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Preparation and reactivity of a non-styrenic polymer-supported organotin chloride catalyst

Alexandre Chemin, Hervé Deleuze* and Bernard Maillard

*Laboratoire de Chimie Organique et Organométallique, UMR 5802-CNRS,
Université Bordeaux I, 33405 Talence, France*

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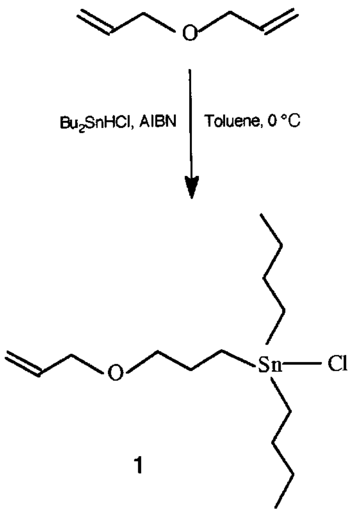
A new type of macroporous polymer-supported organotin hydride has been prepared by suspension copolymerisation of an allyl ether monomer bearing an organotin moiety with *N*-phenylmaleimide and 1,1′-(methylenedi-4,1-phenylene)bismaleimide. Several resins were synthesised using different ratios of toluene–*N*-methylformanilide as the porogen. The swelling characteristics of the resins in different solvents and their specific surface areas were estimated. The organotin chloride-functionalised beads obtained showed good activity and good stability to reduction of bromoadamantane by sodium borohydride. Tin leaching during successive reuses was estimated.

Introduction

In the course of our studies on the preparation and uses of polymer-supported organotin hydrides,[1] we were interested in the use of an easily accessible organotin-bearing monomer and a long storage life.

Chloro(dibutyl)[3-(allyloxy)propyl]tin **1** can be prepared in one step in an essentially pure form by monohydrostannylation of commercially available diallyl ether with the easily prepared dibutylchlorotin hydride[2] (Scheme 1). This new monomer possesses several advantages: (i) As an allylic ether it does not homopolymerise;[3] its long-term storage stabilily is therefore excellent. (ii) The long alkyl chain separating the tin moiety from the allylic group can act as a spacer-arm linking to the polymer backbone. In terms of copolymerisation behaviour, the allylic ethers act as electron donors, so, to form polymers *via* free radical propagation, they have to be copolymerised with electron-acceptor monomers such as maleimides.[4]



Scheme 1 Synthesis of chloro(dibutyl)[3-(allyloxy)propyl]tin **1**.

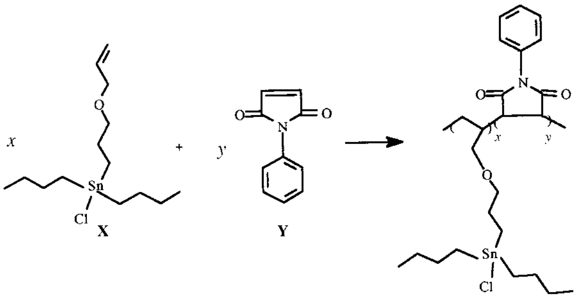
The resulting resins were expected to show different behaviour, in terms of mechanical strength and polarity, from the polystyrenic-based supports usually used in polymer-supported chemistry. There are only a few studies in the literature of the radical copolymerisation of allyl ethers and maleimides. Boutevin[5] made an interesting study of the radical copolymerisation of allyl glycidyl ether with *N*-methyl- and *N*-phenylmaleimide. He found that, in both cases, the insertion of the allylic comonomer did not reach more than 30%. So he proposed that the copolymerisation was more statistical than alternating, and he explained this result using the (*Q*, *e*) scheme. The *N*-phenylmaleimide has a large *Q* value (2.81) compared with allyl alkyl ethers (around 0.09); furthermore, its *e* value (3.24) is of opposite sign to the values calculated for allyl alkyl ethers (−2.5).

