Articles

Solid-State Tin-117 NMR: A Powerful Tool for the Analysis of Organotin Functionalities Anchored to Insoluble Polymers

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Various polymer-supported organotin derivatives of the type $P-(CH_2)_nSnBu_2\Sigma$ (Σ = H, halogen, Ph) were prepared from insoluble polystyrene, and their reactivity was studied. The solid support used in the present report is Amberlite XE 305 (P). Solid-state tin-117 NMR was successfully used for qualitative and quantitative analysis of the different tin species present in the polymers.

Introduction

Many organotin compounds are extremely important reagents in organic synthesis.[1,2] However, removing them or their reaction residues can be difficult. Their utilization is therefore hampered, especially when they are toxic, as is the case for triorganotin derivatives. In order to avoid traces of polluting organotin residues in the reaction products, the organotin reagents can be anchored to insoluble solid supports. The desired reaction products are then isolated by simple filtration.

Several authors have prepared organotin reagents, mainly hydrides, anchored to insoluble polystyrenes.[3−7] It has been demonstrated that such new compounds exhibit reactivities comparing favorably with reagents in usual homogeneous solutions.[8−11] In addition they are significantly less polluting than the usual organotin reagents.[7,12−14]

The general formula of such organotin compounds anchored to an insoluble solid support is $P-(CH_2)_nSnBu_2\Sigma$ (Σ = H, halogen, Ph). The polymer used in the present report is Amberlite XE 305 (P),[6] a macroporous polystyrene. Tin hydride polymers of this type are involved in reduction reactions with halogen and carbonyl derivatives.[7]

So far, as a consequence of their complete insolubility, structural information on these polymers has been obtained essentially only from infrared data and elemental analysis. Accordingly, such data are often unsatisfactory, as they do not provide information as to the nature of the organotin functionalities anchored to the polymer. In turn, this lack of clear information on the nature and relative amounts of the organotin functions involved hampers a good understanding of the chemical reactions these functionalities undergo.

This paper illustrates that solid-state tin-117 NMR is a powerful tool for identifying these functionalities, when combining both chemical shift data extrapolated from solution tin NMR data[15,16] and considerations on chemical properties of the reagents and mechanistic courses of the reactions involved.[1] It is discussed under which conditions solid-state tin-117 NMR can be used to gain quantitative information on the relative amounts of the different tin-containing functionalities anchored to the Amberlite XE 305 support.

Experimental Section

Materials. Amberlite XE 305 was obtained from Rohm and Haas.[6] This polymer is an unfunctionalized macroporous

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polystyrene crosslinked with divinylbenzene and shows an average pore size of 900 Å. All reactions were carried out in a Schlenk tube under a nitrogen atmosphere using dry solvents. After washing, the polymers were dried in vacuo at 60 °C.

P−(CH$_2$)$_4$SnBu$_2$Cl (1) was prepared according to Scheme 1. Chlorotrimethylsilane (1.95 g, 1.8 mmol) was added to a polymer type **6** (12.5 g, 1.6 mmol of Sn) suspended in 60 mL of methanol at 0 °C. The mixture was heated at 60 °C for 12 h. After filtration the polymer was successively washed with THF/H$_2$O (1/1), THF/methanol (1/1), and CH$_2$Cl$_2$. Polymer **1** was found to contain 1.22 mmol of SnCl/g. Anal. Found: Sn, 16.25; Cl, 4.34. IR: ν_{SnCl} 325 cm^{-1}.

P−(CH$_2$)$_4$SnBu$_2$Br (2) was prepared from a tin hydride polymer according to Scheme 1. A solution of 1-bromodecane (0.88 g, 4 mmol) and AIBN (0.08 mmol) in 30 mL of THF was added to a tin hydride polymer (2 g, 2.6 mmol of Sn) suspended in 30 mL of THF. The mixture was heated at 80 °C for 6 h. After filtration the polymer was washed with THF. Polymer **2** was found to contain 0.23 mmol of SnBr/g. Anal. Found: Sn, 14.71; Br, 1.87.

