

Influence of the Support Structure on the Activity, Stability, and Metal Leaching of a Polymer-Supported Organotin Chloride Catalyst

ALEXANDRE CHEMIN, HERVÉ DELEUZE, BERNARD MAILLARD

Laboratoire de Chimie Organique et Organométallique, UMR 5802-CNRS, Université Bordeaux I,
351 Cours de la Libération, 33405 Talence France

Received 2 March 2000; accepted 12 May 2000

ABSTRACT: Polymer-supported organotin chlorides have been synthesized by suspension copolymerization of organotin-functionalized styrenic monomers using a precipitating porogen. Their activities as reducing catalysts have been evaluated in the reduction of bromoadamantane by sodium borohydride. The influence of the length of the spacer arm between the tin atom and the polymer backbone on the activity and the tin leaching of the supported catalyst have been studied. The nature of the alkyl groups (butyl or phenyl) attached on the tin atom plays an important role on the stability toward successive reuse of the supported catalyst. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1297–1308, 2001

Key words: polymer-supported organotin chloride; suspension copolymerization; macroporous supports; tin leaching

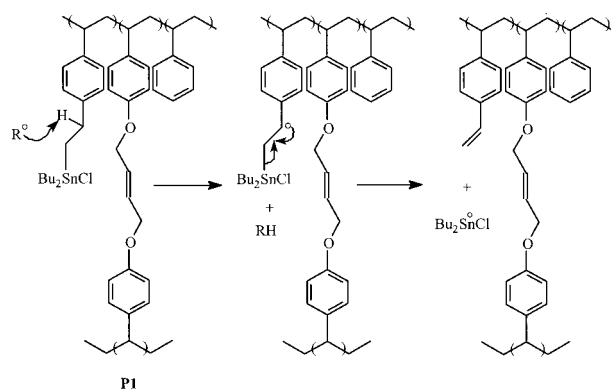
INTRODUCTION

Triorganotin hydrides have proven to be very suitable and very versatile species both for radical generation and kinetically controlled radical trapping.¹ Other uses include replacement of halogen or hydroxy group by hydrogen, and a variety of transition metal catalyzed syntheses using tin hydride.² There is, however, a considerable disadvantage to the use of trialkyltin hydrides in organic synthesis: they produce various potentially toxic products that are difficult to remove completely from the final reaction mixture. This fact has proven to be a severe limitation to the exploitation of these reagents in the synthesis of fine chemicals. This problem has been addressed in two ways. First, an assortment of workup procedures has been devised with the goal of removing trialkyltin products from reaction mixtures. Second, a number of alternative classes of

reagents have been introduced to facilitate separation or to reduce toxicity.⁴ This includes water-soluble⁵ or polar-tailed tin hydrides.⁶ Another promising solution seems to be the immobilization of the tin hydride on insoluble polymer supports.⁷ The functionalization of a crosslinked polystyrene is, by far, the most often used route to prepare polymer-supported reagents and catalysts because it avoids the polymer synthesis steps. However, this approach presents several severe drawbacks. The anchoring of the desired reactive species on the polymer needs several steps that are not always efficient. Furthermore, in the particular case of the grafting of tin hydride onto a gel-type polymer support, it has been clearly demonstrated⁸ that the mobility of the lightly crosslinked macromolecular chains results in coupling and oxidative reactions of the tin hydride functions significantly reducing the long-term stability of the polymer-supported reagent. Having this in mind, some time ago we started a project concerning the synthesis and copolymerization of monomers bearing organotin functionalities to obtain macroporous beads with adjust-

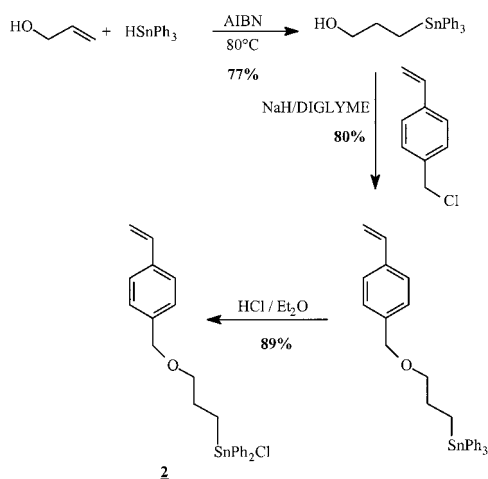
Correspondence to: H. Deleuze (h.deleuze@lcoo.u.bordeaux.fr)

Journal of Applied Polymer Science, Vol. 79, 1297–1308 (2001)
© 2000 John Wiley & Sons, Inc.

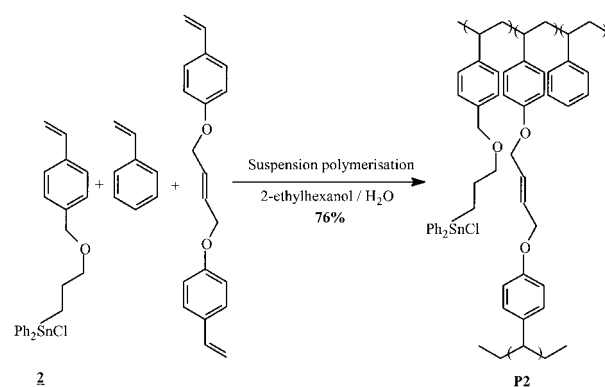


Scheme 1 Leaching of tin from support by a radical elimination.

able crosslinking levels and tin loading.^{9,10} It was expected that better site-isolation obtained with these more rigid network would limit the deactivation of the reactive tin moiety and increase the turnover and life-time of the supported catalysts thus obtained. In a previous article,⁹ we developed a polymer-supported organotin catalyst **P1** based on dibutyl([2-(4-vinylphenyl)ethyl] tin chloride **1**. This macroporous support was synthesized using **1** as the functional monomer, and (E) 1,4-bis(4-vinylphenoxy) but-2-ene (BVPB) as the crosslinking agent showed a good activity and recycling ability when used as a catalyst in the reduction of bromoadamantane to adamantane by NaBH₄. In the supported species **P1**, the tin atom is separated from the aromatic ring of the polystyrenic backbone by only two methylene groups. This short spacer arm could limit the accessibility and, therefore, the activity of the organotin chloride moiety. Furthermore,



Scheme 2 Synthesis of diphenyl (3-((4-vinylphenyl)methyleneoxy)propyl)tin chloride.



Scheme 3 Preparation of support **P2** by suspension copolymerization of **2** with BVPB and styrene.

the benzylic radical R[•] present in solution could abstract a hydrogen atom from the backbone of the polymer. If such a reaction occurs on the moiety carrying the tin entity, the benzylic radical would react by elimination of a tin radical, hence inducing the leaching of the tin group (Scheme 1).

To suppress this radical β-elimination, the organotin moiety should be separated from the aromatic ring by more than two atoms.

RESULTS AND DISCUSSION

Synthesis of a Polymer-Supported Organotin Catalyst with a Long Spacer Arm and Phenyl Group on Tin

Synthesis of the Organotin Monomer **2**

To obtain an organotin monomer with a long spacer arm, we chose to synthesize diphenyl [3-((4-vinylphenyl)methyleneoxy)propyl] tin chloride **2**. This compound was produced in three steps (Scheme 2): (1) hydrostannylation of allylic alcohol, (2) Williamson etherification, and (3) conversion of the Sn—Ph into a Sn—Cl bond using dry HCl. The use of the phenyl substituent on the tin atom instead of the usually preferred butyl groups allowed this bond to be cleaved selectively by HCl. This was justified by the fact that the Sn—Cl function should be introduced at the end of the synthetic path because this bond is sensitive to the basic conditions employed for the etherification step.