Bearing this in mind, we decided to investigate the possibility of inserting a reasonable amount of monomer **1** in an *N*-phenylmaleimide (PMI) macromolecular chain by a radical process. The results obtained being quite positive, we decided to prepare a series of macroporous supports using these two monomers with 1,1′-(methylenedi-4,1-phenylene)bismaleimide (MPBMI) as the crosslinking agent. The reactivity of the polymer-supported tin hydrides obtained was then tested in a series of classical reactions.

Results and discussion

Preparation and structural analysis of the supports

Copolymerisation of chloro(dibutyl)[3-(allyloxy)propyl]tin 1 with *N*-phenylmaleimide. The copolymerisation of **1** and PMI was performed using various molar ratios in toluene at 80 °C with AIBN as a radical initiator (Scheme 2). The results are reported in Table 1. These copolymer compositional data indicate that the copolymerisation is not alternating irrespective of the initial monomer composition used. With equimolar



Scheme 2 Solution copolymerisation of compound **1** and PMI.

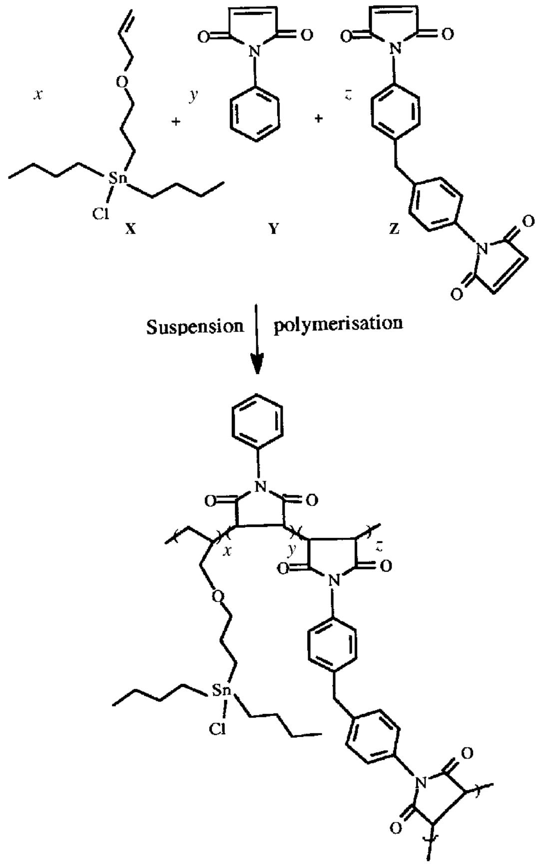
Table 1 Solution copolymerisation of chloro(dibutyl)[3-(allyloxy)-propyl]tin **1** and PMI

Entry	Molar ratio in monomer feed		Molar ratio[a] in polymer		Conversion (%)
	PMI	**1**	PMI	**1**	
1	0.75	0.25	0.93	0.07	14
2	0.50	0.50	0.84	0.16	15
3	0.25	0.75	0.84	0.16	6

[a] Estimated from elemental analysis (% N for PMI, % Sn for **1**).

initial quantities, the molar insertion of the allyl ether, at low conversion, was ~16%. These results are consistent with those obtained by Boutevin.[5] Therefore, the pendant organotin moiety seems to have little effect on the copolymerisation behaviour. The level of insertion of the organotin monomers is, however, high enough for this system to be used in the preparation of functionalised polymer supports.

Macroporous resin synthesis. The different supports were synthesised according to Scheme 3. The comonomer feed consisted of various molar ratios of chloride **1**, PMI as a chain diluent and MPBMI as crosslinking agent with a fixed amount (1 : 1 in volume relative to the monomers) of a mixture of inert solvents as the porogen. The suspension polymerisations were performed as previously described.[1] The influence of the nature of the stabiliser dissolved in the aqueous phase and the composition of the porogenic mixture was investigated. Use of a precipitant diluent in the preparation of macroporous copolymers is known to give resin beads, at least in the case of the styrene–divinylbenzene (DVB) system with low-to-medium specific surface areas and a high-porosity volume.[6] The addition of a solvating diluent to the mixture of styrene–divinylbenzene allows the morphology of the resin to be adjusted to some extent.[7,8] There is, however, much less information in the literature in this context concerning maleimide-based copolymer systems.[9]



Scheme 3 Suspension copolymerisation.

