

Supported Catalysts

Stannylated Vinylic Addition Polynorbornene: Probing a Reagent for Friendly Tin-Mediated Radical Processes

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Abstract: Vinylic addition polynorbornenes (VA-PNB) with stannyl functional groups have been prepared and used in tin-mediated radical dehalogenation reactions. The aliphatic and robust scaffold of VA-PNB is well suited for a support in radical processes. VA-PNB-(CH₂)_nSnHBu₂ can be used as a stoichiometric reagent and VA-PNB-(CH₂)_nSnBu₂Cl as a catalyst in the presence of a hydride donor for the reduction of RBr. The mixture KF (aq.)/polymethylhydrosiloxane (PMHS) is the most convenient hydride source to generate VA-PNB-(CH₂)_nSnHBu₂ in situ. Al-

though quite popular in this context, boron hydrides, being a source of radicals themselves, are not adequate to correctly evaluate the performance of the anchored organotin group. VA-PNB-(CH₂)₄SnBu₂Cl can be recycled and, even if it loses activity upon reuse, it is still useful after ten cycles. The stannylated VA-PNB can be separated from the products by simple filtration, and it leads to very low tin contamination (at least 250 times lower than that with use of conventional separation methods).

Introduction

Tin reagents are extremely useful in radical organic processes and organotin hydrides have been profusely employed in synthetic procedures.^[1] The toxicity of organostannanes has raised a lot of concern about the handling of these derivatives and the contamination of the products obtained, especially if the synthetic protocols are applied to compounds with pharmaceutical applications.^[2] This fact encouraged the search for the so-called tin-free radical processes, which has provided various methods.^[3] However, the synthetic methods based on tin radical reactions can still be very useful in some applications, as long as the problems associated with this type of reagents are solved, namely, the separation of tin byproducts from the target compounds and the unwanted generation of tin waste after each reaction. Finding ways to overcome the drawbacks of the use of organotins has been a long-standing goal and several main approaches have been adopted. One of them is the use of smaller amounts of tin in each reaction, which does not solve the problem but certainly alleviates it. Thus, it has been shown that a stoichiometric amount of a tin hydride reagent, often SnHBu₃,^[4] can be substituted by a mixture of a catalytic amount of either a tin halide or a stannoxane in combination with a hydrogen donor (commonly a borane or a silane).^[5] Also, good separation methods of the tin residue from the product have been developed. They use different strategies that include the use of stannanes with modified substituents, chromatography

on fluoride-containing supports, and so on.^[6,7] Some of these methods are efficient and leave the products with a negligible residual tin content. Unfortunately, they do not address the problem of the generation of tin waste.

An approach that tackles both the separation and byproduct elimination is the support of the stannane on a matrix that could be easily separated and reused.^[6] A few examples of recyclable tin reagents in radical reactions have been reported which consist of stannyl groups anchored to silica or other inorganic supports,^[8] ionic liquids,^[9] and phosphonium salts.^[10] Polymers have also been used and, with the exception of a few examples of polyethylene^[11] and polyimide matrices,^[12] polystyrene is by far the most common polymeric support.^[13–15] Polystyrene resins are easily accessible, most of them commercially available, and they have been widely used in solid-phase synthetic procedures. However, this polymeric backbone has sensitive positions, such as benzylic groups, which can compromise the durability of the support when reused in radical processes. In fact, not all the reported examples of stannylated polystyrenes for these applications can be recycled; in some cases radical-induced β-C–Sn fragmentation has been observed.^[6c]

In contrast to polystyrene, vinylic addition polynorbornene (VA-PNB, Figure 1) has a completely aliphatic backbone, a priori more resistant to a radical attack. We have developed a family of VA-PNBs bearing pendant functional groups (VA-PNB-FG, Figure 1),^[16] and they have proved to be useful supports of organocatalysts or metal catalysts in several transformations.^[17] They can also be functionalized with stannyl groups, and used as recyclable polymeric tin reagents in the Stille reaction.^[18] Our experience with these stannylated reagents led us to study the utility of the robust VA-PNB as a polymeric matrix to support tin reagents in radical transformations. The results on their behavior and recyclability are reported here.

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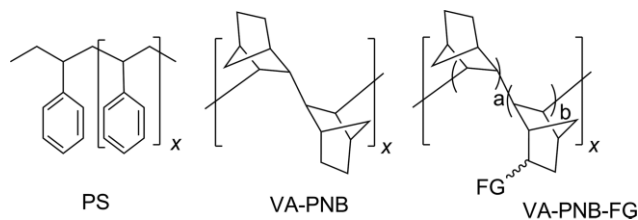
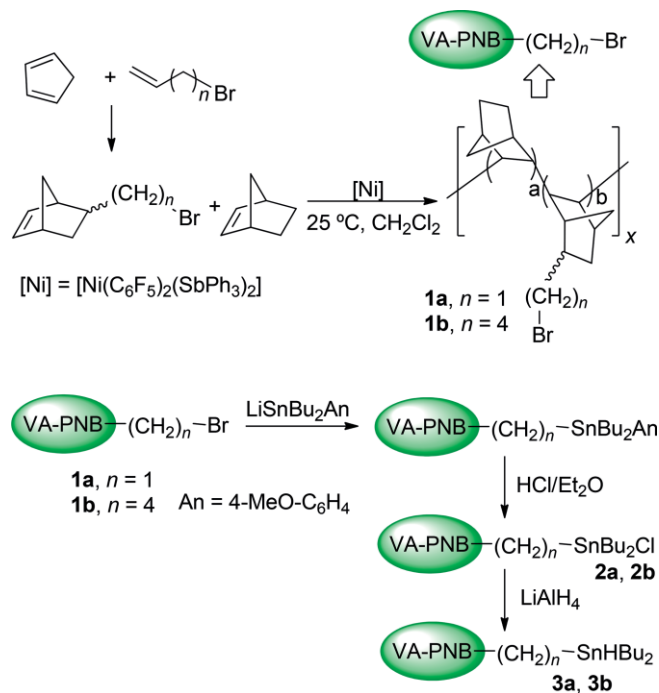


Figure 1. Polystyrene (PS) and vinylic addition polynorbornene (VA-PNB) backbones.