P−(CH$_2$)$_4$SnBu$_2$I (3) was prepared according to Scheme 1. A solution of iodine (3.17 g, 12.5 mmol) in 60 mL of ethanol was added to a polymer type **6** (10 g, 11.6 mmol of Sn). The mixture was heated at 60 °C for 6 h. After filtration the polymer was successively washed with solutions of sodium thiosulfate, ethanol, and THF. Polymer **3** was found to contain 0.68 mmol of SnI/g. Anal. Found: Sn, 9.89; I, 8.66.

P−(CH$_2$)$_6$SnBu$_2$H (4) was prepared according to Scheme 2. Poly[[6-(dibutyliodostannyl)hexyl]styrene] (2 g, 1.6 mmol of SnI) and NaBH$_4$ (3.62 g, 9.6 mmol) were suspended in 40 mL of ethanol. The mixture was heated at 60 °C for 18 h. After filtration the polymer was washed with ethanol and THF. The tin hydride efficiency of this polymer was monitored by reduction of 1-bromodecane.[7] Polymer **4** was found to contain 0.66 mmol of SnH/g. Anal. Found: Sn, 14.56; I, <0.3. IR: ν_{SnH} 1800 cm^{-1}.

P−(CH$_2$)$_4$SnBu$_2$H (5) was prepared according to Scheme 2. Dibutylstannane (6.2 g, 26 mmol) was slowly added to a THF (20 mL)/hexane (12 mL) solution of lithium diisopropylamide (24 mmol) at −70 °C. After 30 min, at −50 °C this solution of (dibutylstannyl)lithium (Bu$_2$SnHLi) was transferred into a Schlenk tube containing poly[(4-chlorobutyl)styrene] (4 g, 9 mmol of Cl) suspended in 20 mL of THF at −70 °C. The mixture was warmed to −10 °C over 12 h. After filtration the polymer was successively washed with THF, THF/H$_2$O (4/1), THF, and ethanol. Polymer **5** contained 1.2 mmol of Sn/g and 0.36 mmol of SnH/g. Anal. Found: Sn, 15.54; Cl, <0.8. IR: ν_{SnH} 1800 cm^{-1}.

P−(CH$_2$)$_4$SnBu$_2$Ph (6) was prepared according to Scheme 3. A solution of Bu$_2$SnPhLi (30 mmol) in 30 mL of THF was added to poly[(4-chlorobutyl)styrene] (8.5 g, 21 mmol of Cl) suspended in 30 mL of THF at 60 °C. The mixture was stirred at 20 °C for 15 h. After hydrolysis and filtration the polymer was washed with THF. Polymer **6** was found to contain 1.23 mmol of Sn/g. Anal. Found: Sn, 14.64; Cl, <0.2%. IR: ν_{SnPh} 730 cm^{-1}.

P−(CH$_2$)$_6$SnBu$_2$Ph (7) was prepared using a similar experimental procedure. It contained 1.2 mmol of Sn/g. Anal. Found: Sn, 14.35; Cl, <0.2%. IR: ν_{SnPh} 730 cm^{-1}.

NMR Experiments. All spectra were recorded on a Bruker AC250 spectrometer, operating at 89.15 MHz for the ^{117}Sn resonance frequency. The spectrometer is interfaced with an Aspect 3000 computer and equipped with a MAS broad-band probe for solid-state experiments. ZrO$_2$ rotors (7 mm o.d.) and a spinning rate of 5 kHz were used. The matching condition for the Hartmann−Hahn cross-polarization for cross-polarization magic angle spinning (CP-MAS) experiments[17] (^{1}H 90° pulse length: 5 μs) was set on the ^{117}Sn resonance of (C$_6$H$_{11}$)$_4$Sn, to which all chemical shifts were referenced (−97.35 ppm relative to (CH$_3$)$_4$Sn).

In order to find the optimal cross-polarization time, a variable contact time experiment was run on two samples. Both led to a maximum signal resonance after 2 ms and showed similar cross-polarization times for all resonances within 15%. Typically ^{117}Sn spectra were obtained by acquiring 32K data points over a spectral width of 166.7 kHz (acquisition time 98 ms), using a 2 ms contact time and a relaxation delay of 2 s with 1000−10 000 scans. A control experiment with a longer relaxation delay of 10 s did not result in any change, within a typical experimental error of no more than 5%, in the relative integrated areas of the resonances of the different species.