Assuming the same behaviour for our system as that for styrene–divinylbenzene, our purpose was to find a porogen which, while able to solubilise the mixture of monomers, was a precipitant for the resulting copolymer. The monomers used, *i.e.* two maleimides and an ether, being of quite different polarity, meant that prediction of a good or a bad solvent for their copolymers was quite difficult to achieve.

PMI and chloro(dibutyl)[3-(allyloxy)propyl]tin **1** are soluble in most common organic solvents, whereas MPBMI, due to its rigid structure, is soluble at rt only in polar solvents such as DMF or DMSO. After an extensive search, *N*-methylformanilide was selected as one of the porogens for the following reasons: it is a good solvent for MPBMI, and therefore for the other monomers, and it is not significantly soluble in water. As *N*-methylformanilide is expected to behave as a solvating diluent of the macromolecular chains, toluene was added, in some experiments, to form a precipitating porogen mixture. The proportion of the latter was limited by the poor solubility of MPBMI in this solvent. The mixtures of toluene and *N*-methylformanilide used allowed each experiment to start with a homogeneous monomer mixture. In all experiments the volumetric ratio monomer : porogen was kept to 1 : 1.

The composition of the organic phases used in the suspension polymerisations is reported in Table 2. The loading and molar composition of the recovered polymers were estimated directly from the elemental content of the heteroatoms (N, Sn and Cl) present in the resins. The mole fractions of the residues from the three monomers involved on the copolymerisation were calculated as follows: n_1, n_2 and n_3 are the molar loadings (mmol g^{-1}) of the moieties corresponding to chloride **1**, PMI and MPBMI, respectively, inserted into the polymer backbone; x, y and z are the corresponding mole fractions and M_1, M_2 and M_3 are the relative molecular masses of the monomers **1**, PMI and MPBMI respectively. These parameters are related as shown in equations (1)–(3).

$$1 = n_1M_1 + n_2M_2 + n_3M_3 \tag{1}$$

$$n_1 = \frac{\%\text{Sn}}{118.69 \times 100} \tag{2}$$

$$n_2 + 2n_3 = \frac{\%\text{N}}{14 \times 100} \tag{3}$$

The assumption that the relative reactivity of PMI and the first double bond of MPBMI are the same during the course of the polymerisation leads to the relationship (4):

$$\frac{n_2}{n_3} = \frac{y}{z} \tag{4}$$

Thus equations (5)–(7) hold:

$$n_3 = \frac{\%\text{N}}{14 \times 100 \times \left(2 + \frac{y}{z}\right)} \tag{5}$$

$$n_2 = \frac{y}{z}n_3 \tag{6}$$

$$x = \frac{n_1}{n_1 + n_2 + n_3} \quad y = \frac{n_2}{n_1 + n_2 + n_3} \quad z = \frac{n_3}{n_1 + n_2 + n_3} \tag{7}$$

The calculated values for x, y and z are reported in Table 3. By comparison of these with the initial composition of the mixture of monomers, it can be seen that the conversions of

Table 2 Suspension copolymerisations—composition of the organic phase

	Molar fractions in monomer mixture[a]						Polymerisation porogenic mixture toluene/*N*-methylformanilide
Entry	**X**	**Y**	**Z**	**Y/Z**	N (%)	Sn (%)	(vol/vol)
P1	0.50	0.27	0.15	1.8	1.8	1.8	1/1
P2	0.62	0.26	0.11	2.4	1.5	2.0	1/1
P3	0.57	0.26	0.17	1.5	1.8	1.8	4/1
P4	0.47	0.34	0.19	1.8	2.4	1.6	4/1
P5	0.47	0.34	0.19	1.8	2.4	1.6	4/1
P6	0.47	0.34	0.19	1.8	2.4	1.6	4/1
P7	0.47	0.34	0.19	1.8	2.4	1.6	0/1
P8	0.23	0.63	0.14	4.1	6.6	3.0	0/1

[a] Molar fractions in monomer mixture: **X** = chloro(dibutyl)[3-(allyloxy)propyl]tin **1**; **Y** = PMI, **Z** = 1,1′-(methylenedi-4,1-phenylene)bismaleimide.