Results and Discussion

Synthesis and Stoichiometric Use of Stannylated Vinylic Addition Polynorbornenes (VA-PNBs)

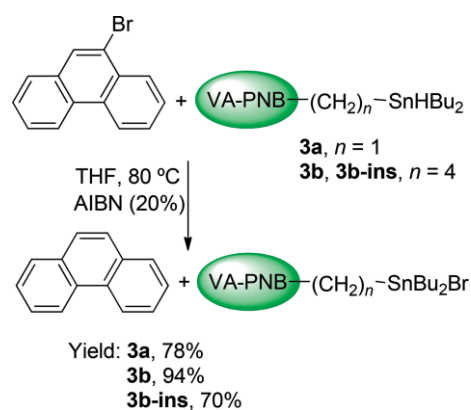
The polymers used in this work were synthesized by the route previously developed in our group and are depicted in Scheme 1. The copolymerization of norbornene and 2-(ω-bromoalkyl)norbornenes catalyzed by $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{SbPh}_3)_2]$ occurs by an insertion mechanism and leads to a material that keeps the bicyclic norbornene structure in the polymer backbone (**1a,b**, Scheme 1).^[16] Polynorbornenes of this type (vinylic addition polynorbornenes, VA-PNBs) are robust materials, both thermally and chemically resistant,^[19] and contain a pendant bromo substituent that can be exchanged for other groups by postpolymerization reactions. The nucleophilic substitution of stannide for bromide and subsequent modification of the tin substituents lead to the stannylated VA-PNBs with $-\text{SnBu}_2\text{Cl}$ groups **2a** and **2b** (Scheme 1).^[18c] Tin-mediated radical reactions rely on the generation of tin-centered radicals by cleavage of a Sn–H bond, and SnHBU_3 is the most common reagent in these transformations. Polymeric tin hydride derivatives can be synthesized from **2a,b**, as shown in Scheme 1, and **3a,b** are analogues to SnHBU_3 . All the stannylated polymers are partially



Scheme 1. Synthesis of polymers 1–3.

soluble or undergo swelling in solvents such as THF, CHCl_3 , or CH_2Cl_2 , but they are insoluble in MeOH, acetonitrile, Et_2O , or hexane. Thus, there is a wide-enough range of solvents that can be chosen to precipitate the polymers and separate them from the target products. However, the lower the solubility of the polymers, the more efficient is the separation and the lower is the expected tin contamination. For this reason, polymer **2b** was subjected to an insolubilization process we have used before on similar polymers which were developed as reagents in the Stille reaction; this proved to be an advantage to reach a low tin contamination.^[18c] The insolubilization is achieved by prolonged heating of VA-PNB in DMF, and this procedure gave polymer **2b-ins**.^[20,21] The synthesis of the insoluble tin hydride polymer, **3b-ins**, was carried out from **2b-ins** as shown in Scheme 1. The presence of the Sn–H moiety is clearly observed in the IR spectra of all polymers **3** [$\nu(\text{Sn–H})$ at about 1800 cm^{-1}] as well as in the ^{119}Sn NMR spectra where the characteristic signal of the $\text{R}_3\text{Sn–H}$ moiety is present between -85 and -90 ppm and no $\text{R}_3\text{Sn–Cl}$ fragment remains ($\delta = 145$ ppm).^[22]

We tested polymers **3** in a model reaction, the dehalogenation of 9-bromophenanthrene, using an excess of the Sn–H moiety in the polymer (1.4 equiv.). As can be seen in Scheme 2, good to moderate yields were obtained, and polymer **3b**, with a longer tether linking the tin fragment to the polymer, is more reactive than **3a**. This is an indication that the tin centers are less encumbered by the polymer backbone when $n = 4$ and, as a result, they are more reactive. We also observed this effect when polymers VA-PNB- $(\text{CH}_2)_n\text{SnBu}_2\text{Ar}$ ($\text{Ar} = \text{Ph}$, 4-MeO- C_6H_4) were used as reagents in the Stille reaction; again those polymers with a higher value of n showed a better performance.^[18c] The insolubilization of the polymer makes it less reactive (cf. **3b** and **3b-ins**), but the expected benefit as far as reaching a low amount of residual tin in the products, makes it a good candidate for further study.



Scheme 2. Use of polymers **3** in the dehalogenation of 9-bromophenanthrene.

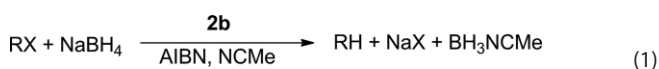
Polymers **3** can be stored at low temperature but they decompose at room temperature in short periods of time, as can be seen by the disappearance of the $\nu(\text{Sn–H})$ IR absorbance. Thus, although they can be synthesized and used in this form if needed, it would be more convenient to generate the Sn–H in situ in the reaction medium from the parent polymer **2** that

can be kept with no special precautions. The experiments that follow were carried out with polymers **2b** ($n = 4$) bearing a longer alkyl chain tether that, as mentioned above, shows a higher reactivity.

In Situ Generation of the Tin Hydride Moiety: The Catalytic Approach

The earliest work on polystyrene supports reports the use of stoichiometric amounts of polymeric tin hydrides,^[15] but soon it was surpassed by the catalytic version of the polymer-supported radical tin chemistry. This relies on the presence of a hydride donor in the reaction mixture capable of regenerating the Sn–H moiety in situ after each cycle. Supported tin chlorides have been used in conjunction with H donors, mainly boron hydrides, and a radical initiator (AIBN, irradiation, etc.).^[12–14] Other hydrogen donors have rarely been used in this context.^[23] It should be taken into account that the evaluation of the activity and recyclability of the tin catalyst in the presence of boron hydrides should be carefully made, as borohydrides in the presence of an initiator can generate boron radical species that have proved to be effective in many transformations.^[24] Pioneer work by the groups of Barltrop,^[24a] Groves,^[24b,24c] and Beckwith^[24d] has been followed by others and, more recently, the group of Ryu has made important contributions to the use of boron-centered radicals.^[24f] In fact, using the dehalogenation of 9-bromophenanthrene or 1-bromodecane as model reactions and NaBH₄ as hydrogen donor [Equation (1)], we found that, although the presence of a catalytic amount of polymer **2b** accelerated the reaction (entries 1 and 2, Table 1), with an excess of NaBH₄ the dehalogenation

went to completion or almost completion in the absence of the tin derivative (cf. entries 3, 4 and 6, 7, Table 1). The reaction does not occur in the absence of a radical initiator (entry 5, Table 1) which points to the crucial role of boron radicals in the reaction. Most reports on the use of catalytic amounts of polymer-supported tin reagents in radical reactions use NaBH₄ as hydrogen donor.^[13,14] Our results show that, at least in dehalogenation reactions, it is not possible to separate the roles of the tin hydride and the tetrahydroborate. As a consequence, it is not possible to find out unequivocally which the activity of the polymeric reagent is or whether the activity is kept upon reuse.



