.85, Sn 13.55; found: H 8.65, C 77.57, Sn 13.11.

A solution of tin tetrachloride (0.57 g, 2.2 mmol) in dry toluene (10 mL) was slowly added to a suspension of $(P-H)_{(1-t)}[P-(CH_2)_4SnCy_3]$ (2 g) in dry toluene (10 mL) at room temperature. After 48 h in the dark, the polymer was filtered and washed eight times with pentane and twice with ethanol. Elemental analysis (%) found: H 5.97, C 58.86, Sn 14.85, Cl 16.15; see Table 2.

**Catalysis experiments on transesterification reactions of ethyl acetate**: Ethyl acetate, used both as reactant ester and solvent, and the appropriate alcohol were engaged in a molar ratio 7/1. The mixture of ethyl acetate, the alcohol and the insoluble Amberlite-supported catalyst was refluxed for 8, 24 or 48 h. The catalyst was filtered off and washed with $CHCl_3$, 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 $CH_2O$ $^1H$ resonances or by GC.

**IR and Raman spectroscopy**: IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer, equipped with an MIR source, KBr beam splitter and a DGTS detector, from dry KBr pellets (200 mg) with about 5 mg of substance. The Raman spectra were recorded on a Perkin–Elmer 2000 NIR FT-Raman spectrometer by using a Raman_dpy2 beam with 310 mW power.

**NMR spectroscopy**: 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 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 magic angle spinning at 4000 Hz. $(CH_3)_4Sn$ was used as internal reference. CP-MAS spectra were recorded on a Bruker Avance 250 spectrometer, equipped with a 4 or 7 mm MAS broad-band probe, operating at 89.15 MHz for $^{117}Sn$. The magic angle was set by using a KBr sample. The chemical shift reference for the $^{117}Sn$ nucleus was set with (cyclo-$C_6H_{11})_4Sn$ (−97.35 ppm relative to $(CH_3)_4Sn$). The $^{117}Sn$ CP-MAS spectra were acquired with 4 K data points over a spectral width of 107 kHz, a relaxation delay of 2 s and 10000 to 40000 scans.

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