Table 3 Suspension copolymerisations—composition of the polymeric supports

				Loading (mmol g^{-1})			Molar fractions[e]					
Entry	Stabilizer	N (%)	Sn (%)	N	Sn	Cl	**X**	**Y**	**Z**	Polymer yield (%)	Usable beads (100–500 μm) (%)	N_2 BET surface area (m^2 g^{-1})
P1	[a]	4.9	5.1	4.9	0.5	0.6	0.12	0.56	0.32	55	80	19
P2	[b]	5.5	7.4	3.9	0.6	0.8	0.17	0.58	0.25	20	62	23
P3	[b]	6.3	4.3	4.5	0.4	0.3	0.13	0.55	0.31	25	83	5
P4	[d]	7.0	3.8	4.2	0.4	0.5	0.11	0.57	0.31	30	75	9
P5	[c]	5.8	5.1	4.2	0.5	0.5	0.15	0.54	0.29	45	82	8
P6	[a]	5.9	5.6	4.2	0.5	0.3	0.15	0.54	0.29	45	59	6
P7	[c]	6.0	6.5	4.3	0.5	0.4	0.14	0.55	0.31	52	78	3
P8	[c]	6.6	3.0	4.7	0.3	0.3	0.06	0.76	0.18	59	67	3

Stabiliser in the aqueous phase: [a] Xanthan gum 0.4%. [b] Xantham gum 0.2%. [c] Xanthan gum 0.1%. [d] Poly(diallyldimethylammonium chloride) 3.5%. [e] Molar fractions in polymer network: **X** = chloro(dibutyl)[3-(allyloxy)propyl]tin **1**; **Y** = *N*-phenylmaleimide; **Z** = 1,1′-(methylenedi-4,1-phenylene)-bismaleimide.

PMI and MPBMI are quite high. In contrast, the insertion of the allyl ether derivative into the backbone is significantly lower (~15%), this level being close to the one obtained in solution copolymerisation (16%). This result indicates that, even at a high conversion, the copolymerisation between chloride **1** and maleimides is not alternating. However, the Sn content of the final supports was found to be remarkably constant (~0.5 mmol Sn g^{-1}) for all the supports synthesised irrespective of the polymerisation conditions. This figure was estimated to be sufficient for the resulting resins to be used as polymer-supported organotin catalyst precursors. The good correlation observed between the Sn and the Cl contents on the different supports is a strong indication of the preservation of the chlorotrialkyltin structure during the polymerisation step. The calculated nominal crosslinking level was found to be ~30% for all the supports prepared (exepted for entry P8). However, the specific surface areas (as estimated by the Brunauer, Emmet and Teller (BET) nitrogen adsorption method) calculated for the spherical polymer beads obtained were quite low.

Swelling behaviour. The swelling behaviour of crosslinked polymers in different solvents gives some information about the internal structure: gel-type resins are usually expected to swell very significantly in compatible solvents and much less in precipitating solvents. Macroporous structures prepared with a precipitating porogen tend to swell only moderately even in the best solvents.[10] In order to quantify the degree of swelling of the beads, swelling ratios were obtained as follows: The apparent volume of the dry beads (2 g) was measured within a cylindrical glass tube (25 cm^3). An organic solvent was added to the tube, the air bubbles entrapped were removed by gentle stirring, then the resin was allowed to swell at rt for 24 h.

The swelling ratio was calculated from the equation (8):[11]

$$S\,(\%) = (V_S - V_D)/V_D \qquad (8)$$

Where V_S = volume of swollen beads (cm^3), and V_d = volume of dry beads (cm^3).

