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Catalytic properties of cross-linked polystyrene grafted diorganotins in a model transesterification and the ring-opening polymerization of ε-caprolactone

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The catalytic properties of cross-linked polystyrene grafted diorganotins of the types $[P{-}H]_{(1-t)}[P{-}(CH_2)_{11}{-}Sn{-}n{-}BuCl_2]_t$ and $[P{-}H]_{(1-t)}\{[P{-}(CH_2)_{11}{-}Sn{-}n{-}BuCl]_2O\}_{t/2}$, in which [P–H] represents the monomeric unit of the cross-linked polystyrene matrix and t is the degree of functionalization, were compared. The grafted chlorodistannoxane catalyst was completely characterized by elemental analysis, IR and Raman, ^{119}Sn high-resolution magic angle spinning (hr-MAS) NMR and ^{117}Sn CP-MAS NMR spectroscopy. In spite of the spatial constraints and the potential steric demand resulting from cross-linking, the grafted C11 chlorodistannoxane exhibited the same dimeric ladder complex arrangement as its nongrafted *n*-butyl analog in the solid state and in solution. Moreover, ^{119}Sn hr-MAS NMR and ^{117}Sn CP-MAS NMR spectroscopy appeared to be complementary techniques for the assessment of the tin(IV) functionality of the grafted tetraalkyldichlorodistannoxane. The catalytic activity of the compounds was assessed in a model reaction, the transesterification reaction of ethyl acetate and *n*-octanol, as well as in the ring-opening polymerization (ROP) of ε-caprolactone. Residual tin trace analysis was performed on the acquired reaction products. Whereas tin contents of the order of 20 ppm were found in the reaction products of the transesterification, tin leaching values were overall higher for the ROP, being less unfavorable, however, for the distannoxane (±70 ppm) than for the dialkyltin dichloride (±290 ppm). Quantitative liquid ^{1}H NMR was applied to assess the conversions in both reactions, but also to determine various molecular parameters of the synthesized poly-caprolactones. Furthermore, size exclusion chromatography was used to determine their polydispersity index. It was also demonstrated that ^{1}H and ^{119}Sn hr-MAS NMR enable the chemical integrity and recycling ability of the catalyst to be assessed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: supported catalyst; grafted organotin; distannoxane; NMR; ROP; transesterification

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INTRODUCTION

Many organotin compounds are efficient catalysts in a large variety of organic reactions with many industrial applications.[1–4] More specifically, 1,3-disubstituted tetraalkyldistannoxanes are known to be among the catalytically most active diorganotin compounds and this under mild and relatively neutral conditions.[5–10] Hence, various functional groups are tolerated and remain unaffected after reaction.[11,12] However, the toxicity of organotins is an important drawback and removing them to their last traces from the reaction mixture remains quite a challenge, especially for reaction products with a high added value.[13–15] Otera *et al.* have reported on a possible approach to overcome the toxicity issue, using perfluoroalkyldistannoxanes.[16–24] These compounds, which are highly soluble in fluorocarbon solvents, combine the above-mentioned advantages of organotin catalysis with fluorous biphasic technology. Fluorous solutions of these distannoxanes become perfectly miscible with the organic reaction phase of interest upon heating. After cooling down the reaction mixture, phase-separation is observed and the catalyst returns into the fluorous phase, making it repeatedly recyclable, thereby creating so-called clean organotin reagents. Another environment friendly strategy consists of grafting the organotin reagent onto an insoluble solid support, producing likewise potentially recyclable and clean catalysts removable from reaction products by simple filtration of the solid support to which it is anchored. In previous investigations, we reported on the synthesis, characterization and catalytic properties of organotins grafted to cross-linked polystyrene of the type $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}[\mathbf{P}{-}(\mathrm{CH_2})_n{-}\mathrm{Sn}{-}n{-}\mathrm{BuX_2}]_t$,[25–29] $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}\{[\mathbf{P}{-}(\mathrm{CH_2})_n{-}\mathrm{Sn}{-}n{-}\mathrm{BuY}]_2\mathrm{O}\}_{t/2}$ ($n = 4, 6, 11$)[27,28] and $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}[\mathbf{P}{-}(\mathrm{CH_2})_n{-}\mathrm{SnZ_3}]_t$ ($n = 4, 11$),[27,30,31] where $[\mathbf{P}{-}\mathrm{H}]$ represents the monomeric unit of the non-functionalized polystyrene, cross-linked by divinylbenzene, X = Ph, Cl, $\mathrm{OOCCH_3}$, Y = Cl, OH, $\mathrm{OOCCH_3}$, Z = Ph, Cl and t is the functionalization degree.

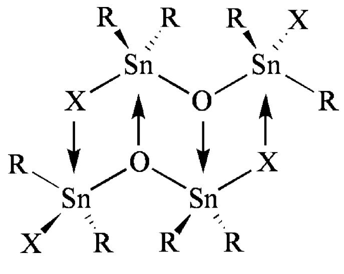
In the present paper the grafted tetraalkyldichlorodistannoxane with the C11 spacer is thoroughly characterized by solid-state ^{117}Sn MAS NMR, ^{119}Sn hr-MAS NMR, IR/RAMAN spectroscopy and elemental analysis. The catalytic properties, chemical stability, recyclability and leaching characteristics of the grafted catalyst $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}[\mathbf{P}{-}(\mathrm{CH_2})_{11}{-}\mathrm{Sn}{-}n{-}\mathrm{BuCl_2}]_t$ were thoroughly investigated for the model transesterification of ethyl acetate with n-octanol, as well as for the ring-opening polymerization of ε-caprolactone (CL), for which the catalytic features of the C11 grafted chlorodistannoxane analog, $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}\{[\mathbf{P}{-}(\mathrm{CH_2})_{11}{-}\mathrm{Sn}{-}n{-}\mathrm{BuCl}]_2\mathrm{O}\}_{t/2}$, were likewise assessed. The relevance to this investigation is that the C11 spacer appears to improve the catalytic properties of the organotin when compared with C6 and C4 spacers,[25,27–29] while on the other hand, molecular tetraalkyldichlorodistannoxanes are known to be among the most efficient and selective catalysts in homogeneous catalyst applications of organotin compounds.[7–12] In non-grafted molecular form, such tetraalkyldichlorodistannoxanes display dimeric ladder structures in solid as well as in solution,[2] with two constitutionally different pairs of mutually homotopic *endo* and *exo* tin atoms involved in a four-ring $\mathrm{Sn_2O_2}$ distannoxane core.[32,33] In spite of numerous data on polystyrene-grafted chlorodistannoxanes with tetramethylene C4- and hexamethylene C6-spacers,[25,28] it has never been elucidated whether such distannoxanes, when grafted, can keep such dimeric configurations, probably submitted to demanding grafting constraints (Scheme 1). The present paper solves this issue.