Control spectra were recorded without cross-polarization on two samples exhibiting all the tin functionalities observable in this work. This was achieved in order to verify that no signals are lost under conditions of cross-polarization. Again, essentially no qualitative and quantitative changes in the resonance patterns were observed.

^{117}Sn NMR was preferred over the more common and theoretically slightly more sensitive ^{119}Sn NMR to overcome a local radio interference problem. Such problems are not unusual.[18] Two control ^{119}Sn NMR runs indicated no differences in resonance patterns and chemical shifts.[19]

Results and Discussion

Methodological NMR Considerations. Solid-state tin NMR has been extensively used over the past few years in structural and molecular dynamics applications of organotin chemistry,[20] yet it remains rather uncommon in solid-phase synthetic organotin chemistry applications, especially in the analysis of tin-containing functional groups. The target polymers of the present paper obey the formula P−(CH$_2$)$_n$SnBu$_2$Σ, with Σ = H, Cl, Br, I or Ph among the functionalities desired and Σ = R′, SnR′$_3$, or O−SnR′$_3$ among the undesired but, unfortunately, predictable ones. In the latter functionalities, R′ is to be understood as an alkyl group in the broad sense, being a polymeric side chain, aliphatic polymethylene fragment comparable to a *n*-butyl group, or an *n*-butyl group itself. It is unnecessary that in SnR′$_3$ all three groups should be identical. It is precisely the purpose of the solid-state tin-117 NMR approach to identify all functionalities obtained under a given set of experimental reaction conditions, in order to determine the nature of side reactions occurring and to design subsequently better synthesis routes.

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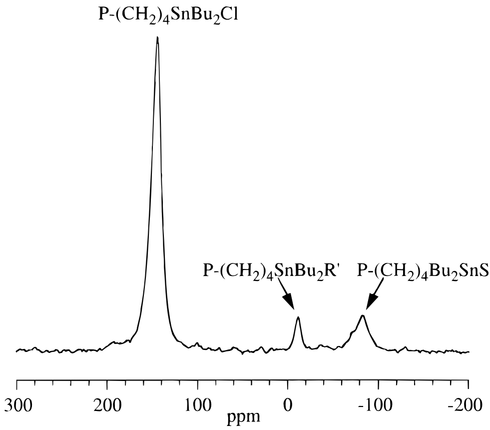

Figure 1. ^{117}Sn CP-MAS NMR spectrum of a sample of the target polymer **1**, $P-(CH_2)_4SnBu_2Cl$.

Qualitatively, the functionalities are identified on the basis of characteristic chemical shift ranges, as found in appropriate reviews.[15,16] The usual risk of errors in the tin chemical shift assignment, related to the possible coordination expansion of tin, is nonexistent here, since the material structure itself imposes a geometrical constraint of four-coordination onto the tin atom, whatever the nature of Σ may be. Stated in other terms, the organotin functionalities are diluted in the solid support, as if they were in a kind of "solid solution", with none of the individual functional organotin groups being able to interact with other groups that might lead to coordination expansion of the tin atom. Accordingly, the chemical shifts characteristic for four-coordinate tin atoms in $P-(CH_2)_nSnBu_2\Sigma$ can be expected in rather narrow ranges, typically within 10 ppm, as is evident from inspection of tin chemical shift data of the appropriate model systems, $Bu_3Sn\Sigma$, in a broad selection of noncoordinating solvents.[15,16] These ranges are +130 to +140 ppm for Σ = Cl or Br, +80 to +90 ppm for Σ = I or $O-SnR'_3$, −10 to +10 ppm for $\Sigma = R'$, around −40 ppm for Σ = Ph, around −80 ppm for $\Sigma = SnR'_3$, and −90 to −95 ppm for Σ = H. A typical example of a ^{117}Sn CP-MAS spectrum, with an assignment obtained by this approach, is displayed in Figure 1. Figure 1 shows the spectrum of $P-(CH_2)_4SnBu_2Cl$, as obtained from the reaction of $P-(CH_2)_4SnBu_2Ph$ with trimethylsilyl chloride in methanol (Scheme 1). We observed small amounts of undesired tetraorganotin and hexaorganoditin functionalities originating from the starting polymer. Another important feature of the spectrum of Figure 1 is that it does not exhibit the typical chemical anisotropy spinning side band pattern often observed in many solid tin-containing products but, rather, a "liquidlike" spectrum with broad resonances. This turned out to be the case for all samples analyzed in this paper, which of course facilitated the resonance identification, especially in the case of overlapping and/or the presence of multiple resonances.