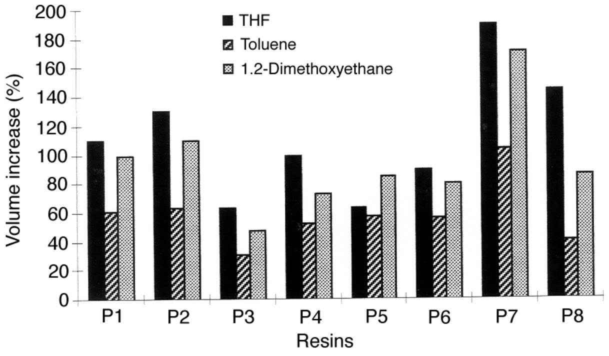


Fig. 1 Swelling of resins in different solvents.

The results obtained are reported in Fig. 1.

The swelling capacities of the resins prepared with toluene–*N*-methylformanilide mixtures as porogen using a volumic ratio of 4 : 1 (resins P3, P4, P5 and P6) are similar in toluene and 1,2-dimethoxyethane and more important in THF. With a volumic ratio of 1 : 1 for the toluene–*N*-methylformanilide porogenic mixtures, the swelling of the resulting resins is more important in the three solvents tested (resins P1 and P2). The volume increase of the resin prepared with *N*-methylformanilide as sole porogen (P7 and P8) was found to be significantly higher in all solvents tested. The swelling capacities of these novel resins are generally higher in toluene than those obtained with macroporous organotin-functionalised polystyrene resins prepared previously.[1] This observation, coupled with the low specific surface area observed, suggests that the real structure is more gel-type than expected due to a low efficiency of the bismaleimide as a crosslinking agent under the conditions of the polymerisation used.

Reactivity tests of the polymer-supported tin hydrides. *1. Stirring conditions.* One of the main problems encountered with the use of insoluble polymeric beads in laboratory batch

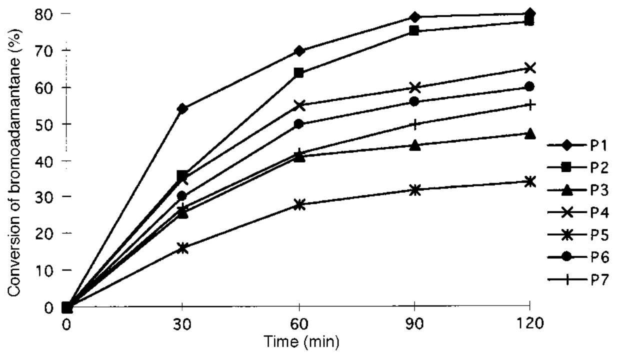


Fig. 2 Catalytic activity of the polymer-supported organotin hydrides. Reduction of 1-bromoadamantane (1 equiv.) with sodium borohydride (5 equiv.) at 95 °C in 1,2-dimethoxyethane using 0.1 equiv. of polymer-supported Sn-Cl.

reactors is the abrasion of the polymer caused by constant magnetic stirring. Seebach described recently[12] an apparatus using the "tea bag" approach.[13] This system looks efficient but requires a rather large amount of solvent.

We considered that the main problem was associated with the "millstone effect" of the stirring bar in contact with the bottom of the reactor. We thus designed a magnetic bar suspended by a flexible nylon wire thread above the container base. The wire, being attached to a swivel, turns torsionlessly at the same speed as the bar. This latter, spinning freely in the solvent without contact with the walls of the reactor, produces a gentle movement of the beads allowing the heterogeneous reaction to occur without degradation of the beads even in a rather low volume of solvent.

2. *Catalytic reduction of 1-bromoadamantane.* The different polymer-supported organotin hydrides synthesised were evaluated as catalysts in a reaction often proposed in the literature as a test of reactivity,[14] *i.e.* the reduction of 1-bromoadamantane by sodium borohydride. The molar amount of tin chloride was fixed at 10% with respect to the 1-bromoadamantane, the sodium borohydride being in a 5-fold excess. The conversions to adamantane reached in 2 h at 95 °C in 1,2-dimethoxyethane for the different resins tested are reported in Fig. 2.