Synthesis of Supported Species **P2**

The monomer **2** was copolymerized in suspension with BVPB and styrene using 2-ethyl hexanol as the porogenic solvent¹¹ (Scheme 3). The results of

Table I Results of the Suspension Copolymerization of the Different Organotin Monomers with BVPB and Styrene

Supported Species	Organotin Monomer	Nominal Crosslinking %	Tin Loading in the Monomer Feed (mmol/g)	Tin Loading in the Polymer (mmol/g)	Chlorine Loading in the Polymer (mmol/g)	Yield of Beads 100 μm < ϕ < 800 μm %
P2	2	20	0.6	0.6	0.6	76
P3	3	20	0.9	0.8	0.8	85
P4	4	20	1.0	1.1	0.9	75

the polymerization of **2** is reported on Table I. Comparison of the tin loading in the monomer feed and that in the final polymer confirms the good incorporation of the organotin monomer in the copolymer chain. The similar values obtained for the tin and chlorine levels in the final polymer confirms the high stability of the Sn—Cl bond toward the suspension conditions. The use of a precipitating solvent as the porogen allowed the formation of a macroporous structure with a specific area in the medium range.¹² The swelling of the beads in different solvents was rather high for a network having a nominal crosslinking level of 20%. It can be compared with those observed with Tantagel S-RAM, which have a gel-type structure and are much less crosslinked (Table II).

Reactivity and Stability of Supported Species P2

The activity of the supported species **P2** was tested in the reduction of bromoadamantane by NaBH_4 catalyzed by tin chloride as previously described.⁹ The results obtained are reported in Figure 1. The conversion of bromoadamantane to adamantane reached 80% after 1 h and is complete within 6 h. These results are comparable with those obtained with supported species **P1**. The stability of the supported functions toward successive reuse was also tested (Fig. 2). Surprisingly, the ability to reuse of polymer **P2** is rather poor, and less so than **P1**.

Tin Leaching Measurements

The leaching of the supported species **P2** was estimated by measurement of the level of contam-

ination of organotin derivatives in the final product (adamantane). After 6 h at 90°, in the presence of **P2**, the leaching of tin from the support was about 0.6%. This value is below the amount of tin loss after the first use of supported species **P1** under the same conditions (3%), but is still too high for most potential applications of organotin hydride in organic synthesis. To have a better knowledge of the origin of the tin leaching we decided to study the influence of three parameters on the observed contamination: (a) the temperature of the reaction, (b) the presence (or absence) of stirring; and (c) the presence (or absence) of AIBN.

The analysis of the results obtained during this study, reported in Table III, lead to the following remarks:

1. The presence of AIBN in the solution, yielding to a high level of radicals, did not increase the tin contamination. Therefore, the elongation of the length of the spacer arm between the tin atom and the aromatic ring, as expected, reduced the tin leaching from the support.
2. The stirring of the solution did not have a great influence on the release of tin, indicating that the stirring device used (see ref. 10) limits the degradation of the support usually induced by a grinding effect.
3. The temperature of the reaction seemed to be the crucial parameter as far as the tin leaching was concerned. The contamination was very low at 20° (but there was no reaction), and was still seven times lower

Table II Characteristics of the Different Supported Species Prepared

Supported Species	Specific Surface Area (m ² /g)	Pore Volume (mL/g)	Swelling in Solvents (mL/g)		
			THF	Toluene	Glyme
P2	100	1.2	3.2	2.5	2.6
P3	120	0.9	1.2	1.0	1.1
P4	80	1.4	3.3	2.3	2.8

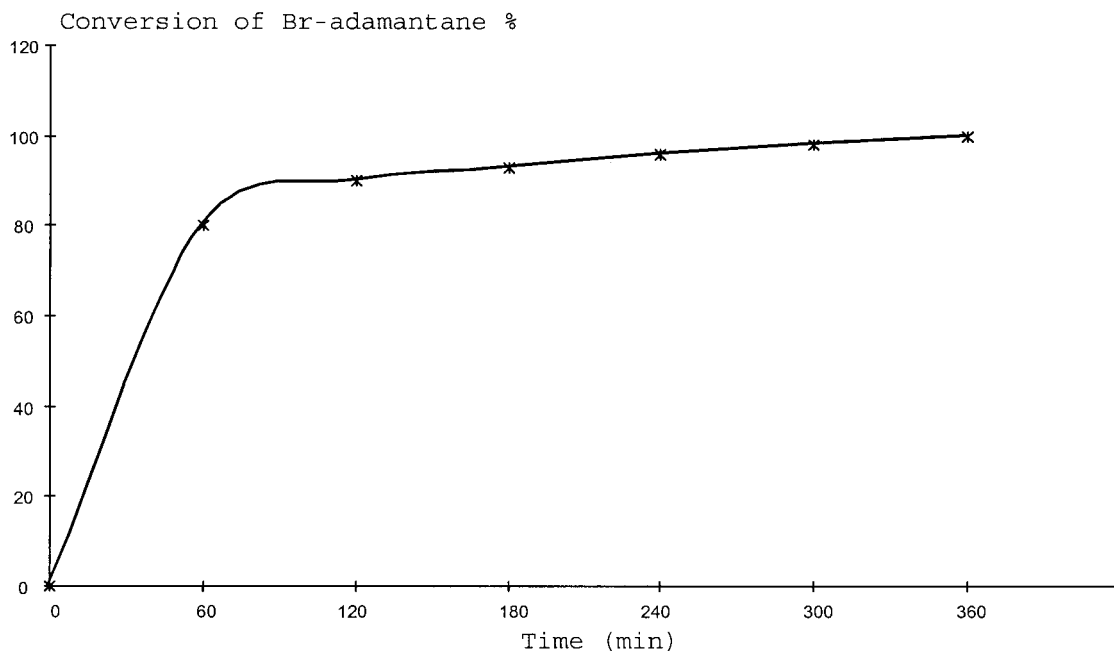


Figure 1 Reactivity of support **P2** used as a catalyst for the reduction of bromoadamantane by NaBH_4 .

at 65° than at 90° . However, at this latter temperature, the activity of the polymer-supported catalyst is rather low (Fig. 3). Therefore, it seems that the main source of tin leaching from the support comes from thermal degradation. This study has shown that the supported species **P2** gives less tin leaching than species **P1**, confirming the attraction in introducing a spacer arm with five atoms between the aromatic

ring and the tin atom. However, supported species **P2** shows a loss of activity as soon as used a second time, and this is not observed with **P1**. An explanation of this difference of behavior could be the nature of the starting organotin monomer. The organotin monomer used in the synthesis of supported species **P1** and **P2** can be differentiated as follows: (a) the nature of the group directly attached to the tin atom (bu-

% Conversion in 2 hours

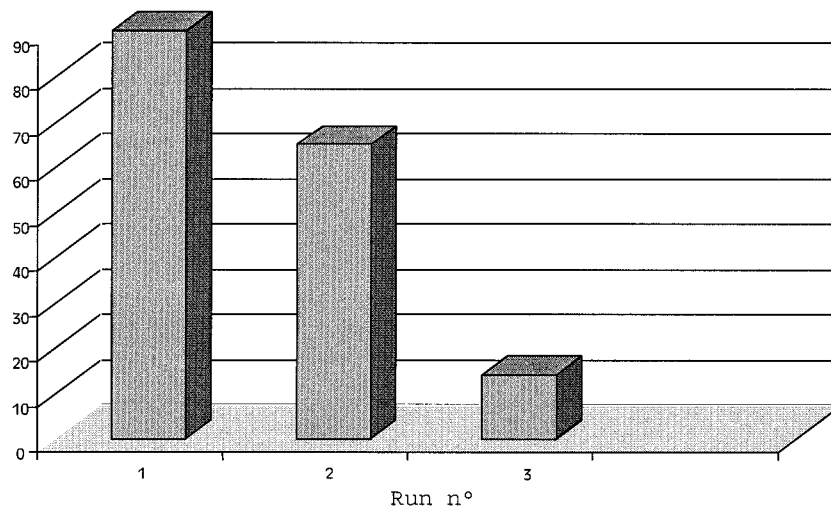


Figure 2 Stability of support **P2** toward successive reuses.