^{1}H and ^{119}Sn high-resolution magic angle spinning (hr-MAS) NMR spectroscopy was applied not only to characterize the graft directly *in situ* at the solid–liquid interface, but also to monitor the catalytic processes. The leaching of tin traces towards the reaction products was investigated for each type of catalyst with inductively coupled plasma/atomic emission spectroscopy (ICP/AES).

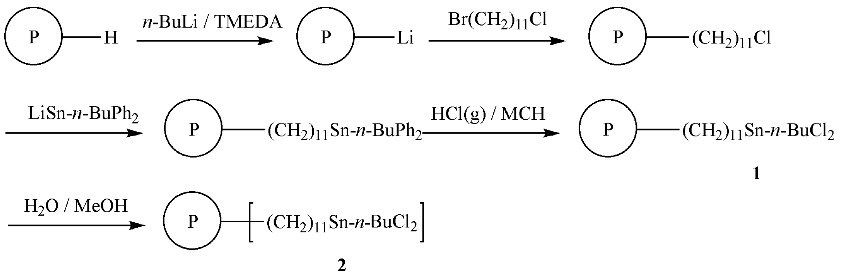
RESULTS AND DISCUSSION

Synthesis and characterization

The general reaction scheme for the synthesis of the polystyrene grafted dialkyldichlorotin compound (**1**)[26] and the corresponding distannoxane (**2**)[25,28] is described in detail elsewhere and recalled in Scheme 2. The complete characterization by infrared/Raman spectrometry, elemental analysis, and one- and two-dimensional hr-MAS NMR spectroscopy has also been described previously for the grafted dialkyldichlorotin.[25,26,34,35] The grafted distannoxane derivative was thoroughly characterized for the C4- and C6-spacers only.[27,28] No direct evidence for the existence of a grafted tetraalkyldichlorodistannoxane with a dimeric ladder structure, similar to that of the soluble molecular non-grafted analog,[2,7–12,32] has been found so far, mainly because the two characteristic isotropic chemical shifts from the *endo* and *exo* tin atoms in the four-membered $\mathrm{Sn_2O_2}$ ring core were never formally identified in the grafted C4- and C6-analogs. This was attributed to additional interface cross-linking arising from the Sn–O–Sn distannoxane bridging inducing so high a conformational rigidity that no dimeric ladder structure could be generated. As this also hampers



Scheme 1. Dimeric ladder structure of the tetraorganodistannoxanes.



Scheme 2. Synthesis of the grafted dialkyltin dichloride (**1**) and tetraorganodichlorodistannoxane (**2**) catalyst (TMEDA = tetramethylethylene diamine; MCH = methylcyclohexane).

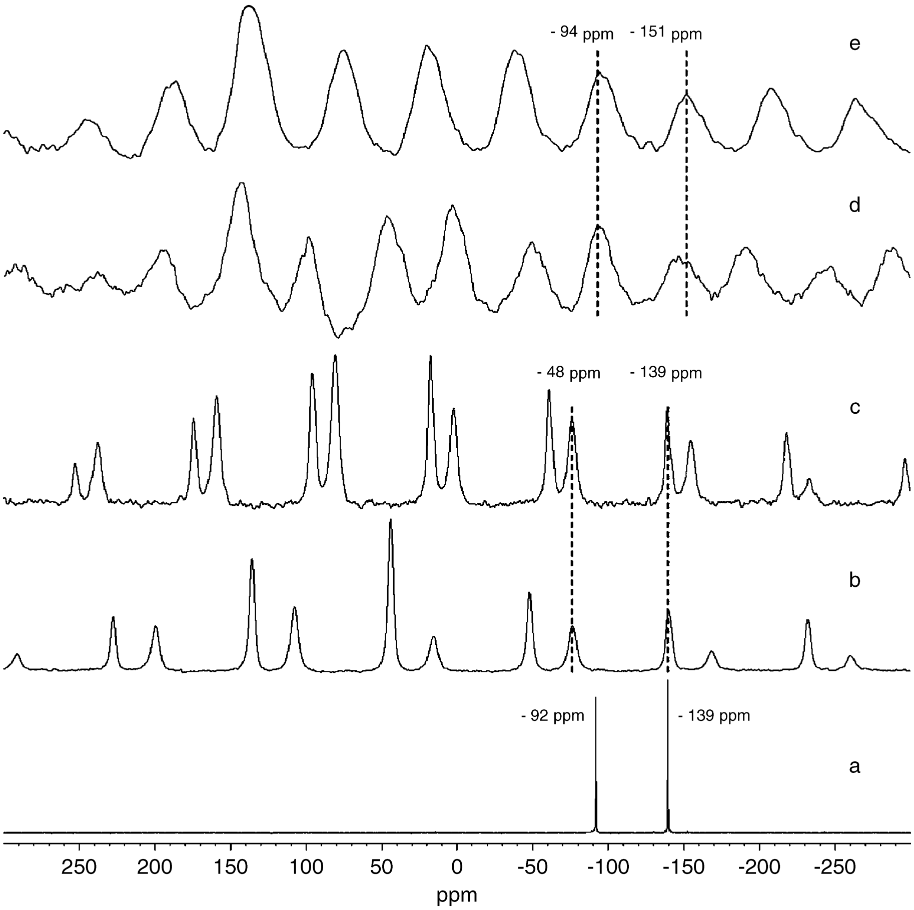


Figure 1. (a) $CDCl_3$ solution state ^{119}Sn NMR spectrum of molecular tetra *n*-butyldichlorodistannoxane; (b, c) solid-state ^{117}Sn MAS NMR spectra of the same molecular tetra *n*-butyldichlorodistannoxane with spinning rates at 8200 Hz (b) and 7000 Hz (c); (d, e) solid-state ^{117}Sn MAS NMR spectra of the grafted $[\mathbf{P}\text{–H}]_{(1-t)}\{[\mathbf{P}\text{–}(CH_2)_{11}\text{–Sn–}n\text{-BuCl}]_2O\}_{t/2}$ (**2**) with spinning rates at 8500 Hz (d) and under cross-polarization conditions at 5000 Hz (e).