The results obtained are the average of at least two duplicate experiments. The data are quite difficult to explain in term of a structure–activity relationship but it seems that the nature of the porogen used plays an important role: The resins P1 and P2, prepared with a 1 : 1 volumic ratio of a mixture of toluene and *N*-methylformanilide, display good activity (almost 80%), whereas, resins P3, P4 and P6, prepared with a ratio 4 : 1 (therefore more rich in toluene), are somewhat less active. Resin P7, prepared using *N*-methylformanilide as sole porogen, is, as well, less efficient. The specific surface area, as estimated by the BET method, seems not to be a good indication of activity in these species. There was almost no reaction in the absence of an organotin catalyst.

3. *Estimation of the leaching.* One of the major claims for using polymer-supported organotin species is the possible reduction in contamination of the final product by organotin species.[15] Therefore, it seemed important to us to try to estimate the level of tin leaching from our resins under different conditions of use. Hence, a sample of resin P1 (amount necessary to reach 0.1 equiv. of Sn) was suspended in 1,2-dimethoxyethane (15 cm^3) containing adamantane (150 mg, 1.1 mmol) for 6 h. After cooling, the polymer was filtered off, then washed with diethyl ether. The collected filtrate was concentrated to dryness then the tin content was analysed by Atomic Absorption Spectroscopy (AAS).[16]

The influence of 2 parameters was investigated: (i) the temperature of the reaction; an increase of temperature may increase the decomposition of the resin; tests were performed at 65 and 95 °C; (ii) the stirring which can break the beads and may release oligomers into the solution; when used, the stirring was performed with a suspended magnetic bar at low speed (50 rpm) as described above. The results are reported in Table 4. It appears from these data that the main parameter influencing the leaching of tin is the temperature of use of the resin. Somewhat unexpectedly the use of an ether–maleimide copolymer instead of the usual styrene–DVB system does not seem to increase the temperature range of use of these tin-containing resins. At 95 °C, a significant thermal degradation occurs leading to the release of tin-bearing oligomers or fragments into solution. The effect of the stirring is much less dramatic (Table 4, entries 1 and 2) probably due to the gentleness of the method we adopted.

Table 4 Leaching of tin under different conditions of use of resin P1

Entry	Temperature (T/°C)	Stirring (yes/no)	Tin content of the product (ppm)	Leaching of initial tin content (%)
1	65	N	220	0.3
2	65	Y	270	0.4
3	95	N	410	1.2
4	95	Y	800	0.6

4. *Recycling tests.* It is very important, when developing a polymer-supported catalyst, to investigate its stability during successive runs in a batch reactor.[14] This study was performed with resin P1 using the reduction reaction described previously. Two kinds of experiments were performed: the first one (method A) with washing of the beads successively with water, ethanol and then diethyl ether between two runs; the other (method B) without washing. Each run was conducted for 2 h after which the polymer was filtered off, then used again with a fresh solution of 1-bromoadamantane, sodium borohydride and AIBN. The results obtained are reported in Fig. 3. From these, it can be concluded that the evolution of the activity on recycling can be divided in three parts; (i) an increase of activity of the resin during the first 3 runs, then (ii) a series of runs with maximum activity (close from 100%) followed by (iii) a slow decrease in activity from run 7. The washing of the beads between two runs clearly reduces the deactivation of the catalyst, probably by removing the water-soluble borate derivatives obstructing the pores of the support.

An estimation of the evolution of the loss of tin from the support during successive runs, using method A, was made using the procedure described above. The results are reported in Table 5. A slow decrease of leaching can be observed with successive runs, with a levelling at ~0.5% per run (the reactions were performed at 95 °C because at 65 °C the rate of reduction was very low). During the 8 runs performed the average conversion in 2 h was 89%; thus 1.85 mmol of 1-bromoadamantane was reduced by NaBH$_4$ in adamantane using 1.5% (molar) of polymer-supported organotin chloride. The total leaching of tin during these experiments (48 h at 95 °C) was estimated to be ~20% (molar) of the initial loading.