Quantitative analysis of the different functionalities by resonance integration in ^{117}Sn CP-MAS spectra requires several cautions.

First, conditions of full T_1 relaxation should be achieved between two successive scans. Spectra recorded on a sample with a maximum of functionalities, using total recycling delays of 2 and 10 s, displayed no differences within experimental error (less than 5%) in the relative integrated areas. Thus, the above requirement is achieved. Second, for relative integrated resonance areas to be proportional to chemical species amounts in CP-MAS spectra, the resonances should grow in parallel to their optimum during the cross-polarization period[17] and the latter optimum be obtained simultaneously for all resonances after the same contact time.[17] In order to check this, CP-MAS ^{117}Sn NMR spectra were recorded on two samples, at 8 and 15 different contact times for polymers **1** and **2**, respectively. For all organotin functionalities observed, no difference in the relative integrated areas was found within 5% as a function of the contact time, its optimal value being 2 ms for all resonances within 10−15%. This finding is further in agreement with the fact that MAS spectra recorded without cross-polarization exhibit no significant difference in the relative integrated resonance areas within the above error margin, as compared to CP-MAS spectra. This demonstrates that no signals are lost under the conditions of cross-polarization.

With these cautions, which imply a careful choice and setting of the instrumental acquisition conditions, it is possible to quantify the relative amounts of the tin-containing species in the different samples on a basis which is estimated to be reliable to within 5−10%. Where confirmation with elemental analysis data is possible, this turns out to be generally the case.

Polymers of the Type $P-(CH_2)_4SnBu_2X$. The target polymers of the type $P-(CH_2)_4SnBu_2X$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) were obtained as shown in Scheme 1. The ^{117}Sn CP-MAS spectrum eventually obtained for compound **1** is shown in Figure 1.

Scheme 1

$$P-(CH_2)_4SnBu_2Ph \xrightarrow[MeOH]{Me_3SiCl} \underset{\mathbf{1}}{P-(CH_2)_4SnBu_2Cl}$$

$$P-(CH_2)_4SnBu_2H \xrightarrow{C_{10}H_{21}Br} \underset{\mathbf{2}}{P-(CH_2)_4SnBu_2Br}$$

$$P-(CH_2)_4SnBu_2Ph \xrightarrow{I_2} \underset{\mathbf{3}}{P-(CH_2)_4SnBu_2I}$$

Table 1 gives the percentage composition of the different organotin functionalities identified in the reaction mixtures associated with the polymers **1**−**3**.

In the target polymer **1**, the desired species $P-(CH_2)_4SnBu_2Cl$ is largely present. The contaminants are $P-(CH_2)_4SnBu_2R'$ and $P-(CH_2)_4Bu_2Sn-SnR'_3$. The latter species are also present in the brominated target analog, polymer **2**. In the brominated polymer **2**, the species $P-(CH_2)_4Bu_2Sn-O-SnR'_3$ is also present to a significant extent. This species, characterized from a ^{117}Sn spectrum recorded on a sample resulting from the reaction of $P-(CH_2)_4Bu_2SnCl$ treated with an excess of potassium hydroxide, is actually already present in the starting material, $P-(CH_2)_4Bu_2SnH$, as discussed below.