the local rotational mobility of the spacer–organotin moiety, the fundamental basic necessary condition for hr-MAS NMR to be feasible was no longer fulfilled and the issue could not be solved by ^{119}Sn hr-MAS NMR spectroscopy. ^{117}Sn MAS NMR spectra did not show the characteristic two isotropic chemical shifts to be expected for such an Sn_2O_2 ring core for C4- and C6-grafted chlorodistannoxane.[25,27,28] The solid-state ^{117}Sn MAS NMR spectra recorded at two different spinning rates for the grafted C11-analog, compound **2**, are shown in Fig. 1(d, e), together with the spectrum for a non-grafted molecular analog, tetra *n*-butyldichlorodistannoxane analog [Fig. 1(b, c)], as well as the liquid-state ^{119}Sn NMR spectrum (a) of the latter, displayed for comparison. The two isotropic chemical shifts at −94 and −151 ppm detected for the grafted distannoxane [Fig. 1(d, e)], very similar to those of the molecular analog in solution, unambiguously evidence the existence of the characteristic pairs of *endo* and *exo* tin atoms in the Sn_2O_2 ring core dimeric ladder structure, which therefore appear to be common to both the non-grafted molecular and the C11-grafted distannoxanes [Fig. 1(a–c)]. Remarkably, the two ^{119}Sn chemical shifts for the tetra *n*-butyldichlorodistannoxane in solution [Fig. 1(a)], at −92 and −139 ppm, are globally closer in value to the isotropic chemical shifts of the grafted distannoxane at −94 and −151 ppm [Fig. 1(d, e)] than those of the crystalline analog at −48 and −139 ppm [Fig. 1(b, c)]. The similarity of the solution spectrum of the molecular distannoxane and the MAS spectrum of the grafted analog is tentatively explained by the fact that the dimeric motif of the grafted distannoxane is surrounded by an organic environment that mimics better the organic solution state than the crystalline state with its packing and stacking constraints.

Apparently, the much more flexible C11 spacers, when compared with the C4 and C6 ones, allow neighboring grafted 'monomeric' distannoxane moieties to get close enough in space to one another, in spite of the grafting constraints, to be able to complex one another toward the extremely stable dimeric ladder configuration with internal four-ring Sn_2O_2 structure.[2] To the best of our knowledge, this is the first time that such a structural motif has been formally identified in a grafted state.[27,28] Figure 2 shows the solid-state MAS ^{117}Sn and hr-MAS ^{119}Sn spectra of both the grafted chlorodistannoxane derivative **2** and its corresponding dialkyldichlorotin precursor **1**.

The solid-state spectrum of the grafted dialkyltindichloride, **1** [Fig. 2(a)], displays a single, albeit broad, ^{117}Sn resonance at its isotropic chemical shift (122 ppm), identical within experimental error to its chemical shift in the ^{119}Sn hr-MAS spectrum [123 ppm; Fig. 2(b)], indicating that the tin atom has the same four-coordination sphere in dry solid state and at the solid–liquid interface. This is in strong contrast with the ^{117}Sn solid-state MAS spectrum of **2** [Fig. 2(c)], which displays a very broad anisotropy pattern, resulting in the pairs of isotropic chemical shifts discussed above. Comparison of the ^{117}Sn solid state MAS spectra of **1** and **2** does not enable one to identify whether a residue of the single resonance of **1**, precursor of **2**, is hidden under the anisotropy pattern of the latter, making it impossible to assess whether or not a complete conversion of **1** into **2** is obtained. The ^{119}Sn hr-MAS spectrum of compound **2** [Fig. 2(d)], however, unambiguously reveals the total absence of any residual ^{119}Sn hr-MAS resonance from its precursor **1**, which unmistakably evidences the complete conversion from **1** to **2**, at least within the detection limits of the method. It also confirms that the additional cross-linking of the diorganotin units at the interface, resulting both from the Sn–O–Sn bridge formation and the rather unexpected dimerization of two such moieties to the ladder structure with central Sn_2O_2 four-ring core, dramatically decreases the conformational flexibility and mobility of the organotin moieties, with the consequence that any ^{119}Sn hr-MAS resonance from the interface of **2** simply becomes invisible [Fig. 2(d)], in strong contrast with **1** [Fig. 2(b)].

The functionalization degree *t* of the grafted C11-distannoxane was determined from elemental analysis data using a previously described non-linear least-squares procedure.[25] The elemental analysis results are given in the experimental section, along with the corresponding calculated data.[27] The values are pair-wise in excellent agreement with each other, which evidences the high functional purity of compound **2**.