We moved to other hydrogen donor systems and tested polymethylhydrosiloxane (PMHS). This reducing agent has been used to generate Sn–H moieties, and the groups of Fu and Maleczka found out suitable conditions for an efficient hydride transfer to tin that needs the presence of a specific Sn–X precursor. Fu developed the in situ generation of a stannoxane moiety, which then reacts with PMHS.^[5g,25] Maleczka et al. used the so-called “Sn–F approach” that consists of the use of a fluoride source in solution, which binds to silicon in PMHS and activates it towards hydride transfer to a preformed tin fluoride derivative.^[5h,26] In our hands, this second approach proved to be useful, and Table 2 shows the optimization experiments we carried out for the dehalogenation of 9-bromophenanthrene using polymers **2b** and **2b-ins** as catalysts, an aqueous KF solution as the fluoride source, and PMHS as hydride donor (Scheme 3).

Table 1. Dehalogenation reactions using NaBH₄ as hydrogen donor.^[a]

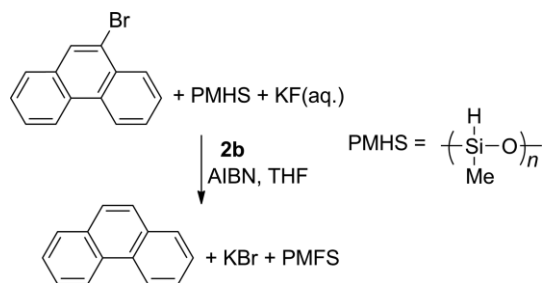
Entry	RBr	NaBH ₄ /RBr ^[b]	2b [mol-%] ^[c]	AIBN [mol-%]	Time [h]	Crude yield [%] ^[d]
1 ^[e]	BrPhen	2	20	20	10	>99
2 ^[e]	BrPhen	2	0	20	10	68
3 ^[f]	BrPhen	4	20	20	5	>99
4 ^[f]	BrPhen	4	0	20	5	92
5 ^[f]	BrPhen	4	0	0	5	2
6 ^[f]	C ₁₀ H ₂₁ Br	4	20	20	0.5	>99
7 ^[f]	C ₁₀ H ₂₁ Br	4	0	20	1	>99

[a] BrPhen: 9-bromophenanthrene. All reactions were carried out under a nitrogen atmosphere in MeCN at 80 °C. [b] Molar ratio. [c] **2b** has a functionalization of 1.29 mmol Sn–Cl/g polymer. [d] Crude yield determined by ¹H NMR spectroscopic analysis of the reaction mixture. [e] [RX] = 0.0257 M. [f] [RX] = 0.0214 M.

Table 2. Dehalogenation of 9-BrPhen (RBr) using PMHS as hydrogen donor.^[a]

Entry	Si–H/RBr ^[b]	KF/RBr ^[b]	Polym. [mol-%] ^[c]	Time [h]	Crude yield [%] ^[d]
1	1.2	2.5	2b (20)	2	37
2	2	4	2b (20)	2	96
3	2	3	2b (20)	20	82
4 ^[e]	2	4	2b (10)	2	37
5 ^[f]	2	4	2b (20)	2	19
6 ^[g]	2	4	–	2	0
7	2	4	2b-ins (20)	2	60
8	2	4	2b-ins (20)	4	83
9	3	6	2b-ins (20)	4	>99

[a] PMHS = polymethylhydrosiloxane. All reactions were carried out under a nitrogen atmosphere, with THF (1.3 mL) and water (0.1 mL) as the solvents, 80 °C, AIBN (20 mol-%) unless otherwise noted. [b] Molar ratio. [c] The tin polymers have a functionalization of: **2b**, 1.83 mmol Sn–Cl/g polymer; **2b-ins**, 1.43 mmol Sn–Cl/g polymer. [d] Crude yield determined by ¹H NMR spectroscopic analysis of the reaction mixture. [e] 10 % of AIBN used. [f] Reaction temperature 60 °C. [g] An additional blank reaction using a ratio 9-BrPhen/PMHS/KF of 1:140:5 for 20 h was also carried out, and 9-BrPhen remained unreacted.



Scheme 3. Dehalogenation of 9-bromophenanthrene using **2b** as the catalyst and KF/PMHS as hydride-donor system.

As can be seen in Table 2 (entry 6) the mixture PMHS/KF/AIBN is inactive in the dehalogenation reaction; so this system is adequate to evaluate the performance of the polymeric tin reagents. The best reaction conditions when using the more soluble polymer **2b** as the catalyst (20 mol-%) are a twofold molar amount of PMHS and a fourfold molar amount of KF (aq.) at 80 °C. The insoluble polymer **2b-ins** is less reactive, and a larger excess of both PMHS and KF (aq.) is necessary to reach the same conversion (cf. entries 2 and 9, Table 2). THF proved to be the best solvent. Under the conditions of entry 9 (Table 2) other solvents such as dioxane (24 % yield) or toluene (50 % yield) gave worse results. Acetonitrile is not a suitable solvent since PHMS is not soluble in it.

We also tested other hydride donors. Low molecular weight silane derivatives are less efficient than PMHS: both SiH(OEt)₃ and 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (OMTS) gave lower yields (30 and 60 % yield, respectively, under the conditions of entry 9, Table 2). This is not really a problem since PMHS, being an abundant byproduct in the manufacture of silicones, is inexpensive and readily available. We tested the possibility of using sodium formate but, even if the tin formate formation is fast at room temperature, the decarboxylation step does not occur in the reaction conditions we use.

Using the optimized conditions for polymer **2b-ins** we tested the dehalogenation reaction of other substrates (Table 3). The system is inactive for chlorides (entries 2 and 6, Table 3) but dehalogenates alkyl and aryl bromides. In some cases, longer reaction times (8 h) are needed to obtain good yields. As expected, the reaction is more efficient for aryl bromides with electron-withdrawing groups (entries 7–9),^[27] and, interestingly, the system dehalogenates ketones and esters without significant reduction of the carbonyl group (entries 4 and 5, Table 3).