Experimental

Fourier transform IR (FTIR) spectra were recorded on a Perkin-Elmer Paragon 100 spectrometer; ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer with CDCl$_3$ solutions and Me$_4$Si as internal standard. ^{119}Sn NMR spectra were recorded on a BRUKER AC 250 spectrometer operating at 89.15 MHz. Elemental microanalytical data were provided by the Service central d'analyse du CNRS, Vernaison, France, with an error of 0.3% for C, H, N and 0.5% for Cl, Br and Sn.

Nitrogen adsorption isotherms were obtained using a Micromeritics Acusorb 2100E apparatus, University of Strathclyde, Glasgow, UK and the resultant data were subjected to a Brunauer, Emmet and Teller (BET) treatment for the determination of the specific surface area.

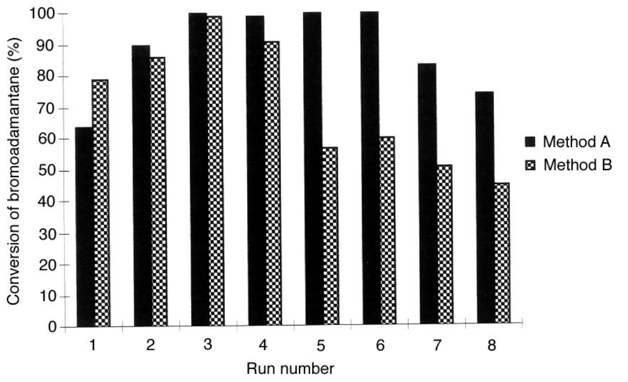


Fig. 3 Catalytic stability of the polymer-supported organotin hydride. Reduction of 1-bromoadamantane (1 equiv.) with sodium borohydride (5 equiv.) at 95 °C in 1,2-dimethoxyethane using 0.1 equiv. of polymer-supported Sn-Cl (% conversion in adamantane after 2 h). Method A: washing of beads between the runs. Method B: without washing.

Table 5 Tin leaching of resin P1 during successive runs

Run	1	2	3	4	5	6	7
Tin content of the product (ppm)	570	450	420	370	380	350	350
Leaching of initial tin content (%)	0.8	0.65	0.6	0.55	0.55	0.5	0.5

Catalytic reduction (0.1 equiv. Sn-Cl) of 1-bromoadamantane (1 equiv.) by $NaBH_4$ (5 equiv.) at 95 °C in 1,2-dimethoxyethane using method A (see Fig. 3).

Materials

PMI (Aldrich), MPBMI (Aldrich), styrene (Dow-Chemical.Co) and diallyl ether (Aldrich) were used as supplied.

Stabilisers

The suspension stabilisers poly(diallyldimethylammonium chloride) (PDDAC, high viscosity, 20% aq. solution) (Aldrich) and Xanthan gum (Aldrich) were also used as received. The remaining solvents and chemicals were general purpose species.

Synthesis of dibutylstannane (Bu_2SnH_2). Dibutylstannane was synthesised according to a procedure previously described.[1]

Synthesis of chloro(dibutyl)[3-(allyloxy)propyl]tin 1. A two-necked flask was charged with diallyl ether (52.9 g, 538.9 mmol) and dibutyltin dichloride (16.5 g, 53.9 mmol). The flask was purged with N_2, and dibutylstannane (12.8 g, 53.9 mmol) was added dropwise. The mixture was stirred overnight and the unchanged allyl ether was evaporated off under vacuum. The residue was then filtered to yield an oil (37.8 g, 95%), ^{1}H-NMR $\delta(CDCl_3)$ 0.8–2.0 (m, 22 H, aliphatic), 3.4 (t, 2 H, $^3J_{H\text{-}H}$ 5.5 Hz, CH_2CH_2O), 3.9 (d, 2 H, $^3J_{Hd\text{-}Hc}$ 6 Hz, $OCH_2CH{=}CH_2$), 5.2 (m, 2 H, $CH{=}CH_2$) and 5.7–5.8 (m, 1 H, $CH{=}CH_2$); ^{13}C-NMR $\delta(CDCl_3)$ 13.7 (CH_3), 15.0 and 18.7 (CH_2Sn, $^1J_{C\text{-}Sn}$ 220 Hz), 26.0, 26.8 and 27.9 (CH_2), 71.2 (CH_2CH_2O), 72.4 (CH_2O-$CH{=}CH_2$), 119.3 ($CH_2{=}CH$) and 133.1 ($CH{=}CH_2$); ^{119}Sn-NMR $\delta(CDCl_3)$ +66 (complexation) (Calc. for $C_{14}H_{29}ClSn$: C, 45.4; H, 7.8; Sn, 32.1; Cl, 9.6%. Found: C, 45.1; H, 7.8; Sn, 32.6; Cl, 10.2%).