Table III Tin Leaching from the Support P2 after Use Under Several Different Conditions

Entry	<i>T</i> (°C)	Stirring Yes/no	AIBN Yes/no	Conversion of Br-adamantane in 1 h %	Tin Leaching % of Tin Initially on Support
1	20	Y	N	0	0.02
2	65	N	N	0	0.07
2	65	Y	N	0	0.07
4	65	Y	Y	40	0.08
5	90	N	N	0	0.45
6	90	Y	N	0	0.57
7	90	Y	Y	85	0.60

tyl for **P1** and phenyl for **P2**); and (b) The length and the nature of the spacer arm (two atoms for **P1** and five atoms for **P2**).

To complete our study of the structural parameters controlling the reactivity and stability of our organotin polymer-supported reagents we decided to investigate the influence of the above two factors in the case of supported species **P3**, an analog of **P1** with phenyl substituents on the tin atom and species **P4** which is similar to **P2** with butyl substituents.

Synthesis of a Polymer-Supported Organotin Catalyst with a Short Spacer Arm and Phenyl Group on Tin, **P3**, and a Long Spacer Arm and Butyl Groups on Tin, **P4**

Synthesis of Monomer **3**

By analogy with the synthesis of dibutyl[2-(4-vinylphenyl)ethyl] tin chloride, **1**, we realized the

hydrostannylation of *p*-divinylbenzene with chlorodiphenyltin hydride formed *in situ* from Ph_2SnH_2 and Ph_2SnCl_2 to obtain diphenyl[2-(4-vinylphenyl)ethyl] tin chloride, **3** (Scheme 3). Compound **3** was obtained with a yield of 86% as a mixture 85/15 with the product of dihydrostannylation, and was used without further purification (Scheme 4).

Preparation of Supported Species **P3**

Monomer **3** was copolymerized in suspension with styrene and BVPB as crosslinking agents using the same conditions reported for **P2** to yield supported species **P3** (Scheme 5).

The results of the copolymerization are reported in Table I. This supported species was obtained in good yield, and possesses characteristics similar to the analogous species **P1** bearing butyl groups on the tin atom (Table II). It can be seen that with the same crosslinking level (20%)

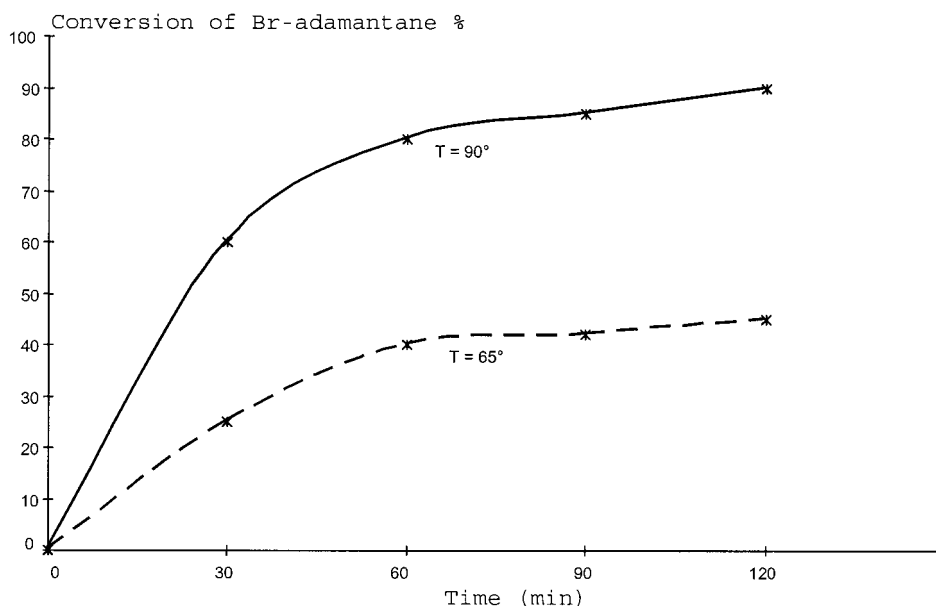
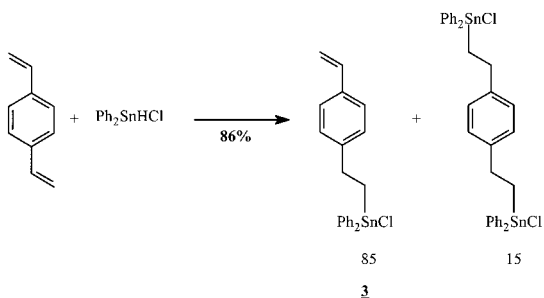


Figure 3 Influence of the reaction temperature on the reactivity of support **P2**.



Scheme 4 Synthesis of diphenyl (2-(4-vinylphenyl)ethyl)tin chloride **3**.

as **P2** and similar specific surface area, the swelling of **P3** in solvents is almost three times higher than **P2**.

Reactivity and Stability of Supported Species **P3**

The activity of **P3** was tested in the reduction of 1-bromoadamantane under the usual conditions. The conversion curve for the reaction is shown in Figure 4. The stability in successive reuse was also studied and the results are reported in Figure 5. Here it is seen that the activity is considerably reduced soon after the second reuse.

Synthesis of Monomer **4**

The monomer dibutyl[3-(4-vinylphenyl)methyleneoxypropyl] tin chloride, **4**, was synthesized using the same approach as that used for monomer **2** replacing Ph_3SnH by Bu_2SnPhH (Scheme 6). Compound **4** was obtained with an overall yield of 60% from dibutylphenyltin hydride.

Synthesis of Supported Species **P4**

Monomer **4** was copolymerized in suspension with styrene and BVPB as the crosslinking agents under the same conditions as reported for **P2** (Scheme 7). Supported species **P4** was obtained in a yield of 75%. This supported species, **P4**, shows similar characteristics to **P2** (Tables I and II).

Reactivity and Stability of Supported Species **P4**

The reduction of bromoadamantane to adamantane by NaBH_4 using a catalytic amount of dibutyl chloride supported on polymer **P4** gave similar results to those obtained with **P3** (Fig. 4). A similar activity was observed for **P3** and **P4** on the first use (**P3** being somewhat less active than **P4**). The stability of **P4** in successive reuse in this reaction has also been studied and compared with the behavior of **P1**, **P2** and **P3** (Fig. 6).