The system was also tested in the dehalogenative cyclization of 1-bromo-2-(prop-2-en-1-yloxy)-naphthalene (**4**, Scheme 4). The radical cyclization of **4** leads to a mixture of 5-exo and 6-endo products, a reaction that was studied in detail by Beckwith et al.^[28] They found that the 6-endo product arises mainly from a neophyl rearrangement of the methylcyclopentenyl radical formed by the favored 5-exo cyclization. The 5-exo/6-endo ratio is a result of the competing (i) trap of the 5-exo cyclopentenyl radical by the Sn–H moiety through hydrogen abstraction and (ii) rearrangement to the 6-endo product. We rationalized that this reaction could give us information about the relative availability of the Sn–H moiety anchored to the polymer in

Table 3. Dehalogenation reactions with **2b-ins** as the catalyst.^[a]

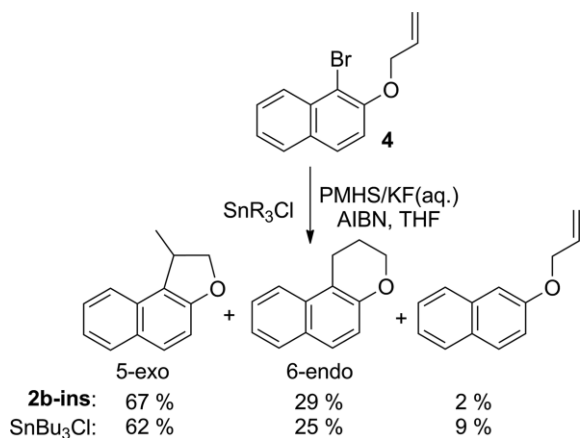
Entry	RX	RH	Yield [%], 4 h (yield [%], 8 h) ^[b]
1	C ₁₀ H ₂₁ Br	C ₁₀ H ₂₂	79
2	C ₁₀ H ₂₁ Cl	C ₁₀ H ₂₂	0
3			> 99
4			> 99
5			> 99 ^[c]
6			7
7			58 (78)
8			46 (65)
9			79 (> 99) ^[d]
10			69 (> 99)
11			> 99

[a] All reactions carried out under a nitrogen atmosphere, with THF (1.3 mL) and water (0.1 mL) as the solvents, 80 °C, 4 h, Sn–Cl (0.2 equiv., polymer **2b-ins**), PMHS (3 equiv.), KF (6 equiv.). Compound **2b-ins** has a functionalization of 1.43 mmol Sn–Cl/g polymer. [b] Determined by ¹H NMR spectroscopic analysis of the crude mixture. [c] A trace amount of 1-phenylethanol was detected by GC–MS. [d] Determined by ¹⁹F NMR in the crude mixture.

comparison to SnHBu₃: the less available the Sn–H moiety the higher the amount of rearranged (6-endo) product.

Scheme 4 depicts the reaction of **4** in the presence of the mixture SnR₃Cl/PMHS/KF (aq.) where SnR₃Cl is either SnBu₃Cl or polymer **2b-ins**. A conversion of 96 % (SnBu₃Cl) or 98 % (**2b-ins**) was achieved within 4 h, and a mixture of the 5-exo and 6-endo cyclization products along with some dehalogenation product was formed (ratios of products are given in Scheme 4).

The results show that the reactivity of both tin sources is comparable, with little amount of the noncyclized dehalogenated product (even less with **2b-ins**) and a similar 5-exo/6-endo ratio. As far as reactivity is concerned, the stannyl



Scheme 4. Dehalogenative cyclization of **4** using a tin catalyst and KF/PMHS as hydride donor system.

groups in **2b-ins** are not encumbered by the polymer backbone structure.

Recyclability of the Stannylated VA-PNBs

Polymer **2b-ins** was used several times in subsequent dehalogenation reactions of 9-bromophenanthrene under the conditions shown in Scheme 3 and Table 2 (entry 9). After the allotted reaction time, the polymer was recovered by filtration, washed, and used again in a new reaction without any additional treatment. The results collected in Table 4 show that the polymer can be recycled and it stays active for five reuses; however, a strong fluctuation in the yields is observed in different cycles. A second recycling experiment was carried out by changing the conditions in order to favor a steady initiation and radical concentration. Thus, the amount of **2b-ins** was increased from 20 mol-% (Table 4) to 50 mol-% (Table 5) and a second addition of AIBN was made after two hours. The use of an excess of the tin derivative, a serious drawback when SnBu₃X derivatives are used, is not a problem for this polymeric reagent since the separation from the product is easy and no tin waste is produced. As can be seen in Table 5, the yields still show a large variation from cycle to cycle up to about the seventh reuse. In addition to the yield fluctuation, the activity of the tin polymer decreases; however, from the eighth cycle on the yields stay close to 50 %. After ten consecutive uses, the stannylated polymer **2b-ins** is still useful. Considering the amount of catalyst used (50 mol-%) and the crude yield obtained (around 50 %) the polymer is playing the role of a stoichiometric tin reagent. As mentioned above, this is not a problem for these stannylated polymers since, even when using a large

Table 4. Recyclability of polymer **2b-ins** as catalyst in the reaction shown in Scheme 3.^[a]

Cycle	1	2	3	4	5
Crude yield [%] ^[b]	100	82	100	57	92

[a] All reactions were carried by using the conditions of entry 9, Table 2: **2b-ins** (20 mol-% Sn-Cl). Compound **2b-ins** has a functionalization of 1.33 mmol Sn-Cl/g polymer. [b] Determined by ¹H NMR spectroscopic analysis of the crude mixture.

amount of tin, the separation from the products is easy and **2b-ins**, however limited its activity, is not discarded.

Table 5. Reuse of polymer **2b-ins** as catalyst in the reaction shown in Scheme 3.^[a]

Cycle	Crude yield [%] ^[b]	Isolated yield [%]	Residual Sn [wt.-%]
1	100	96	0.0155
2	84	72	0.0113
3	100	63	–
4	62	49	–
5	100	67	0.008
6	61	41	–
7	79	43	–
8	53	34	–
9	63	44	–
10	52	39	0.0455

[a] All reactions were carried out by using the conditions of entry 9, Table 2 except that a higher amount of **2b-ins** was used (50 mol-% Sn-Cl) and a second addition of AIBN was made after the first 2 h. Compound **2b-ins** has a functionalization of 1.33 mmol Sn-Cl/g polymer. [b] Determined by ¹H NMR spectroscopic analysis of the crude mixture.

Analysis of the residual tin content in the dehalogenated product was carried out by ICP-MS, in different cycles of the reuse experiment. The tin content of the product is very small and varies from 80 to 155 ppm (entries 1, 2, 5, Table 5). A larger amount of residual tin was observed after ten uses ($\delta = 455$ ppm), but it is low when compared to the contamination resulting from conventional separation methods of monomeric tin derivatives: phenanthrene obtained by dehalogenation of 9-bromophenanthrene with SnBu₃Cl (50 mol-%) instead of **2b-ins** and subjected to a similar workup procedure contained 10 wt.-% of tin ($\delta = 10^5$ ppm).