Transesterification of ethyl acetate and *n*-octanol

The catalytic activity of compound **1** ($t = 0.22$) was

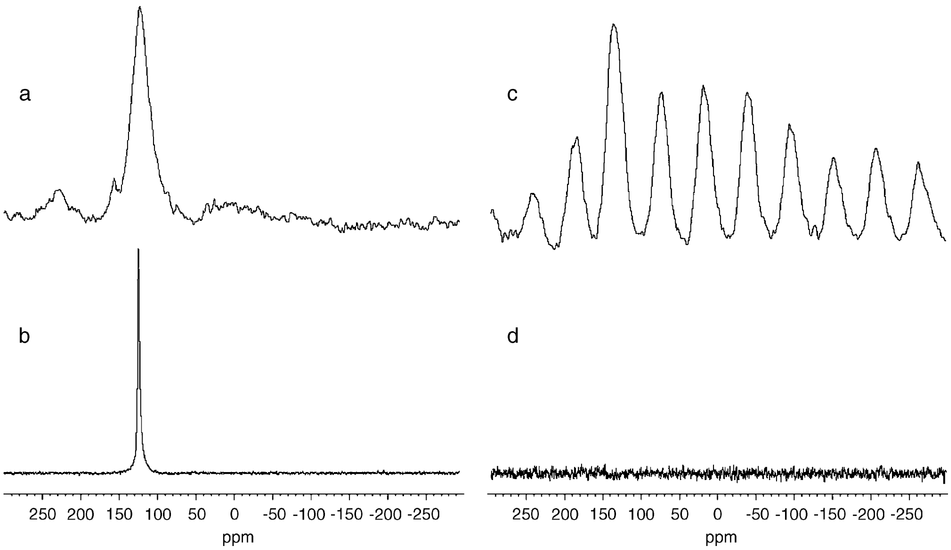


Figure 2. ^{117}Sn MAS spectrum (a, c) and ^{119}Sn hr-MAS NMR spectrum (b, d) of compounds **1** and **2**, respectively.

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investigated in the transesterification of ethyl acetate with *n*-octanol [equation (1)], a model reaction used previously to assess the catalytic activity of various grafted organotin compounds.[25,27,28,30,31]

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

As for one series of experiments performed previously with the C11-SnCl$_3$ catalyst,[30] the reaction was performed with a stoichiometric 1 : 1 mixture of ester and alcohol, without driving the reaction to completion, so as to keep reaction volumes strictly under control for the purpose of kinetic studies. The time evolution towards thermodynamic equilibrium was monitored by proton NMR on small aliquots of the reaction mixture collected at regular times, after which ethyl acetate and ethanol were distilled off. The rate of conversion into octyl acetate was assessed on the basis of the half-life time of the reactants in their evolution towards chemical equilibrium of the reaction. In all experiments, 1 mol% of grafted tin, with respect to the initial molar amount of reactant, was used. In order to demonstrate the recycling ability of the catalyst, several successive transesterification reactions were performed. The catalyst was recovered by filtration after each run, briefly washed with ethyl acetate and then re-used in a subsequent reaction.

The chemical state of the catalyst was assessed by ^{1}H and ^{119}Sn hr-MAS NMR spectroscopy after each catalytic run. Longitudinal eddy current delay (LED) diffusion-filtered ^{1}H hr-MAS NMR spectra[26,30,34–36] of the actual reaction mixture were used to monitor the catalyst *in situ* during the reaction. Figure 3 (top) shows the standard ^{1}H hr-MAS NMR spectrum of compound **1** in the presence of its reaction mixture, i.e. ethyl acetate, *n*-octanol, ethanol and octyl acetate, in which the resonances of the reaction mixture completely dominate the spectrum, while those of the catalyst at best hardly show up above noise level as broad bands.

Upon applying the diffusion filter (Fig. 3, bottom), only the broader resonances from the translationally immobile but the rotationally mobile moieties from the spacer, and to a lesser extent, from the polystyrene matrix, remained visible, those from the translationally mobile species being completely filtered away.

Two sets of transesterification experiments were performed in parallel in order to determine the half-life times[30] of the reaction toward equilibrium under catalysis of compound **1**, which amounted to 5–6 h in the first couple of catalytic runs. The catalytic efficiency improved in both series as the number of catalytic runs increased, under identical transesterification conditions. This observation might be related to the appearance of low amounts of grafted R$_2$Sn(OOCCH$_3$)$_2$ moieties after several runs, as evidenced by ^{119}Sn hr-MAS NMR (Fig. 4). After seven to eight runs, the half-life time was about half its value in the first couple of runs, but then increased again from run 9 in both series. Overall, for a total of 10 runs, statistically significantly identical average half-life times of 3.66 ± 1.21 and 3.73 ± 1.10 h were obtained for the first and second series, respectively, being much longer than for the corresponding C11-grafted tin trichloride ($t_{1/2} = 0.47 \pm 0.04$ h; $N = 10$), investigated elsewhere.[30] Fitting of the experimental data sets for compound **1** to a mechanistic model where both reactants complex simultaneously the tin atom before the rate-determining step[30] resulted in a calculated average half-life time of 4.01 ± 1.88 h for the first series and 3.61 ± 1.04 h for the second, in satisfactory agreement with the experimental values. Average turnover frequencies for compound **1** amounted to $1.8 \pm 0.6 \times 10^{-3}$ s^{-1}

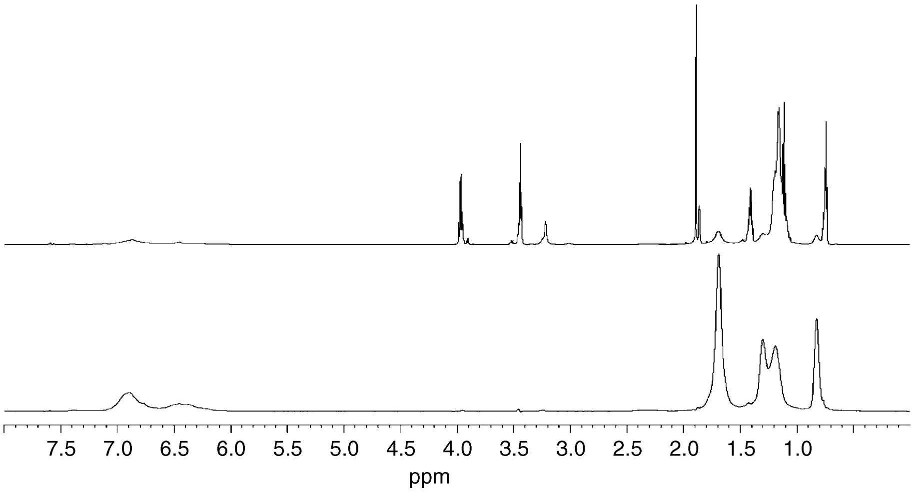

Figure 3. ^{1}H hr-MAS NMR spectrum of $[\mathbf{P}\text{–H}]_{(1-t)}[\mathbf{P}\text{–(CH}_2)_{11}\text{–Sn} - n\text{-BuCl}_2]_t$ in the presence of its reaction mixture (ethyl acetate, *n*-octanol, octyl acetate and ethanol) (top), and the corresponding DOSY-filtered ^{1}H hr-MAS NMR spectrum (bottom), recorded on the same sample, displaying only the resonances of the grafted catalyst, upon full suppression of the spectrum of the reaction mixture.