Suspension polymerisation. The macroporous supports were prepared by a conventional aq. suspension polymerisation using a parallel-side flanged glass reactor specially designed according to the literature.[17] The organic comonomer mixture was suspended, with continuous stirring, in an aq. phase containing either mixtures of Xanthan gum (0.1, 0.2 or 0.4% w/v) and ethylcellulose (0.2% w/v) or a mixture of high-molecular-mass PDDAC (3.5% w/v) and gelatin (0.15%) as, respectively, stabiliser and dispersant.

In a typical reaction a mixture of comonomers (15 cm^3), porogen (toluene–*N*-methylformanilide 1 : 1 v/v, 15 cm^3) and AIBN (100 mg) as the free-radical source was suspended in 240 cm^3 of aq. phase (aq : organic ratio 8 : 1). The stirring speed was adjusted (usually between 500 and 600 rpm) at rt in order to obtain, visually, droplets of satisfactory size. The reactor was then placed in a thermostatted bath and the polymerisation was run at 80 °C for 8 h. After cooling, the reaction mixture was filtered and washed successively with copious quantities of water, ethanol, then DMF, then was continuously extracted for 24 h with, successively, toluene, ethanol, then THF in a Soxhlet apparatus. After a last washing with diethyl ether, the beads were dried under vacuum at 60 °C for 24 h. The dry beads were sieved and both the very fine and the large particles were discarded.

Catalytic dehalogenation experiments. All reactions were performed under argon with carefully degassed solvents.

A typical catalytic reduction run was performed as follows: A 50 cm^3 three-necked flask was charged with 1,2-dimethoxyethane (15 cm^3), 1-bromoadamantane (0.26 mmol, 55.9 mg), the polymer-supported tin chloride (0.026 mmol SnCl) and dodecane (40 mg, 0.26 mmol) as an internal standard. The reactor was purged with argon, then sodium borohydride (25 mg, 0.52 mmol) and AIBN (4 mg, 0.026 mmol) were added and the flask was heated with an oil-bath at 95 °C. Aliquots (0.1 cm^3) of reaction mixture were withdrawn periodically and analysed by gas chromatography (DB5 column; N_2 carrier; 10 °C min^{-1} temperature gradient from 95 to 200 °C; injector 200 °C; detector 220 °C; 15 psi). The reaction was stopped at completion or by cooling to rt. In the recycling experiments another solution of $NaBH_4$, 1-bromoadamantane and AIBN in 1,2-dimethoxyethane was added and the reaction was performed again. In some recycling experiments the beads were recovered by suction filtration, and washed successively with water, ethanol and finally diethyl ether before being reused (see Results and discussion section).

Conclusions

We have developed the use of a non-styrenic organotin functionalised monomer synthesised in one step from readily available materials. The copolymerisation of this monomer with commercially available maleimides was investigated and insoluble macroporous supports containing reasonable levels of tin (≈0.5 mmol g^{-1}) were obtained using different suspension polymerisation conditions. The activity and stability toward recycling of the polymer-supported organotin hydride were demonstrated in the catalytic reduction of 1-bromoadamantane to adamantane by $NaBH_4$.

The major cause of the rather important leaching of tin from the support was attributed to the high temperature used (95 °C) in the reaction.

Our present work is now directed toward lowering the reaction temperature—using other kinds of initiator than AIBN—and to a better understanding of the influence of the structure of the support on its activity. Applications of the polymer-supported organotin hydrides to radical cyclisation reactions are underway.

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