The loss of tin in each cycle is obviously too small to account for the decrease in activity of the polymer. In order to find out the reason for the deactivation observed, we looked into the spectroscopic features of polymer **2b-ins** recovered after the 10th cycle (Table 5). The IR spectrum shows strong absorption, characteristic of the polysiloxane derivatives coming from the residual fluorinated or oxygenated polymers derived from PMHS [$\nu(\text{Si-O-Si})$ 1100–1000 cm⁻¹, $\nu(\text{Si-C})$ 740 cm⁻¹, see Supporting Information].^[29] These polysiloxane derivatives are very difficult to eliminate since they do not dissolve in organic solvents or aqueous acidic or basic media. We could not quantify the amount of residual polysiloxanes present. The Si-O and Si-C absorbances in IR are intrinsically strong, so there is no direct correlation between the intensity of those bands and the residual silicon species in the polymer. Compound **2b-ins** is recovered almost quantitatively after each use in Table 5 (90–100 % of the initial weight), and no significant increase in weight is observed. Even if the polysiloxane byproducts are not expected to induce any competing reaction, their presence could influence the accessibility of the tin centers.

The nature of the tin centers in this recovered polymer can be analyzed by solid-state ¹¹⁹Sn NMR spectroscopy. The ¹¹⁹Sn resonance for the VA-PNB-SnBu₂Cl centers in **2b-ins** before use ($\delta = 147.7$ ppm) disappears in the reacted polymer. Two new resonances at $\delta = 82$ and -11 ppm are present, and these chemical shifts are characteristic of R₃Sn-OR and R₃Sn-F moieties, respectively (cf. SnBu₃-O-SnBu₃ at $\delta = 85$ ppm and SnBu₃F

at -9 ppm, see Supporting Information).^[30,31] This is not unexpected since the reactions are carried out in the presence of an aqueous KF solution and, under these conditions, the Sn–Br bonds in the VA-PNB-SnBu₂Br polymer formed in the first dehalogenation turnover can be easily transformed into the stronger Sn–F and Sn–O bonds. These moieties can contribute to crosslink the polymer since both the tin oxide and fluoride derivatives have a strong tendency to oligomerize through the formation of F or O bridges, increasing the tin coordination number.

The absence of Sn–X (X = Cl, Br) bonds is not the main reason of the deactivation of the polymer. VA-PNB-SnBu₂Cl can be regenerated by treatment of the polymer recovered after cycle 10 (Table 5) with concentrated hydrochloric acid, as has been described before for monomeric tin derivatives.^[32] The ¹¹⁹Sn NMR spectrum of the polymer obtained shows that most of the tin centers in the polymer bear Sn–Cl bonds ($\delta = 146$ ppm) and a signal corresponding to the Sn–F moiety (-10 ppm) still remains. This polymer was used in the dehalogenation reaction of 9-bromophenanthrene under the same conditions used in Table 5 leading to a 53 % crude yield, almost equal to the one obtained in the preceding 10th cycle. Thus, the presence of the Sn–Cl moieties does not reactivate the polymer. This experiment indicates that Sn–Cl bonds are probably not necessary for the reaction to occur, Sn–F and Sn–O bonds being transformed into Sn–H bonds in the same way as reported for the monomeric tin derivatives.^[25,26]

The decrease in the activity observed is likely derived from the structural changes imposed on the polymer by the possible crosslinking because of the Sn–F and Sn–O moieties as well as the contamination with residual polymeric siloxane byproducts in the reaction. Altogether, they may affect the accessibility of the tin centers to react with the hydride source and RBr reactants.

Conclusions

Vinyl addition polynorbornenes are suitable supports for tin hydrides, and they can be used in tin-mediated radical reactions, as has been shown for a model dehalogenation reaction. VA-PNB-SnBu₂X can be used both in stoichiometric reactions (X = H) and catalytic processes (X = Cl) in the presence of a suitable hydride donor. The behavior of the polymers does not substantially differ from the monomeric SnBu₃X derivatives.

Being insoluble, they can be easily separated from the final products, and the amount of residual tin is at least 250 times lower than that obtained when SnBu₃X is used. Also, the stannylated polynorbornenes can be reused a minimum of 10 times in a radical process catalytic in tin. The polymer is not fully recyclable since it loses efficiency upon reuse up to an activity value that stays almost constant from the seventh use on. The evaluation of the recyclability of the polymers has been made by using a hydride donor that does not mask the actual performance of the stannyl matrix, that is the KF (aq.)/PMHS combination, developed by Malezcka et al. Although very much used in combination with supported tin derivatives, borohydrides are not convenient for this purpose since they are a

source of radicals on their own that may conceal the loss of reactivity of the anchored stannyl reagent.

Experimental Section

Materials and General Considerations

NMR spectra in solution were recorded at 293 K with Bruker AV-400 and Agilent MR-500 and MR-400 instruments. Chemical shifts (δ) are reported in ppm and referenced to SiMe₄ (¹H and ¹³C), CFCl₃ (¹⁹F), and SnMe₄ (¹¹⁹Sn). The solid-state NMR spectra were recorded at 293 K under magic angle spinning (MAS) with a Bruker AV-400 spectrometer by using a Bruker BL-4 probe with zirconia rotors (4 mm diameter) spinning at 8 kHz. ¹³C CP-MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with a 90° pulse length of 4.5 μ s and a contact time of 3 ms and recycle delay of 3 s. ¹¹⁹Sn MAS NMR spectra were measured at 149.21 MHz by using pulses of 4 ms corresponding to a flip angle of $\pi/3$ radians and recycle delay of 60 s. The ¹³C and ¹¹⁹Sn NMR spectra were referred to glycine (CO signal at $\delta = 176.1$ ppm) and SnMe₄ ($\delta = 0$ ppm), respectively. IR spectra were recorded on solid neat samples with a Perkin-Elmer FTIR spectrum frontier spectrophotometer with Csl + ATR diamond accessory. Polymer functionalization was determined by quantitative analyses of the halogen content (Br in **1** or Cl in **2**). It was determined by oxygen-flask combustion of a polymer sample and analysis of the residue by the mercurimetric titration of the halide.^[33] Residual tin in the dehalogenation products was determined by ICP-MS with use of Agilent 7500i equipment. Solvents were dried with a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen prior to use. The reactants employed in the dehalogenation reactions, SnBu₃Cl, SnHBU₃, PMHS, and OMTS, were purchased from commercial sources and used as received. Compound **4** was prepared by modification of the synthesis reported in the literature (see Supporting Information).^[34]

Synthesis of Polymers: Polymers VA-PNB-NBCH₂Br (**1a**) and VA-PNB-NB(CH₂)₄Br (**1b**) were synthesized as described before by copolymerization of norbornene and the corresponding 2-(ω -bromoalkyl)norbornene.^[16] The polymers have a functionalization in the range 1.7–2.8 mmol Br/g polymer. VA-PNB-NBCH₂SnBu₂Cl (**2a**) and VA-PNB-NB(CH₂)₄SnBu₂Cl (**2b**) were prepared from **1a** or **1b** as described elsewhere.^[18c] Polymer **2b** was subjected to the insolubilization procedure that involves heating in DMF at 120 °C for 24 h, as reported before.^[18c]

Compound 2b: ¹H NMR (CDCl₃, 499.72 MHz): $\delta = 2.5$ – 0.5 (br., PNB backbone), 1.64 (br., CH₂, Bu), 1.35 (br., CH₂, Bu), 1.29 (br., CH₂, Bu), 0.92 (br., CH₃, Bu) ppm. ¹¹⁹Sn{¹H} NMR (CDCl₃, 186.38 MHz): $\delta = 156.2$ (br.) ppm. IR (neat): $\tilde{\nu} = 2900, 2860, 1450, 325$ (v, Sn–Cl) cm⁻¹.