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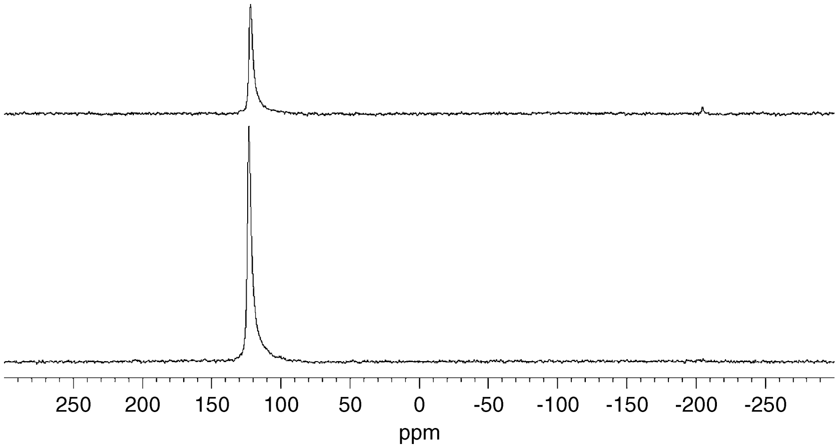

Figure 4. ^{119}Sn hr-MAS NMR spectrum of $[\mathbf{P}{-}\mathrm{H}]_{(1-t)}[\mathbf{P}{-}(\mathrm{CH_2})_{11}{-}\mathrm{Sn}{-}n{-}\mathrm{BuCl_2}]_t$ prior to any catalytic transesterification (bottom) and after the tenth run (top).

and $1.7 \pm 0.5 \times 10^{-3}\ \mathrm{s^{-1}}$ for the first and second series, respectively, whereas the turnover frequency (TOF) for the tin trichloride was about an order of magnitude higher ($\mathrm{TOF} = 1.1 \pm 0.2 \times 10^{-2}\ \mathrm{s^{-1}}$).[30]

The ^{1}H hr-MAS NMR spectrum of the grafted diorganotin dichloride after its use as a catalyst showed some additional resonances that were assigned to residues of ester and/or alcohol inside the pores of the beads that were not washed away. Nevertheless, the ^{119}Sn chemical shift of the catalyst remained unaltered by the reaction (i.e. at 123 ppm). After the first run, a minor additional resonance (integrating for 2%) was observed at −203 ppm, indicating only a limited modification of the catalyst into a functionality of the type $R_2Sn(OOCCH_3)_2$ (R = *n*-Bu, spacer).[37] For all subsequent runs, the ^{119}Sn spectra of the catalyst showed the characteristic resonance at 123 ppm next to the minor additional resonance, integrating between 2 and 4% of the main catalyst resonance (Fig. 4).

The signal-to-noise ratio was lower by 43 and 49% after the tenth run for the first and second series, respectively. The limited tin leaching (see below) only negligibly accounted for the dramatic S/N loss. Rather,[30] this effect was traced to the formation upon each catalytic run of diorganotin moieties immobilized at the interface, making their observation by hr-MAS NMR impossible, as demonstrated in Fig. 2(d) for the immobilized grafted distannoxane.

ROP of *ε*-caprolactone

Poly-*ε*-caprolactone (PCL) is readily synthesized by a ring-opening polymerization (ROP) of CL.[38–40] Compound **1** has already been proven to catalyze this reaction initiated by *n*-propanol.[29,30] The importance of the long C11 spacer to maintain the control over the polydispersity index has also been reported.[29] The work presented here focuses on the catalyst's recycling ability. The polymerizations were initiated by 10 mol% *n*-propanol, using 5 mol% of tin catalyst with respect to the initial amount of alcohol, i.e. 0.5 mol% with respect to CL monomer. The reaction was carried out for 2 h in dry toluene under an inert, moisture-free N_2 atmosphere at 100 °C in the presence of **1** or **2** as a catalyst. These experimental conditions were similar to those used with other catalysts, making comparison with previous results possible.[31] The PCL chain length was limited to 10 monomer units in order to prevent a partial burst of the grafted catalyst through polymer formation inside the pores of the polystyrene beads.[29] Hr-MAS NMR spectroscopy was used to evaluate the status of compound **1** as a catalyst after every reaction run, so as to assess whether and how much polymerization residue was retained in the material pores after a catalytic run, and to investigate the chemical integrity and recycling conditions of the grafted catalyst. Catalysts **1** and **2** were recycled in 10 consecutive polymerization runs. After each run they were filtered off from the reaction medium and briefly washed with toluene and dried under vacuum. An aliquot of the reaction mixture was taken to analyze the conversion degree and the degree of polymerization by quantitative liquid ^{1}H NMR spectroscopy.