From the NMR data, it is calculated that in polymer **1** the molar percentage of tin atoms bound to a chlorine atom (Sn−Cl), at 82%, amounts to of the total number of tin atoms present in the material. This result is in fair agreement with the elemental analysis results. These show that polymer **1** contains 1.22 mmol of SnCl

Table 1. ^{117}Sn Chemical Shifts (in ppm) and Mole Percent Composition, As Determined from Resonance Integration, of the Different Organotin Species Obtained in the Polymer Mixtures of the Target Species 1−3

$P-(CH_2)_4SnBu_2X$[a]	$P-(CH_2)_4SnBu_2X$	$P-(CH_2)_4Bu_2SnOSnR'_3$	$P-(CH_2)_4SnBu_2R'$	$P-(CH_2)_4Bu_2SnSnR'_3$
1, X = Cl	+146.0 88%		−11.4 5%	−83.0 7%
2, X = Br	+128.3 33%	+83.0 39%	−12.0 12%	−82.4 16%
3, X = I	+81.9 87%[b]			

[a] Target polymers. [b] 13% of an unidentified functionality.

Table 2. ^{117}Sn Chemical Shifts (in ppm) and Mole Percent Composition, As Determined from Resonance Integration, of the Different Organotin Species Obtained in the Polymer Mixtures of the Target Species 4 and 5

$P-(CH_2)_nSnBu_2H$[a]	$P-(CH_2)_nBu_2SnOSnR'_3$	$P-(CH_2)_nSnBu_2R'$	$P-(CH_2)_nSnBu_2H$
4, $n = 6$	+81.6 26%		−91.6 74%
5, $n = 4$	+83.3 44%	−12.2 10%	−90.4 46%

[a] Target polymers.

moieties for a total of 1.35 mmol of tin atoms/g of material, which corresponds to a ratio $SnCl/Sn_{total}$ of 90%.

The agreement is even slightly better for polymers **2** and **3**, where the ratios $SnBr/Sn_{total}$ and SnI/Sn_{total} were found to be respectively 21% (elemental analysis, 19%) and 87% (elemental analysis, 82%).

Polymers of the Type $P-(CH_2)_nSnBu_2H$. The target polymers $P-(CH_2)_6SnBu_2H$ (**4**) and $P-(CH_2)_4SnBu_2H$ (**5**) were prepared according to Scheme 2.[6,7]

Scheme 2

$$P-(CH_2)_6SnBu_2I \xrightarrow{NaBH_4} P-(CH_2)_6SnBu_2H$$

4

$$P-(CH_2)_4Cl \xrightarrow{Bu_2SnHLi} P-(CH_2)_4SnBu_2H$$

5

The infrared spectra of the target polymers **4** and **5** exhibit a characteristic ν_{SnH} band at 1800 cm^{-1}. Table 2 gives the percentage composition of the different organotin functionalities identified in the target hydride polymers **4** and **5**.

The ^{117}Sn CP-MAS NMR spectrum of polymer **4** reveals that the hydride functionality is present in major amount (74%). However, because of the rather close values of the chemical shifts of the Sn−H (around −90 ppm) and Sn−Sn (around −80 ppm) functionalities and the rather large line widths, it cannot be excluded entirely that there is no contamination of the desired former one by the undesired latter one. It should be stressed, however, that no NMR spectral evidence, like for instance a high-frequency shoulder appearance at the tin hydride resonance due to the distannane species, could be observed in the spectrum of **4**. This is somewhat surprising, as the generation of such a distannane species is not unusual during the reduction of a Sn−I polymer of this type by $NaBH_4$.[5] In contrast, significant amounts of a distannoxane species, Sn−O−Sn, is observed. It is likely that the latter results from the oxidation of the Sn−H or the unobserved Sn−Sn species. Similar considerations hold for **5**.

Elemental analysis enables us to evaluate the total amount of tin present in **4** to be 1.22 mmol/g of material. Its hydride content, as assessed from its reactivity toward 1-bromodecane (see Scheme 1), is 0.66 mmol/g of material. The resulting ratio SnH/Sn_{total} of 54% is in good agreement with the ratio of 58% deduced from the ^{117}Sn NMR CP-MAS spectra. For polymer **5**, the ratio SnH/Sn_{total} was found to be 28% by elemental analysis and 32% by CP-MAS ^{117}Sn NMR.