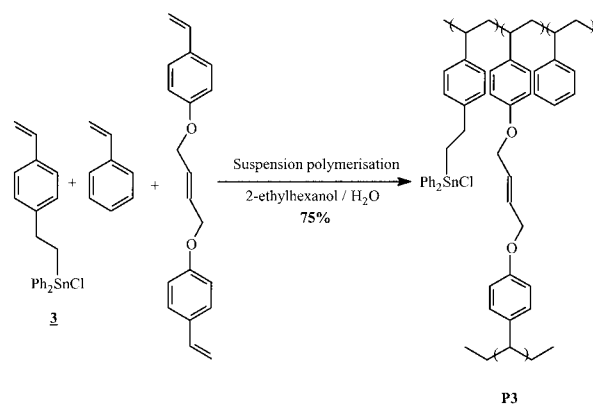
The results obtained clearly establishes that supported species prepared with monomers bearing two butyl groups attached to the tin atom are much more stable toward successive reuse than those prepared with diphenylchlorotin moieties. In contrast, the length of the spacer arm between the tin atom and the aromatic ring (three bonds for **P1** and **P3**; and six bonds for **P2** and **P4**) does not seem to have a significant influence on the reactivity and stability of these polymer-supported organotin catalysts under the conditions used in this study.

Tin Leaching Measurements

Estimation of the level of tin leaching from **P4** has been conducted under the same conditions as for the other supported tin species. The value obtained corresponds to a loss of about 0.6% of the initial tin present on the support. This is very similar to that observed with the analogous support bearing alkyldiphenyltin functions (**P2**).

CONCLUSION

The replacement of a short spacer arm (two methylene groups) by a longer one (four methylene groups and one oxygen atom) considerably reduces the tin leaching from the polymer-supported organotin chloride catalysts. However, the tin contamination of the final product still corresponds to a loss of about 0.6% mol of the tin initially present on the support when the species are used as catalyst in the reduction of 1-bromoadamantane at 90°C. This contamination is attributed to thermal degradation of the supported tin moiety under the conditions of the test reaction.



Scheme 5 Preparation of support **P3** by suspension copolymerization of **3** with BVPB and styrene.

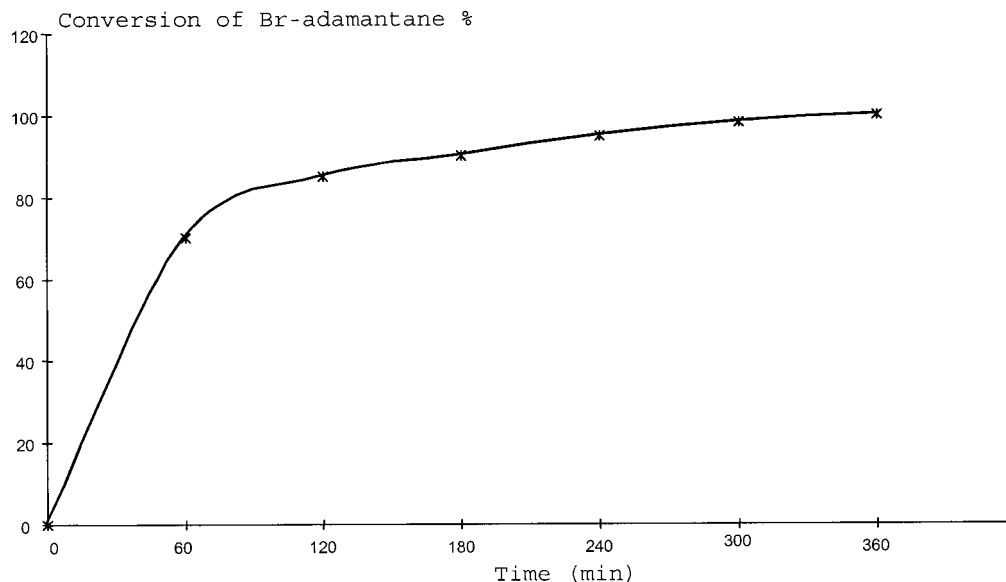


Figure 4 Reactivity of support **P3** used as a catalyst for the reduction of bromoadamantane by NaBH_4 .

The nature of the alkyl groups attached to the tin atom plays an important role in determining the stability of the supported catalysts in successive reuse. The dibutylchlorotin moiety leads to a much more stable supported catalyst than its diphenylchlorotin counterpart. The length of the spacer arm does not play an important role in this instance. The reasons for this behavior are not clearly understood. A polymer-supported organotin chloride with a dibutylchlorotin group separated from the polymer backbone by a long spacer

arm (six bonds) shows good activity as a catalyst in the reduction of bromoadamantane by NaBH_4 as well as a good stability in successive reuse (at least 10) in the same test reaction

EXPERIMENTAL

The tin contents were estimated by ICP-AES at the "Service Central d'Analyse," Vernaison, France.

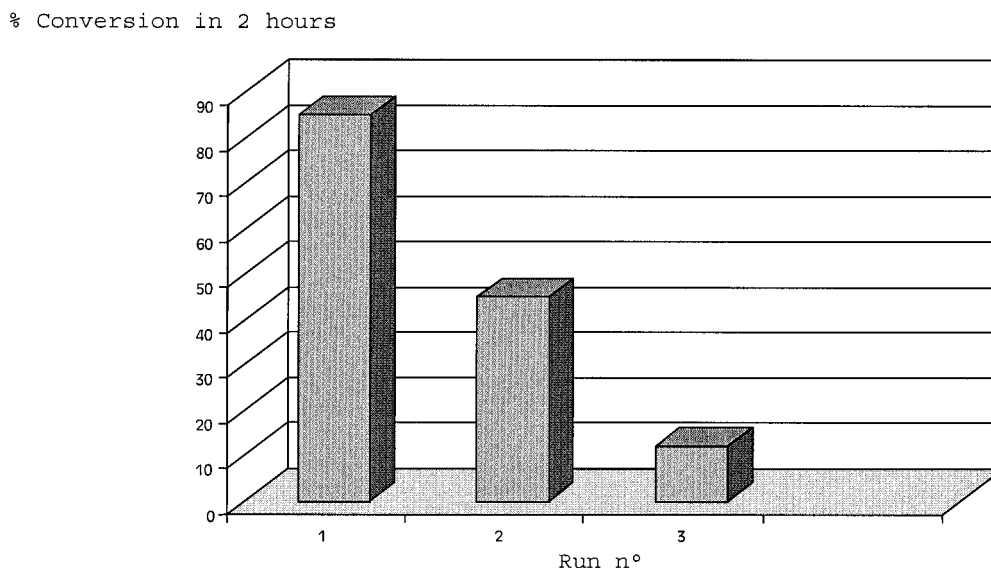
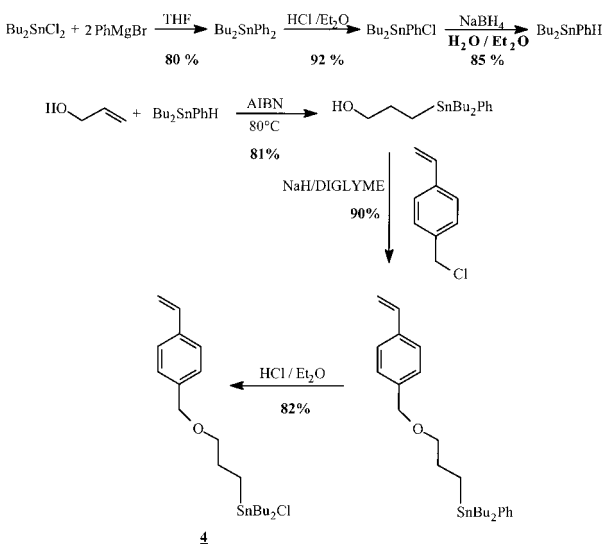


Figure 5 Stability of support **P3** toward successive reuses.