The conversion degree of CL to PCL was calculated from the relative integrated intensities of the methylene proton resonances of the PCL repetitive units (PCL; $CH_2{-}O{-}CO$) at $\delta = 4.1$ ppm and the corresponding ones in the monomeric form (CL; $CH_2{-}O{-}CO$) at $\delta = 4.2$ ppm. For compound **1** a rather poor average conversion degree over 10 catalytic runs of 18 ± 8 % (SD) was found after 2 h of reaction. Compound **2** provided a better catalytic activity under the same reaction conditions, averaging at 63 ± 23%. As could also be deduced from the half-life times of the transesterification reaction (see above), the conversions achieved for the ROP tended to be statistically dispersed for catalysts **1** and **2**, which indicated that no constantly reproducible conversions could be achieved without thorough washing. The overall catalytic activity of **1** and **2** was significantly lower than that of the grafted C11-SnCl3 catalyst, giving full monomer conversion under the same reaction conditions.[31] The yield of PCL was determined by weighing the isolated dried material after three selective precipitation cycles from heptane for the polymerizations with **2** as a catalyst. Only two cycles of precipitation could be performed for ROPs with **1**, since the low yields prevented a third cycle being performed. The purified polymer yields obtained averaged 8 ± 9% (varying from 3 to 8% with one outlier of 32%) for **1** and 42 ± 20 (varying from 36 to 65% with two outliers of 7 and 14%) for **2**. They were slightly lower than the conversion degrees, because of the loss into the solution of the lower molar weight fractions during the precipitation–dissolution cycles. The appearance of outliers in these yields and their broad statistical dispersion reflected the difficulty of achieving reproducible washing conditions in the recycling process. Overall it can be stated that the grafted chlorodistannoxane derivative exhibited a higher catalytic activity than the dialkyltin dichloride catalyst. The conclusion is that, unlike the grafted tin trichloride,[31] the *n*-butyl tin dichloride and *n*-butylchlorodistannoxane analogs do not appear to be suitable as catalysts for practical applications, since no quantitative conversions were achieved for **1** and **2**.

The degree of polymerization (DP) was assessed with quantitative liquid ^{1}H NMR,[31] the integration data of the methylene proton resonances of the PCL repeat units (PCL $CH_2–O–CO$; $\delta = 4.1$ ppm) being compared with those of the end-group α-hydroxy methylene protons ($CH_2–OH$; $\delta = 3.6$ ppm). Whenever monomer conversion is quantitative and takes place according to a living polymerization mechanism, the DP should theoretically equal 10. It should be kept in mind that the DPs obtained from the NMR data are sensitive to variability because the resonance intensities of the hydroxy ends are low, and therefore subject to a large relative error. Moreover, in the case of catalyst **2** a decrease of the resonance intensity of the CH_3 end-group ($\delta = 0.9$ ppm) with regard to the signal of the $CH_2–OH$ protons ($\delta = 3.6$ ppm) was observed as the number of catalytic runs increased. This indicated that the polymerization was increasingly initiated by remnants in the material pores, e.g. opened ε-caprolactone as the catalyst was increasingly recycled. Such a trend was not observed with catalyst **1**. For the reaction duration of 2 h, the DP averaged at 4.6 ± 1.5 for catalyst **2**, while it was negligibly small for **1**, being 1.2 ± 0.8.

The mean theoretical number average molar mass ($< M_{n,\mathrm{th}} >$) over 10 reaction runs was calculated from the initial monomer-to-alcohol molar ratio with the assumption of a living coordination–insertion mechanism only initiated by *n*-PrOH $\{M_{n,\mathrm{th}} = ([\mathrm{CL}]_0/[n\text{-PrOH}]_0 \times \text{conversion} \times M_{\mathrm{CL}}) + M_{n-\mathrm{PrOH}}\}$. Experimental number average PCL molar masses ($M_{n,\mathrm{exp}}$) were determined by quantitative liquid ^{1}H NMR spectroscopy, using the already acquired degrees of functionality and conversion degree [$M_{n,\mathrm{exp}} = (\mathrm{DP} \times \text{conversion} \times M_{\mathrm{CL}}) + M_{n-\mathrm{PrOH}}$], and by size exclusion chromatography (SEC) with reference to polystyrene standards in combination with the Mark–Houwink–Sakaruda relationship.[29,41–43] Therefore, values for $M_{n,\mathrm{exp}}$ calculated from NMR data were subject to the same uncertainty as mentioned above for DP. For the polymers synthesized with catalyst **1** the mean number average molar masses were $< M_{n,\mathrm{th}} >= 260 \pm 90$ g/mol, to be compared with $< M_{n,\mathrm{exp}}(\mathrm{NMR}) >= 190 \pm 90$ g/mol, indicating that they were hardly more, on average, but dimers, even though $< M_{n,\mathrm{exp}}(\mathrm{SEC}) >= 470 \pm 190$ g/mol. For catalyst **2**, higher mean values were obtained both from SEC and NMR, with $< M_{n,\mathrm{exp}}(\mathrm{NMR}) >= 580 \pm 180$ g/mol being effectively lower than $< M_{n,\mathrm{exp}}(\mathrm{SEC}) >= 710 \pm 200$ g/mol, for an expected $< M_{n,\mathrm{th}} >= 780 \pm 260$ g/mol. The higher values found by SEC on isolated and purified polymers suggested that the assumption of a living polymer did not hold when catalyst **1** was used, but since the Mark–Houwink–Sakaruda relationship.[29,41–43] was questionable for such low molar masses, they are not discussed further. The differences between the mean number average molar masses from NMR on the reaction mixture, and SEC on isolated and purified polymers, were due to the fact that for NMR all polymers generated were accounted for, while the dissolution–precipitation cycles eliminated lower molar mass fractions to a larger extent, the solubility of the oligomers decreasing upon increasing molar mass. Moreover, size exclusion chromatography data showed a bimodal molar mass distribution, and polydispersity indices averaging at higher than unity, 1.9 ± 0.6 and 1.7 ± 0.2 for catalysts **1** and **2** respectively. Hence, the polymerization mechanism could not be purely of the living type, probably being hampered by diffusion issues.

The chemical stability of compound **1** and catalytic processes was monitored *in situ* with hr-MAS NMR spectroscopy, by recording the spectra of the organotin graft before and after polymerization runs. The ^{119}Sn resonance was shifted upfield from 123 ppm for the unused catalyst to 112 ppm after the first catalytic run, but recovered its original chemical shift after thorough Soxhlet extraction.

The catalytic processes at the level of the tin atoms of the grafted dichlorodistannoxane **2**, more particularly the evolution of the catalyst from its non-used initial state up to its state after the tenth catalytic run, were monitored by ^{117}Sn solid-state MAS NMR. Figure 5 compares the spectrum of the unused catalyst with the one recorded under the same acquisition conditions, on the same catalyst sample after 10 consecutive polymerization runs alternating brief washings with toluene.