Compound 2b-ins: ¹³C CP-MAS NMR (100.61 MHz): $\delta = 70$ – 36 (br.), 35 (br.), 24.7 (br.), 21 (br.) ppm. ¹¹⁹Sn MAS NMR (149.21 MHz): $\delta = 147.7$ ppm. IR (neat): $\tilde{\nu} = 2900, 2860, 1450, 325$ (v, Sn–Cl) cm⁻¹.

Synthesis of VA-PNB-NB(CH₂)₄SnHBU₂ (3b**):** Polymer **2b** (0.11 g, 0.2 mmol of SnCl), LiAlH₄ (0.015 g, 0.4 mmol), and Et₂O (40 mL) were mixed under a nitrogen atmosphere. The reaction mixture was heated to reflux for 24 h. A small amount of hydroquinone (0.08 g) was added, followed by the addition of an aqueous solution of potassium and sodium tartrate (40 mL, 20 % w/w); a greyish suspension was formed. MeOH (20 mL) and then water (20 mL) were poured into the suspension. The polymer was filtered, washed with a mixture of MeOH/aqueous tartrate solution (3 \times 15 mL), MeOH/

H₂O (1:1 v/v, 40 mL), MeOH (3 × 15 mL) and air-dried. A brownish solid was obtained. Yield: 98 % (0.1 g). ¹³C CP-MAS NMR (100.61 MHz): δ = 65–39 (br., PNB backbone), 37.9 (br.), 35 (br.), 21.7 (br.), 15.9 (br.) ppm. ¹¹⁹Sn CP-MAS NMR (149.21 MHz): δ = –84.8 (br.) ppm. IR (neat): $\tilde{\nu}$ = 1804 [s, ν(Sn–H)] cm^{–1}. The polymer contains 3.16 mg (0.089 mmol) of Cl/g of polymer, which indicates 95 % of chloride substitution. Polymers VA-PNB-NBCH₂SnHBu₂ (**3a**) and VA-PNB-NB(CH₂)₄SnHBu₂ (**3b-ins**) were prepared from **2a** and **2b-ins** by following the same procedure.

Compound 3a: Yield: 82 %. ¹H NMR (CDCl₃, 400.14 MHz): δ = 4.7 (br., Sn–H), 2.4–0.3 (br., PNB backbone), 1.5 (br., CH₂, Bu), 1.3 (br., CH₂, Bu), 0.9 (br., CH₃, Bu) ppm. ¹³C CP-MAS NMR (100.61 MHz): δ = 70–40 (br., PNB backbone), 38 (br.), 35 (br.), 21.6 (br.), 16.4 (br.) ppm. ¹¹⁹Sn CP-MAS NMR (149.21 MHz): δ = –90.5 (br.) ppm. IR (neat): $\tilde{\nu}$ = 1803 [s, ν(Sn–H)] cm^{–1}. The polymer contains 2.43 mg (0.069 mmol) of Cl/g of polymer, which indicates 96 % of chloride substitution.

Compound 3b-ins: Yield: 97 %. ¹³C CP-MAS NMR (100.61 MHz): δ = 65–35 (br., PNB backbone), 37.9 (br.), 35.1 (br.), 21.7 (br.), 16.1 (br.) ppm. ¹¹⁹Sn CP-MAS NMR (149.21 MHz): δ = –85 (br.) ppm. IR (neat): $\tilde{\nu}$ = 1803 [s, ν(Sn–H)] cm^{–1}. The polymer contains 3 mg (0.085 mmol) of Cl/g of polymer, which indicates 96 % of chloride substitution.

Dehalogenation Reactions

General Dehalogenation Procedure Using VA-PNB-NB(CH₂)₄SnBu₂Cl: In a Schlenk flask with a screw cap, the corresponding RX (0.027 mmol), polymer **2b-ins** (3.84 mg, 5.48 × 10^{–3} mmol of Sn–Cl), AIBN (0.9 mg, 5.48 × 10^{–3} mmol), PMHS (5 mg, 0.084 mmol Si–H), and KF (9.51 mg, 0.162 mmol) were mixed in THF (1.3 mL) and water (0.1 mL) under a nitrogen atmosphere and stirred at 80 °C for 4 h. After this time, the crude reaction mixture was analyzed by ¹H NMR spectroscopy. MeOH (10 mL) was added, and the polymer was filtered and washed with MeOH (3 × 5 mL), Et₂O (3 × 5 mL) and air-dried. The polymer was quantitatively recovered. All the dehalogenated products in Table 3 are commercial and were identified by comparison to the NMR spectroscopic data of authentic samples.

Dehalogenation Procedure Using VA-PNB-NB(CH₂)₄SnHBu₂: In a Schlenk flask with a screw cap, 9-bromophenanthrene (7.19 mg, 0.027 mmol), polymer **3b** (20.25 mg, 0.040 mmol of Sn–H), and AIBN (0.9 mg, 5.48 × 10^{–3} mmol) were mixed in THF (1.4 mL) under a nitrogen atmosphere and stirred at 80 °C for 4 h. The crude reaction mixture was analyzed by ¹H NMR spectroscopy. MeOH (10 mL) was added, and the polymer was filtered and washed with MeOH (3 × 10 mL), Et₂O (3 × 10 mL) and air-dried. It was quantitatively recovered.

Recycling Procedure: In a Schlenk flask with a screw cap, 9-bromophenanthrene (0.2 g, 0.76 mmol), polymer **2b-ins** (0.29 g, 0.38 mmol of Sn), PMHS (0.14 g, 2.29 mmol), and KF (0.0581 g, 4.57 mmol) were mixed in THF (36 mL) and water (2.8 mL) under a nitrogen atmosphere and stirred at room temperature for 15 min.^[35] A solution of AIBN (0.025 g, 0.15 mmol) in THF (2 mL) was added, and the mixture was stirred at 80 °C for 2 h. A new solution of AIBN (0.025 g, 0.15 mmol) in THF (2 mL) was added, and the mixture was stirred at 80 °C for 2 h. The resulting reaction mixture was concentrated at reduced pressure to ca. 15 mL, and MeOH (30 mL) was added. The polymer was filtered, washed with MeOH (3 × 30 mL), Et₂O (3 × 30 mL), and air-dried. It was almost quantitatively recovered (90–100 % yield) and stored to be reused in a subsequent reaction. The MeOH solution was evaporated, and the residue was extracted with Et₂O. The ethereal solution was evaporated to dryness and was subjected to preparative TLC (silica) with use of hexane as the eluent. A yellowish solid was obtained.