Scheme 6 Synthesis of dibutyl (3-((4-vinylphenyl)methyleneoxy)propyl)tin chloride **4**.

Synthesis of (E)-1,4-bis (4-vinylphenoxy) but-2-ene (BVPB)

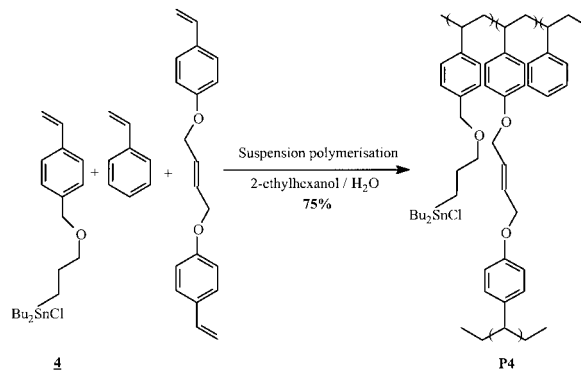
(E)-1,4-bis (4-vinylphenoxy) but-2-ene (BVPB) was synthesised as previously described.⁹

Synthesis of Triphenyl(3-hydroxypropyl)tin

The procedure was adapted from the literature.¹⁴ A 100-mL three-necked flask fitted with a condenser was charged with allyl alcohol (7.5 g, 129.1 mmol) and AIBN (0.2 g, 1.2 mmol), and purged with N₂. Triphenyl tin hydride (19 g, 54.3 mmol), synthesized according to the procedure described by Podesta et al.,¹⁵ was then added dropwise with a syringe and the flask was heated at 80°C for 2 h. The mixture was then allowed to cool to room temperature, and the white precipitate obtained was dissolved in acetone. The suspension was filtered and the filtrate was concentrated under vacuum. The white precipitate was then recrystallized from cyclohexane to give 17.6 g (Y = 77%) of triphenyl (3-hydroxypropyl)tin as white needles. (a) F = 104°C. (b) ¹H-NMR (CDCl₃): δ(ppm): 1.6 (m, 2H, CH₂—Sn); 1.8 (broad s, 1H, OH); 2.0 (m, 2H, —CH₂—CH₂—CH₂—); 3.7 (t, 2H, ³J_{H—H} = 6 Hz, —CH₂—OH); 7.4–7.6 (m, 15H, H aromatic). (c) ¹³C-NMR (CDCl₃): δ(ppm): 6.8 (¹J_{C—Sn} = 204 Hz, —CH₂—Sn); 29.4 (CH₂—CH₂—CH₂, ²J_{C—Sn} = 16 Hz); 65.7 (CH₂—OH, ³J_{C—Sn} = 31 Hz); 128.7 (³J_{C—Sn} = 28 Hz, C aromatic); 129.0 (C aromatic); 137.2 (²J_{C—Sn} = 18 Hz, C aromatic); 139.1 (C aromatic). (d) ¹¹⁹Sn NMR (CDCl₃): δ(ppm): –98.

Synthesis of Triphenyl{3-[(4-vinylphenyl)methyleneoxy]propyl}tin

In a two-necked flask fitted with a condenser and a dropping funnel, sodium hydride (1.9 g, 47.5 mmol, 60% in oil) were suspended in freshly distilled DMF (5 mL) and DIGLYME (10 mL). The flask was purged with N₂ and a solution of triphenyl(3-hydroxypropyl)tin (14.0 g, 34.3 mmol) dissolved in DMF (15 mL) was then added dropwise at 0–5°C. The mixture was stirred at room temperature for an additional 30 min before *p*-chloromethylstyrene (5.2 g, 34.3 mmol) was added dropwise. The mixture was stirred overnight at room temperature. Excess NaH was destroyed with a few drops of ethanol. Water (25 mL) and ether (25 mL) were added and aqueous phase was extracted with ether (3 × 25 mL). The combined organic phase was washed with H₂O, dried over MgSO₄, and concentrated under vacuum. The orange oil obtained was purified by chromatography (eluent : petroleum ether / ether: 90 / 10) to yield a colorless oil that solidifies when stored at 0–5°C (14.1 g, Y = 80%). (a) F = 33–35°C. (b) ¹H-NMR(CDCl₃): δ(ppm): 1.8 (m, 2H, —CH₂—Sn); 2.2–2.3 (m, 2H, —CH₂—CH₂—CH₂—); 3.6 (t, 2H, ³J_{H—H} = 6 Hz, CH₂O); 4.5 (s, 2H, Ph—CH₂—O); 5.4 (d, 1H, ³J_{cis} = 11 Hz, Ha); 5.9 (d, 1H, ³J_{trans} = 18 Hz, Hb); 6.9 (dd, 1H, ³J_{cis} 1 z and ³J_{trans} = 18 Hz, Hc); 7.4–7.8 (m, 19H, H aromatic). (c) ¹³C-NMR (CDCl₃): δ(ppm): 7.5 (¹J_{C—Sn} = 204 Hz, CH₂—Sn); 26.8 (²J_{C—Sn} = 15 Hz, —CH₂—CH₂—Sn); 72.7 (Ph—CH₂—O—); 73.1 (³J_{C—Sn} = 31 Hz, —CH₂—CH₂—O—); 113.9 (C vinylic); 126.5; 128.2; 128.4; 128.8; 129.1; 137.1; 137.4; 137.6; and 138.4 (7 C aromatic and 1 C vinylic); 139.4 (¹J_{C—Sn} = 236 Hz, C aromatic). (d) ¹¹⁹Sn NMR (CDCl₃): δ(ppm): –99. (e) Found: %C: 69.6; %H: 6.0; %O: 2.8; %Sn: 21.0 (calc.: %C: 68.6; %H: 5.8; %O: 3.0; %Sn: 22.6).



Scheme 7 Preparation of support P4 by suspension copolymerization of **4** with BVPB with styrene.

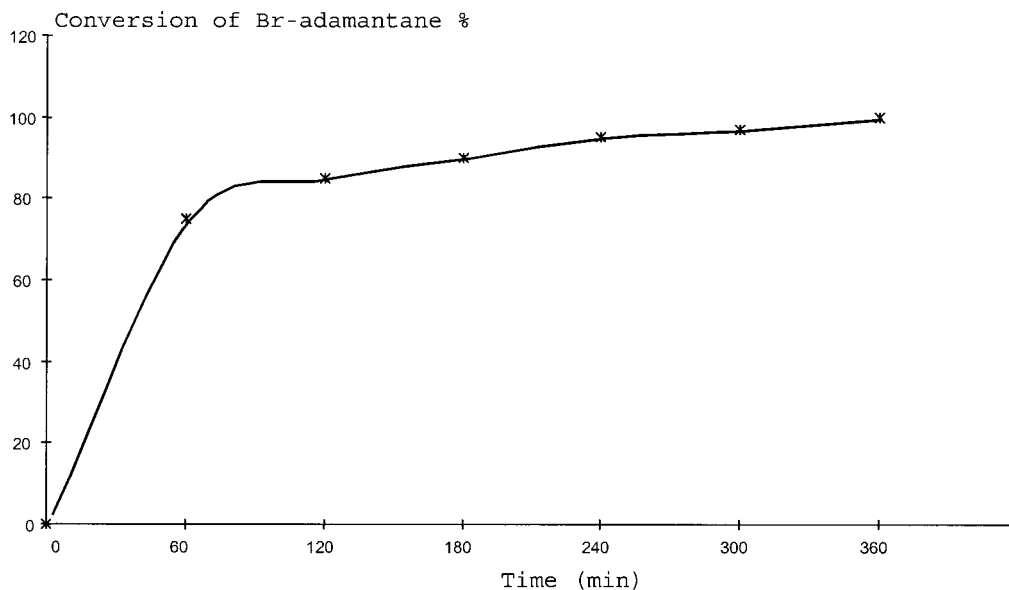


Figure 6 Reactivity of support **P4** used as a catalyst for the reduction of bromoadamantane by NaBH_4 .