Since no significant differences can be observed in the anisotropy patterns of the two spectra, it can be concluded that no alteration of the catalyst has occurred.

Tin leaching

Residual tin contents in all transesterification reaction products were measured by inductively coupled plasma/atomic emission spectroscopy (ICP-AES).

Reasonably low values of tin amounts were measured for two independent series of 10 consecutive catalytic runs when the transesterification was catalyzed by compound **1**. However, there was a clear trend towards the existence

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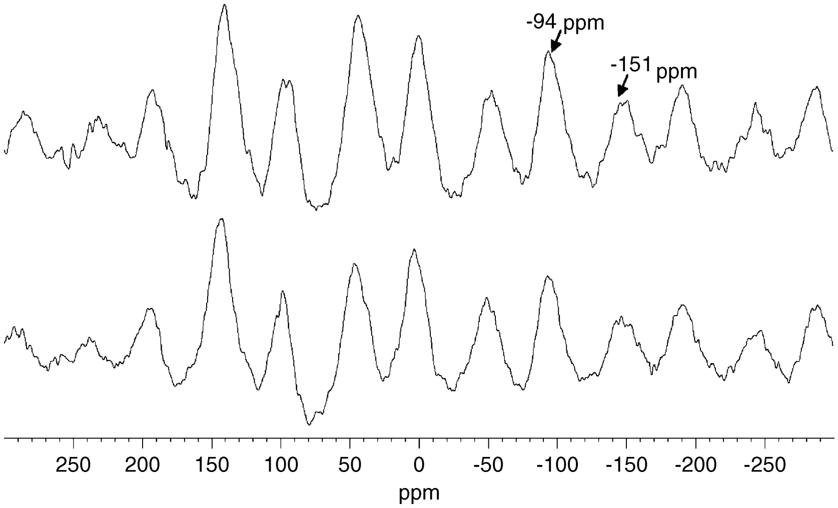

Figure 5. ^{117}Sn MAS NMR spectra, at a spinning rate of 8500 Hz, of non-used $[\mathbf{P}\text{–H}]_{(1-t)}\{[\mathbf{P}\text{–(CH}_2)_n\text{–Sn-}n\text{-BuCl}]_2\text{O}\}_{t/2}$ (bottom) and the same catalyst after 10 consecutive polymerization runs (top) recorded at a spinning speed of 8500 Hz.

of a correlation between tin leaching and contact time between the catalyst and the refluxing reaction mixture, as observed previously for the grafted C11-SnCl$_3$ catalyst.[30] In the first run, where refluxing time lasted 10 h, 16 ppm of tin was detected in the reaction mixture. However, the values averaged 51 ± 56 and 53 ± 13 ppm for the next three runs which were conducted with reaction times of 30 h or more, the first leaching value being rather dispersed because of an unexplained peak value of 115 ppm for the fourth run. Overall, this shows the relatively unpredictable thermal instability of the catalyst upon prolonged exposure to the refluxing temperature of the reaction mixture, since also in the second series, three peak values well over 50 ppm were obtained in addition to the one of 115 ppm in the first series. In contrast, they averaged 20 ± 8 and 9 ± 5 ppm for the last six runs conducted with much shorter reaction times of 5–6 h, in experiment series 1 and 2, respectively.

In order to investigate the organotin contamination of the synthesized polymer in ring-opening polymerizations, PCL was digested with concentrated nitric acid prior to investigation with ICP-AES. For compound **1**, an average tin contamination of 288 ± 46 ppm was found, which was unsatisfactorily high for practical applications. For compound **2**, the tin leaching values were less unfavorable, since they averaged 70 ± 23 ppm, however remaining slightly higher than the average of 50 ± 5 ppm per run observed previously for the grafted C11-SnCl$_3$ catalyst.[31] This suggests that the dimeric distannoxane core of catalyst **2** does not have a higher thermal stability when compared with the tin trichloride, even though it does with respect to the tin dichloride. The overall higher leaching values observed for the ring-opening polymerizations than for the transesterifications are therefore probably due to the higher reaction temperature for the former than the latter by approximately 20 °C.

CONCLUSION

The grafted dialkyltin dichloride appeared to be recyclable at least nine times in the transesterification of ethyl acetate, revealing reasonable catalytic activities under mild reaction conditions and leaching amounts of tin, at least within 2 h of reaction.

The ROP experiments with the grafted C11-chlorodistannoxane, for which the existence of a dimeric structure could be proven for the first time for a grafted distannoxane, displayed fairly good catalytic activities, notwithstanding the more rigid structure, while the dialkyltin dichloride only reached low conversion degrees of 15% on average during the same reaction time of 2 h. Tin leaching figures were higher for the ring-opening polymerization than for the model transesterification; however, they were less unsatisfactory for the distannoxane than for the dialkyltin dichloride.

^{1}H and especially ^{119}Sn hr-MAS NMR spectroscopy proved their full potential as tools, not only for monitoring the synthesis of the grafted catalysts and assessing their functional purity, but also in the assessment of their chemical integrity and recyclability after use in catalytic processes. This technique showed its limitations, however, when the grafted organotins lost their rotational mobility at the solid–liquid interface, even under good material swelling conditions, as proven to be the case for the C11-grafted chlorodistannoxane.

EXPERIMENTAL

Materials

ε-Caprolactone (Fluka, ≥99%), toluene (Aldrich, 99%) and 1-propanol (n-PrOH, Aldrich, 99.5+%) were dried over calcium hydride (CaH$_2$) and distilled before reaction. Ethyl acetate (Aldrich, 99.5+%) and n-octanol (Aldrich, 99+%)

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were distilled prior to use. Prior to catalytic experiments, the polystyrene-supported organotin catalysts were dried at 60 °C under reduced pressure.