Yield: 96 % (130.9 mg). The experiments summarized in Table 5 were carried out in the same way.

Cyclization Reaction: In a Schlenk flask with a screw cap, 1-bromo-2-(prop-2-en-1-yloxy)naphthalene (**4**, 7.21 mg, 0.027 mmol), polymer **2b-ins** (3.84 mg, 5.48 × 10^{–3} mmol of Sn–Cl), AIBN (0.9 mg, 5.48 × 10^{–3} mmol), PMHS (5 mg, 0.084 mmol Si–H), and KF (9.51 mg, 0.162 mmol) were mixed in THF (1.3 mL) and water (0.1 mL) under a nitrogen atmosphere and stirred at 80 °C for 4 h. The crude reaction mixture was analyzed by ¹H NMR spectroscopy. MeOH (10 mL) was added, and the polymer was filtered and washed with MeOH (3 × 5 mL), Et₂O (3 × 5 mL) and air-dried. The polymer was recovered quantitatively. The MeOH solution was evaporated, and the residue was extracted with Et₂O. The ethereal solution was evaporated to dryness. The residue was subjected to preparative TLC (silica) with use of hexane as the eluent to separate the residual silicon polymeric byproducts from the mixture of reaction products: 5.4 mg (mixture of isomers). The dehalogenated products were identified by comparison to the NMR spectroscopic data reported in the literature.^[28]

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Keywords: Radical reactions · Tin · Supported catalysts · Polynorbornene · Dehalogenation

- [1] a) W. P. Neumann, *Synthesis* **1987**, 665–683; b) M. Pereyre, J. P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, **1987**; c) A. G. Davies, M. Gielen, K. H. Pannell, R. T. Tiekink (Eds.), *Tin Chemistry: Fundamentals, Frontiers and Applications*, Wiley, Chichester, **2008**.
- [2] The toxicity of organotin compounds SnR₃X strongly depends on the nature of the R group and, for alkyl derivatives, it decreases upon increasing the length of the alkyl chain, R = Me being the most toxic; a) Y. Arakawa, O. Wada, T. H. Yu, *Toxicol. Appl. Pharmacol.* **1981**, *60*, 1–7; b) B. Buck, A. Mascioni, L. Que Jr., G. Veglia, *J. Am. Chem. Soc.* **2003**, *125*, 13316–13317 and references cited therein; c) K. E. Apple, *Drug Metab. Rev.* **2004**, *36*, 763–786.
- [3] a) P. A. Baguley, J. C. Walton, *Angew. Chem. Int. Ed.* **1998**, *37*, 3072–3082; *Angew. Chem.* **1998**, *110*, 3272; b) A. Studer, S. Amrein, *Synthesis* **2002**, 835–849.
- [4] SnHBu₃ is actually the correct IUPAC name (see IUPAC Red Book) even though organic chemists are more used to Bu₃SnH.
- [5] Borane derivatives: a) E. J. Corey, W. Suggs, *J. Org. Chem.* **1975**, *40*, 2554–2555; b) G. Stork, P. M. Sher, *J. Am. Chem. Soc.* **1986**, *108*, 303–304; c) D. E. Bergbreiter, J. R. Blanton, *J. Org. Chem.* **1987**, *52*, 472–473. Silanes: d) J. Lipowitz, S. A. Bowman, *J. Org. Chem.* **1973**, *38*, 162–165; e) D. S. Hays, G. C. Fu, *J. Org. Chem.* **1996**, *61*, 4–5. PMHS: f) K. Hayashi, J. Iyoda, I. Shihara, *J. Organomet. Chem.* **1967**, *10*, 81–91; g) R. M. Lopez, D. S. Hays, G. C. Fu, *J. Am. Chem. Soc.* **1997**, *119*, 6949–6950; h) I. Terstiege, R. E. Maleczka Jr., *J. Org. Chem.* **1999**, *64*, 342–343.
- [6] A discussion of these methods as well as the use of polymeric and other tin supports can be found in several reviews: a) D. Young in *Tin Chemistry – Fundamentals, Frontiers and Applications* (Eds.: A. G. Davies, M. Gielen, K. H. Pannell, R. T. Tiekink), Wiley, Chichester, **2008**, ch. 5, pp. 653–665; b) N. Carrera, A. C. Albéniz, *Eur. J. Inorg. Chem.* **2011**, 2347–2360; c) E. Le Grogneq, J.-M. Chrétien, F. Zammattio, J.-P. Quintard, *Chem. Rev.* **2015**, *115*, 10207–10260.
- [7] D. L. J. Clive, J. Wang, *J. Org. Chem.* **2002**, *67*, 1192–1198.