Synthesis of Diphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin chloride (**2**)

In a 100-mL two-necked flask fitted with a condenser and a dropping funnel, triphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin (13.3 g, 25.4 mmol) was dissolved in CH_2Cl_2 (25 mL). A solution of HCl 1.8 M in Et_2O (14 mL), was then added dropwise at $0-5^\circ\text{C}$ over a period of 30 min. The solution was stirred for an additional hour and water (25 mL) was added. The organic phase was

washed with brine, dried over MgSO_4 , and concentrated under vacuum to yield a pale yellow oil which solidifies when stored at $0-5^\circ\text{C}$ (10.9 g, $Y = 89\%$). (a) $F = 63-64^\circ\text{C}$. (b) $^1\text{H-NMR}(\text{CDCl}_3)$: $\delta(\text{ppm})$: 1.8 (m, 2H, $\text{CH}_2\text{-Sn}$); 2.1 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$); 3.5 (t, 2H, $^3J_{\text{H-H}} = 5$ Hz, $\text{CH}_2\text{-CH}_2\text{-O}$); 4.1 (s, 2H, $\text{Ph-CH}_2\text{-O}$); 5.2 (d, 1H, $^3J_{\text{cis}} = 11$ Hz, Ha); 5.7 (d, 1H, $^3J_{\text{trans}} = 18$ Hz, Hb); 6.7 (dd, 1H, $^3J_{\text{cis}} = 11$ Hz, $^3J_{\text{trans}} = 18$ Hz, Hc); 6.8 (d, 2H, $^3J_{\text{H-H}} = 9$ Hz, H aromatic); 7.2 (d,

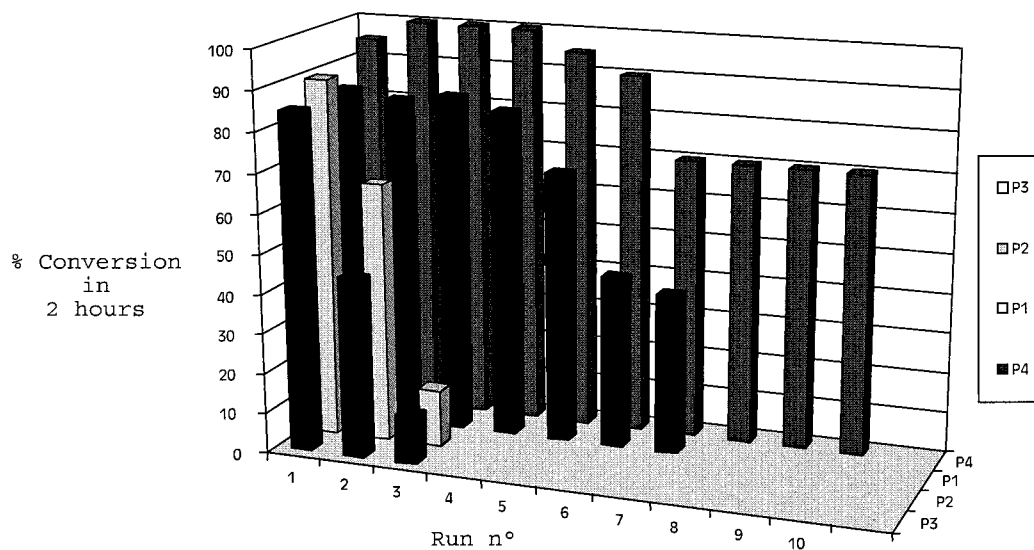


Figure 7 Comparison of the stability toward successive reuses of the different supports.

2H, $^3J_{\text{H-H}} = 9$ Hz, H aromatic); 7.4–7.8 (m, 10H, H aromatic). (c) $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm): 15.0 ($^1J_{\text{C-Sn}} = 267$ Hz, $\text{CH}_2\text{-Sn}$); 25.8 ($\text{CH}_2\text{-CH}_2\text{-Sn}$, $^2J_{\text{C-Sn}} = 19$ Hz); 69.7 ($^3J_{\text{C-Sn}} = 25$ Hz, $\text{-CH}_2\text{-CH}_2\text{-O-}$); 72.8 ($\text{Ph-CH}_2\text{-O-}$); 114.4 (C vinylic); 126.2 (C aromatic); 128.8 ($^3J_{\text{C-Sn}} = 38$ Hz, C aromatic); 129.6 (C aromatic); 135.2 (C aromatic); 136.0 ($^2J_{\text{C-Sn}} = 20$ Hz, C aromatic); 136.2 and 137.6 (1 C vinylic and 3 C aromatic); 140.9 (C aromatic). (d) $^{119}\text{Sn NMR}$ (CDCl_3): δ (ppm): -74. (e) Found: %C: 59.6; %H: 5.3; %Cl: 7.0; %Sn: 24.5 (calc.: %C: 59.6; %H: 5.3; %Cl: 7.3; %Sn: 24.5).

Synthesis of Diphenyl{2-(4-vinylphenyl)}tin chloride (3)

Diphenyl{2-(4-vinylphenyl)}tin chloride **3** was synthesised by hydrostannylation of *p*-DVB obtained by a Wittig reaction according to a published procedure.¹⁶

A two-necked flask was charged with *p*-DVB (4.0 g, 31 mmol), dichlorodiphenyltin (2.1 g, 6 mmol) and AIBN (280 mg, 1.7 mmol). The flask was purged with N_2 and diphenyltin dihydride (2.1 g, 8 mmol) was added dropwise keeping the reaction temperature below 30°C . The mixture was stirred overnight and the unreacted *p*-DVB was evaporated under vacuum to give a gray oil (6.5 g, 86%) containing a mixture of the mono and dihydrostannylation products (molar composition 85/15% as estimated by $^1\text{H-NMR}$). This mixture was used in the polymerization without further purifications. (a) $^1\text{H-NMR}$ (CDCl_3): δ (ppm): 1.8 (t, 2H, $\text{CH}_2\text{-Sn}$, $^3J_{\text{H-H}} = 8$ Hz); 3.0 (t, 2H, $^3J_{\text{H-H}} = 8$ Hz, $\text{Ph}_2\text{-CH}_2\text{-CH}_2$); 5.2 (d, 1H, $^3J_{\text{cis}} = 10$ Hz, $\text{CH}_{\text{cis}}=\text{CH-}$); 5.7 (d, 1H, $^3J_{\text{trans}} = 18$ Hz, $\text{CH}_{\text{trans}}=\text{CH-}$); 6.7 (dd, 1H, $^3J_{\text{trans}} = 18$ Hz and $^3J_{\text{cis}} = 10$ Hz, $=\text{CH-Ph}$); 7.5 (m, 14H, H aromatics). (b) $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm): 15.3 ($^1J_{\text{C-Sn}} = 204$ Hz, $\text{CH}_2\text{-Sn}$); 30.6 ($\text{CH}_2\text{-CH}_2\text{-Sn}$, $^2J_{\text{C-Sn}} = 15$ Hz); 114.4 (C vinylic); 126.2 (C aromatic); 128.8 ($^3J_{\text{C-Sn}} = 38$ Hz, C aromatic); 129.6 (C aromatic); 135.2 (C aromatic); 136.2 and 137.6 (1 C vinylic and 3 C aromatic); 140.9 (C aromatic).