Polymers of the Type $P-(CH_2)_nSnBu_2Ph$. The target polymers $P-(CH_2)_4SnBu_2Ph$ (**6**) and $P-(CH_2)_6SnBu_2Ph$ (**7**) were prepared according to Scheme 3 by stannylation from the corresponding chlorinated precursors $P-(CH_2)_4Cl$ and $P-(CH_2)_6Cl$, respectively.

Scheme 3

$$P-(CH_2)_nCl \xrightarrow{Bu_2SnPhLi} P-(CH_2)_nSnBu_2Ph$$

$n = 4$, **6**
$n = 6$, **7**

The only data available on these polymers are a characteristic ν_{SnPh} IR band at 730 cm^{-1} and the total tin mass percentages, 14.64% for **6** and 14.35% for **7**, as determined by elemental analysis. The latter unambiguously excludes the presence of chlorine in these materials. Accordingly, even more than in the cases above, ^{117}Sn CP-MAS NMR turned out to be essential to characterize the organotin functionality compositions of **6** and **7**. They are presented in Table 3.

In both cases the NMR data reveal the presence of almost 90% of the desired $P-(CH_2)_nSnBu_2Ph$. Only minor amounts of tetraorganotin and hexaorganoditin compounds are observed. Noteworthy is the total absence of oxidation products of the distannoxane type.

Conclusion

The various polymer-supported organotin derivatives were obtained, in some cases, as a mixture of different tin species. Their usual analysis (IR and elemental analysis) does not enable a satisfactory determination of their composition. The main merit of the present ^{117}Sn CP-MAS NMR approach is that it enables the

Table 3. ^{117}Sn Chemical Shifts (in ppm) and Mole Percent Composition, As Determined from Resonance Integration, of the Different Organotin Species Obtained in the Polymer Mixtures of the Target Species 6 and 7

$P-(CH_2)_nSnBu_2Ph$[a]	$P-(CH_2)_nSnBu_2R'$	$P-(CH_2)_nSnBu_2Ph$	$P-(CH_2)_nBu_2SnSnR'_3$
6, $n = 4$	−9.9 5.5%	−42.9 88%	−82.3 6.5%
7, $n = 6$	−12.0 6%	−43.1 89%	−84.2 5%

[a] Target polymers.

Table 4. Comparative Overview of the Ratio of SnΣ/Sn$_{total}$ (%), As Obtained from Elemental Analysis and Quantitative ^{117}Sn CP-MAS NMR[a]

target polymer	elemental anal.	^{117}Sn CP-MAS NMR
$P-(CH_2)_4Bu_2Sn-Cl$ (**1**)	90	82
$P-(CH_2)_4Bu_2Sn-Br$ (**2**)	19	21
$P-(CH_2)_4Bu_2Sn-I$ (**3**)	82	87
$P-(CH_2)_6Bu_2Sn-H$ (**4**)	54	58
$P-(CH_2)_4Bu_2Sn-H$ (**5**)	28	32

[a] SnΣ = number of moles of tin atoms bound to Σ (Cl, Br, I, H) per gram of polymer; Sn$_{total}$ = total number of moles of tin per gram of polymer.

characterization of totally insoluble, polymeric organotin materials, from the point of view of the nature of the organotin functionalities generated, as well as their relative yields. Especially the latter information is essential in the design of experimental variants or novel synthesis routes aiming at better selectivity toward the target organotin polymers.

Table 4 provides a summarizing, comparative overview of functionality compositions as obtained from ^{117}Sn CP-MAS NMR and elemental analysis.

While the merit in the identification of organotin functionalities is indisputable, Table 4 stresses both the scope and the limitation of the quantitative aspects of the ^{117}Sn CP-MAS NMR analysis method. Quantitative determinations are satisfactory to within 10% deviation approximately. Most important, in our view, is the global semiquantitative insight gained into the nature of side products obtained during these reactions involving insoluble organotin polymer−solution interfaces.

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