- [8] Q. J. Fu, A. M. Steele, S. C. Tsang, *Green Chem.* **2001**, *3*, 71–73.
- [9] P. D. Pham, S. Legoupy, *Tetrahedron Lett.* **2009**, *50*, 3780–3782.
- [10] J. P. Poupon, D. Marcoux, J. M. Cloarec, A. B. Charette, *Org. Lett.* **2007**, *9*, 3591–3594.
- [11] D. E. Bergbreiter, S. A. Walker, *J. Org. Chem.* **1989**, *54*, 5138–5141.
- [12] A. Chemin, H. Deleuze, B. Maillard, *J. Chem. Soc. Perkin Trans. 1* **1999**, 137–142.
- [13] a) Y. Ueno, K. Chino, M. Watanabe, O. Moriya, M. Okawara, *J. Am. Chem. Soc.* **1982**, *104*, 5564–5566; b) G. Dumartin, M. Pourcel, B. Delmond, O. Donard, M. Pereyre, *Tetrahedron Lett.* **1998**, *39*, 4663–4666; c) A. Chemin, H. Deleuze, B. Maillard, *Eur. Polym. J.* **1998**, *34*, 1395–1404; d) A. Mercier, H. Deleuze, B. Maillard, O. Mondain-Monval, *Adv. Synth. Catal.* **2002**, *344*, 33–36.
- [14] Other reports of radical reactions using tin derivatives supported on polystyrene where no reuse of the polymer is reported: a) J. R. Blanton, J. M. Salley, *J. Org. Chem.* **1991**, *56*, 490–491; b) E. J. Enholm, J. P. Schulte II, *Org. Lett.* **1999**, *1*, 1275–1277.
- [15] a) N. M. Weinschenker, G. A. Crosby, J. Y. Wong, *J. Org. Chem.* **1975**, *40*, 1966–1971; b) L. Miller, J. W. Hershberger, *J. Polym. Sci. Part C Polym. Lett.* **1987**, *25*, 219–221; c) U. Gerigk, M. Gerlach, W. P. Neumann, R. Vieler, V. Weintritt, *Synthesis* **1990**, 448–452.
- [16] S. Martínez-Arranz, A. C. Albéniz, P. Espinet, *Macromolecules* **2010**, *43*, 7482–7487.
- [17] a) J. A. Molina de la Torre, A. C. Albéniz, *ChemCatChem* **2014**, *6*, 3547–3552; b) I. K. Sagamanova, S. Sayalero, S. Martínez-Arranz, A. C. Albéniz, M. A. Pericàs, *Catal. Sci. Technol.* **2015**, *5*, 754–764; c) J. A. Molina de la Torre, A. C. Albéniz, *ChemCatChem* **2016**, *8*, 2241–2248.
- [18] a) N. Carrera, E. Gutiérrez, R. Benavente, M. M. Villavieja, A. C. Albéniz, P. Espinet, *Chem. Eur. J.* **2008**, *14*, 10141–10148; b) I. Meana, A. C. Albéniz, P. Espinet, *Adv. Synth. Catal.* **2010**, *352*, 2887–2891; c) S. Martínez-Arranz, N. Carrera, A. C. Albéniz, P. Espinet, A. Vidal-Moya, *Adv. Synth. Catal.* **2012**, *354*, 3551–3560.
- [19] The VA-PNB skeleton is all-aliphatic and devoid of benzylic positions that may favor degradation of the scaffold by radical processes. To check this assumption and to compare the stability of both the aliphatic and the benzylic substitution, we subjected two model tin compounds (fluorine-labeled for convenience) to heating in acetonitrile with AIBN as a radical initiator: 30 % of $\text{SnBu}_3(\text{CH}_2\text{CH}_2\text{CH}_2\text{-C}_6\text{F}_5)$ decomposed after 48 h at 80 °C, whereas $\text{SnBu}_3(\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3)$ remained unaltered for 48 h under the same conditions (see Supporting Information for details).
- [20] Polynorbornenes are known to undergo structural changes upon heating that involve rotation of the bicyclic units to the stable thermodynamic conformation. These changes modify the properties of the polymers (solubility and T_g). See: P. P. Chu, W. J. Huang, F. C. Chang, S. Y. Fan, *Polymer* **2000**, *41*, 401–404.
- [21] The spectroscopic features of **2b** and **2b-ins** are the same and, according to the ^{119}Sn NMR spectra, all the tin centers correspond to $\text{R}_3\text{Sn-Cl}$ units (see Experimental Section). The functionalization of **2b-ins** was determined by a new analysis of the amount of chloride present. A small but significant loss was observed when compared to the initial polymer **2b**. The reason for this loss was not determined but it could be due to the loss of the lower molecular weight polymer chains or even of residual tin species trapped in the polymer synthesis.
- [22] We cannot completely exclude the presence of a small amount of Sn–Sn species resulting from partial decomposition of the tin hydride moieties. See for example: A. G. Davies, D. K. Osei-Kissi, *J. Organomet. Chem.* **1994**, *474*, C8–C10. The ^{119}Sn NMR resonance for $\text{R}_3\text{Sn-SnR}_3$ species is very close to that of SnHR_3 . Thus, the broad signals in the solid-state ^{119}Sn NMR spectra of polymers **3** do not allow to completely rule out the occurrence of Sn–Sn bonds.
- [23] A. G. Hernán, P. N. Horton, M. B. Hursthouse, J. D. Kilburn, *J. Organomet. Chem.* **2006**, *691*, 1466–1475.
- [24] a) J. A. Barltrop, D. Bradbury, *J. Am. Chem. Soc.* **1973**, *95*, 5085–5086; b) J. T. Groves, K. W. Ma, *J. Am. Chem. Soc.* **1974**, *96*, 6527–6529; c) J. T. Groves, S. Kittisopikul, *Tetrahedron Lett.* **1977**, *18*, 4291–4294; d) A. N. Abeywickrema, A. L. J. Beckwith, *Tetrahedron Lett.* **1986**, *27*, 109–112; e) T. Kawamoto, S. Uehara, H. Hirao, T. Fukuyama, H. Matsubara, I. Ryu, *J. Org. Chem.* **2014**, *79*, 3999–4007; f) T. Kawamoto, I. Ryu, *Org. Biomol. Chem.* **2014**, *12*, 9733–9742.
- [25] a) R. M. López, G. C. Fu, *Tetrahedron* **1997**, *53*, 16349–16354; b) D. S. Hays, G. C. Fu, *J. Org. Chem.* **1998**, *63*, 2796–2797.
- [26] a) R. E. Maleczka Jr., L. R. Terrell, D. H. Clark, S. L. Whitehead, W. P. Gallagher, I. Terstiege, *J. Org. Chem.* **1999**, *64*, 5958–5965; b) R. E. Maleczka, W. P. Gallagher, *Org. Lett.* **2001**, *3*, 4173–4176; c) W. P. Gallagher, R. E. Maleczka, *J. Org. Chem.* **2005**, *70*, 841–846.
- [27] D. H. Lorenz, P. Shapiro, A. Stern, E. I. Becker, *J. Org. Chem.* **1963**, *28*, 2332–2335.
- [28] A. N. Abeywickrema, A. L. J. Beckwith, S. Gerba, *J. Org. Chem.* **1987**, *52*, 4072–4078.
- [29] D. Cai, A. Neyer, R. Kuckuk, H. M. Heise, *J. Mol. Struct.* **2010**, *976*, 274–281.
- [30] A. G. Davies, *Organotin Chemistry*, Wiley-VCH, Weinheim, **2004**.
- [31] R. K. Harris, K. J. Packer, P. Reams, *Chem. Phys. Lett.* **1985**, *115*, 16–18.
- [32] G.-X. Wang, B.-P. Sun, C.-H. Peng, *Org. Process Res. Dev.* **2011**, *15*, 986–988.
- [33] D. C. White, *Microchim. Acta* **1961**, *49*, 449–456.
- [34] Y. Suzuki, Y. Okita, T. Morita, Y. Yoshimi, *Tetrahedron Lett.* **2014**, *55*, 3355–3357.
- [35] The experiments described herein were carried out by keeping the concentration values used in Table 3, but the amount of solvent (THF) can be reduced.

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