Synthesis of Dibutyldiphenyltin

The procedure was adapted from the literature.¹⁷ A 500-mL three-necked flask was charged with dry magnesium (16.9 g, 696 mmol) and dry THF (50 mL). The flask was purged with N_2 , and a solution of bromobenzene (54.6 g, 348 mmol) diluted in THF (200 mL) was added dropwise over a period of 2 h. The mixture was then heated at

45°C for 1 h. The Grignard reagent solution was transferred into an other 500 mL three-necked flask purged with N_2 , and Bu_2SnCl_2 (48 g, 157 mmol) dissolved in THF (125 mL) added dropwise over a period of 1 h. The solution was then refluxed for an additional hour and the excess of Grignard reagent was hydrolyzed with HCl 0.1 *M* (50 mL). The aqueous layer was then extracted with Et_2O (3×50 mL). The combined organic layer were washed with H_2O (3×50 mL), dried over MgSO_4 , and concentrated under vacuum. The product was then purified by column chromatography (petroleum ether / ether: 90 / 10) to yield Bu_2SnPh_2 (48.6 g, $Y = 80\%$). (a) $^1\text{H-NMR}$ (C_6D_6): δ (ppm): 0.8–2.0 (m, 18H, H aliphatic); 7.2 (m, 10H, H aromatic). (b) $^{119}\text{Sn NMR}$ (CDCl_3): δ (ppm) : -70.

Synthesis of Dibutylphenyltin Chloride

Dibutyldiphenyltin (15.0 g, 38 mmol) were diluted in Et_2O (25 mL) in a 250-mL two-necked flask. A solution of HCl (85 mL at 0.5 *M* in Et_2O) was then added dropwise at $0\text{--}5^\circ\text{C}$ over a period of 30 min. The mixture was stirred for an additional hour at room temperature, and H_2O (25 mL) was poured in. The organic layer was washed with brine, dried over MgSO_4 , and concentrated under vacuum to yield Bu_2SnPhCl as a pale yellow oil (12.4 g, $Y = 92\%$). (a) $^1\text{H-NMR}$ (CDCl_3): δ (ppm): 0.8 (t, 6H, $^3J_{\text{H-H}} = 8$ Hz, CH_3); 1.1–1.9 (m, 12H, H aliphatic); 6.8–7.5 (m, 5H, H aromatic). (b) $^{119}\text{Sn NMR}$ (CDCl_3): δ (ppm): +90.

Synthesis of Dibutylphenyltin Hydride

The procedure was adapted from the literature.¹⁵ In a 500-mL three-necked flask, dibutylphenyltin chloride (10 g, 29 mmol) were dissolved in Et_2O (90 mL). The flask was purged with N_2 , and a solution of NaBH_4 (5.4 g, 143 mmol) dissolved in H_2O (90 mL) was added dropwise at $0\text{--}8^\circ\text{C}$ over a period of 45 min. The mixture was stirred for an additional 45 min at room temperature, and the organic phase was washed with H_2O (2×50 mL), dried over MgSO_4 , and concentrated under vacuum to yield PhBu_2SnH as a pale yellow oil (7.7 g, $Y = 88\%$). (a) IR: $\nu_{\text{SnH}} = 1800$ cm^{-1} . (b) $^1\text{H-NMR}$ (C_6D_6): δ (ppm): 0.6–1.6 (m, 18H, H aliphatiques); 5.5 (m, 1H, Sn—H); 7.4 (m, 5H, H aromatiques). (c) $^{119}\text{Sn NMR}$ (C_6D_6): δ (ppm): -110.

Synthesis of Dibutylphenyl(3-hydroxypropyl)tin

A 100-mL three-necked flask fitted with a condenser was charged with allyl alcohol (7.5 g, 129.1

mmol) and AIBN (0.2 g, 1.2 mmol), and purged with N₂. Dibutylphenyl tin hydride (6.5 g, 20.8 mmol) was then added dropwise with a syringe, and the flask was heated at 70°C for 2 h. The mixture was then concentrated under vacuum and purified by column chromatography (petroleum ether / ether: 95 / 5) to yield dibutylphenyl(3-hydroxypropyl)tin as a yellow oil (6.3 g, Y = 81%). (a) ¹H-NMR (CDCl₃): δ(ppm): 0.9–1.9 (m, 22H, H aliphatic); 2.2 (broad s, 1H, OH); 3.6 (t, 2H, ³J_{H–H} = 7 Hz, –CH₂–O–); 7.3–7.5 (m, 5H, H aromatic). (b) ¹³C-NMR (CDCl₃): δ(ppm): 5.0 (¹J_{C–Sn} = 158 Hz, –CH₂–SnBu₂); 9.6 (CH₃–CH₂–CH₂–CH₂–Sn, ¹J_{C–Sn} = 173 Hz); 13.8 (CH₃–); 27.5 (CH₃–CH₂–CH₂–CH₂–Sn, ³J_{C–Sn} = 29 Hz); 29.1 (CH₃–CH₂–CH₂–CH₂–Sn, ²J_{C–Sn} = 11 Hz); 29.8 (–CH₂–CH₂–SnBu₂, ²J_{C–Sn} = 10 Hz); 66.1 (CH₂–OH, ³J_{C–Sn} = 32 Hz); 128.1 (C aromatic); 128.1 (³J_{C–Sn} = 21 Hz, C aromatic); 136.5 (²J_{C–Sn} = 15 Hz, C aromatic); 141.6 (C aromatic). (c) ¹¹⁹Sn NMR(CDCl₃): δ(ppm): –41. (d) Found: %C: 54.5; %H: 8.1; %O: 4.4; %Sn: 33.0 (calc.: %C: 55.2; %H: 8.1; %O: 4.3; %Sn: 32.4).