Synthesis and characterization

The catalysts $\mathbf{1}^{25-29}$ and $\mathbf{2}^{27,28}$ were prepared according to a procedure described previously, as summarized in Scheme 2. The full characterization of **1** has been given in previous reports.[27,29]

$(\boldsymbol{P}\text{–}H)_{(1-t)}\{[\boldsymbol{P}\text{–}(CH_2)_{11}Sn\text{-}n\text{-}BuCl]_2O\}_{t/2}$ (**2**)

Elemental analysis (%) found: H 8.17, C 73.76, Sn 13.51, Cl 4.50, O 0.93; calcd: H 7.91, C 72.94, Sn 14.02, Cl 4.19, O 0.95; $t = 0.20$; IR (cm^{-1}): ν (Sn–Cl) 347 (m), ν (Sn–O–Sn)$_{sym}$ 602 (w), ν (Sn-*n*-Bu)$_{asym}$ 600 (w), ν (Sn-*n*-Bu)$_{sym}$ 522 (w); ^{117}Sn solid state MAS NMR: isotropic chemical shifts $\delta = -94$ and -151 ppm.

Catalysis experiments on transesterification reaction

Ethyl acetate and *n*-octanol were used in a 1 : 1 molar ratio. A mixture of ethyl acetate, *n*-octanol and insoluble polystyrene supported catalyst (1 mol% Sn with respect to *n*-octanol) was refluxed until chemical equilibrium was achieved. The catalyst was filtered off and gently washed with ethyl acetate. The ethyl acetate and ethanol were distilled off from the reaction mixture. The ratio of initial alcohol to obtained ester was determined by integration (±1%) of the respective CH_2O ^{1}H NMR resonances.

Catalysis experiments on ring opening polymerization

Typically, in a first run 200 mg of polystyrene-supported catalyst (0.220 mmol tin/g) was introduced into a preliminarily flamed and nitrogen purged round-bottom flask equipped with a three-way stopcock and a rubber septum. Next, three vacuum/nitrogen purging cycles were further applied to make the round-bottom completely moisture free. After distilling azeotropically off its head fraction, 2 ml of toluene and 4.66 ml of ε-CL (43.95 mmol) were injected into the flask. The reaction medium was heated up to 100 °C before adding 330 µl of *n*-PrOH (4.395 mmol). After a polymerization reaction time of 2 h under low-speed shaking, the reaction medium was rapidly cooled down by tap water. An aliquot of about 50 µl was taken from the reaction mixture to determine the degree of conversion, the polymerization degree and molar mass parameters with quantitative liquid ^{1}H NMR. Next, 25 ml of dry toluene was added in order to reduce the viscosity of the obtained mixture and to make it possible to separate the polystyrene-supported catalyst by simple filtration. The grafted catalyst was then washed five times with 5 ml of dry toluene and dried under vacuum at 60 °C. After 24 h of drying, 20 mg of catalyst was taken to perform hr-MAS NMR experiments to investigate its status. The remaining fraction was then re-used in a next polymerization experiment. The PCL synthesized with compound **2** was precipitated three times by adding drop by drop a 7-fold excess of heptane to the liquid reaction mixture. For compound **1**, only two precipitation cycles could be performed, as explained in the Results and Discussion. The precipitate was filtered and dried under reduced pressure at 60 °C until constant weight to assess the yield of polymer.

Size exclusion chromatography

Size exclusion chromatography (SEC) was performed in THF at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 ml min^{-1}), a Marathon auto-sampler (loop volume = 200 µl, solution concentration = 1 mg ml^{-1}), a PL-DRI refractive index detector and three columns : a PL gel 10 µm guard column and two PL gel Mixed-B 10 µm columns (linear columns for separation of PS molecular weight ranging from 500 to 10^6 Da). Molar masses were calculated by reference to a polystyrene standard calibration curve, using the Mark–Houwink–Sakaruda relationship $(\eta) = KM^a$ for PS and PCL ($K_{PS} = 1.25 \times 10^{-4}$ dl g^{-1}, $a_{PS} = 0.707$, $K_{PCL} = 1.09 \times 10^{-3}$ dl g^{-1}, $a_{PCL} = 0.600$).

IR and Raman spectroscopy

IR spectra are recorded on a Bruker Equinox 55 FT-IR spectrometer, equipped with a MIR source, KBr beam splitter and a DGTS detector, from 200 mg dry KBr pellets with ca. 5 mg of substance. The RAMAN spectra are recorded on a Perkin Elmer 2000 NIR FT-Raman spectrometer using a Raman_dpy2 beam with 310 mW power.

NMR spectroscopy

The ^{1}H, ^{13}C and ^{119}Sn hr-MAS NMR spectra were recorded on a Bruker AMX500 and Avance II 500 instruments operating respectively at 500.13, 125.77 and 186.50 MHz, with a dedicated Bruker ^{1}H/^{13}C/^{119}Sn hr-MAS probe equipped with gradient coils; full rotors were filled with approximately 20 mg of resin beads, swollen in approximately 85 µl of $CDCl_3$; magic angle spinning was at 4000 Hz. ^{119}Sn measurements were referenced to $\Xi = 37.290665$ MHz.[44] On the 700 MHz Bruker Avance II spectrometer, also equipped with a dedicated Bruker^{1}H/^{13}C/^{119}Sn hr-MAS probe with gradient coils, a diffusion LED sequence was used to eliminate the contributions of any mobile species from one-dimensional ^{1}H hr-MAS spectra to monitor the catalyst in the presence of the reaction mixture.[26,36] The solid-state MAS spectra of compound **2** were recorded on the Bruker DRX250 spectrometer, operating at 89.25 MHz for the ^{117}Sn nucleus using procedures described previously.[45,46] Samples used for the determination of the ratio initial alcohol/obtained ester by solution ^{1}H NMR were prepared by dissolving about 10 mg of mixture in $CDCl_3$ (0.5 ml). In the case-study of the transesterification reaction of *n*-octanol with ethyl acetate, the quantitative liquid ^{1}H NMR spectra were recorded on a Bruker DRX250 Avance I spectrometer operating at 250.13 MHz. In the ring-opening polymerization experiments, the quantitative ^{1}H NMR spectra were recorded on a Bruker AMX500 or Avance II 500 instrument.

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