Synthesis of Dibutylphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin

The same procedure as for the synthesis of triphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin was used, with sodium hydride (1.6 g, 40 mmol, 60% in oil), dibutylphenyl(3-hydroxypropyl)tin (10.0 g, 27 mmol), and *p*-chloromethylstyrene (4.1 g, 27 mmol). The desired product was thus obtained with 90% yield (11.9 g). (a) ¹H-NMR (CDCl₃): δ(ppm): 0.8–1.9 (m, 20H, H aliphatic); 3.3 (t, 2H, ³J_{H–H} = 5 Hz, CH₂–CH₂–O); 4.4 (s, 2H, Ph–CH₂–O); 5.2 (d, 1H, ³J_{cis} = 11 Hz, Ha); 5.7 (d, 1H, ³J_{trans} = 18 Hz, Hb); 6.6 (dd, 1H, ³J_{cis} = 11 Hz and ³J_{trans} = 18 Hz, Hc); 7.2 (m, 9H, H aromatic). (b) ¹³C-NMR (CDCl₃): δ(ppm): 5.8 (¹J_{C–Sn} = 160 Hz, –CH₂–Sn–Bu₂); 9.7 (¹J_{C–Sn} = 173 Hz, CH₃–CH₂–CH₂–CH₂–Sn); 13.9 (CH₃); 27.1 (²J_{C–Sn} = 10 Hz, CH₃–CH₂–CH₂–CH₂–Sn); 27.6 (³J_{C–Sn} = 30 Hz, CH₃–CH₂–CH₂–CH₂–Sn); 29.2 (²J_{C–Sn} = 10 Hz, O–CH₂–CH₂–CH₂–Sn); 72.7 (Ph–CH₂–O–); 73.7 (³J_{C–Sn} = 31 Hz, –CH₂–CH₂–CH₂–O–); 113.7 (C vinylic); 128.0; 128.1; 128.3; 136.7; 138.4; 142.5 (8C aromatic et 1C vinylic). (c) ¹¹⁹Sn NMR (CDCl₃): δ(ppm): –41. (d) Found: %C: 64.4; %H: 8.0; %O: 3.5; %Sn: 24.0 (calc.: %C: 64.3; %H: 7.0; %O: 3.3; %Sn: 24.5).

Synthesis of Dibutyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin chloride (4)

The same procedure was used for the synthesis of diphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin chloride employing dibutylphenyl{3-[(4-vinylphenyl)methylenoxy]propyl}tin (3.3 g, 6.8 mmol). The desired product was obtained in 82% yield (2.5 g). (a) ¹H-NMR (CDCl₃): δ(ppm): 0.8–1.9 (m, 20H, H aliphatic); 3.3 (t, 2H, ³J_{H–H} = 5 Hz, CH₂–CH₂–O); 4.4 (s, 2H, Ph–CH₂–O); 5.2 (d, 1H, ³J_{cis} = 11 Hz, Ha); 5.7 (d, 1H, ³J_{trans} = 18 Hz, Hb); 6.6 (dd, 1H, ³J_{cis} = 11 Hz, ³J_{trans} = 18 Hz, Hc); 7.2 (d, 2H, ³J_{ortho} = 9 Hz, H aromatic); 7.4 (d, 2H, ³J_{ortho} = 9 Hz, H aromatic). (b) ¹³C-NMR (CDCl₃): δ(ppm): 13.7 (CH₃); 15.0 (CH₂–SnBu₂); 18.6 (CH₃–CH₂–CH₂–CH₂–Sn, ¹J_{C–Sn} = Hz); 26.1 (CH₂–CH₂–O, ²J_{C–Sn} = Hz); 26.9 (CH₃–CH₂–, ³J_{C–Sn} = Hz); 28.0 (CH₃–CH₂–CH₂–, ²J_{C–Sn} = Hz); 71.4 (–CH₂–CH₂–O–, ³J_{C–Sn} = Hz), 73.2 (Ph–CH₂–O–); 114.5 (C vinylic); 126.5; 128.6; 135.7; 136.2; 137.9 (4C aromatic and 1C vinylic). (c) ¹¹⁹Sn NMR(CDCl₃): δ(ppm) : +68. (d) Found: %C: 54.2; %H: 7.6; %O: 4.5; %Sn: 25.3; %Cl: 7.7 (calc.: %C: 54.1; %H: 7.5; %O: 3.7; %Sn: 26.7; %Cl: 8.0).

Suspension Polymerization

The macroporous supports were prepared by a conventional aqueous suspension polymerization using a parallel-side flanged glass reactor especially designed according to the literature.¹⁸ The organic comonomer mixture was suspended, with continuous stirring in an aqueous phase containing the dissolved suspension stabilizer. The stabilizing systems used consisted of a mixture of a solution of poly(diallyldimethylammonium chloride) (3.5%, PDDAC), high molecular weight as the stabilizer and a solution of gelatin (0.15%).

In a typical reaction, a mixture of comonomers (15 mL), 2-ethylhexanol (15 mL), and AIBN (100 mg) as the free radical source were suspended in 240 mL of aqueous phase (aqueous organic ratio of 8 : 1). The stirring speed was adjusted (usually between 500 to 600 rpm) at room temperature to obtain droplet of, visually, a satisfactory size. The reactor was then placed in a thermostated bath and the polymerization was run out at 80°C for 8 h. After cooling, the reaction mixture was filtered and then washed copiously with water and ethanol, then continuously extracted with THF in a Soxhlet apparatus for 24 h. After the last washing with ether, the beads were dried under vacuum at 60°C for 24 h. The dry beads were sieved,

and the very fine and large particles were discarded.

REFERENCES

1. Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987.
2. Regittz, M.; Giese, B., Ed. *C-Radical Houben-Weyl Methoden der Organischen Chemie*; Thieme: Stuttgart, 1989, vol. E19a.
3. Some recent references: Edelson, B. S.; Stoltz, S. M.; Corey, E. J. *Tetrahedron Lett* 1999, 30, 6729; Crich, D.; Sun, S. X. *J Org Chem* 1996, 61, 7200; Farina, V. *J Org Chem* 1991, 56, 4985; Curran, D. P.; Chang, C. T. *J Org Chem* 1989, 54, 3140; Merge, J. M.; Roberts, S. M. *Synthesis* 1979, 471.
4. Baguley, P. A.; Walton, J. C. *Angew Chem Int Ed Engl* 1998, 37, 3072.
5. Light, J.; Breslow, R. *Tetrahedron Lett* 1990, 31, 2957.
6. Ferkous, F.; Massadi, D.; de Jeso, B.; Degueil-Castaing, M.; Maillard, B. *J Organometal Chem* 1991, 420, 315.
7. Neumann, W. P.; Peterseim, M. *React Polym* 1993, 20, 189; Ruel, G.; The, N. G.; Dumartin, G.; Delmond, B.; Pereyre, M. *J Organomet Chem* 1993, 444, C18.
8. Dumartin, G.; Kharboutli, J.; Delmond, B.; Pereyre, M.; Biesemans, M.; Gielen, M.; Willem, R. *Organometallics* 1996, 15, 19; Gerlack, M.; Joerdens, F.; Kuhn, H.; Neumann, W. P.; Peterseim, M. *J Org Chem* 1991, 56, 5971.
9. Chemin, A.; Deleuze, H.; Maillard, B. *Eur Polym J* 1998, 10, 1395.
10. Chemin, A.; Deleuze, H.; Maillard, B. *J Chem Soc Perkin Trans* 1999, 1, 137.
11. Sherrington, D. C. *Chem Commun* 1998, 2275.
12. Guyot, A. G.; Bartholin, B. *Prog Polym Sci* 1982, 8, 277.
13. Richard, S.; Griffith, M. C.; Qu, M. *Tetrahedron Lett* 1998, 39, 8951.
14. Van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J Appl Chem* 1957, 7, 356.
15. Chopa, A. B.; Podesta, J. C. *Anal Asoc Quim Argent* 1977, 65, 181.
16. Campbell, T. D.; Mc Donald, R. *J Org Chem* 1959, 24, 1296.
17. Rosenberg, S. D.; Debreczeni, E.; Weinberg, E. L. *J Am Chem Soc* 1959, 81, 972.
18. Sherrington, D. C. Appendix in *Polymer-Supported Reactions in Organic Synthesis*; Sherrington, D. C.; Hodge, P., Eds.; Wiley: New York, 1980, p. 469.