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Cross-linked resins functionalized with triorganotin carboxylates: synthesis, characterization and preliminary catalytic screening in transesterification

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Cross-linked polymers containing triorganotin carboxylate functionalities were synthesized from ionic exchange resins bearing carboxylic groups. The organic tin substituents selected were methyl and butyl in order to ensure different accessibility at the metal centre. The functionalization degree depends on the different substituents and strongly affects the thermal stability of the final product. Catalytic screenings were performed in order to assess the activity of the above resins in transesterification reactions, using ethyl acetate as a substrate, together with differently hindered alcohols. The results obtained point to a negligible role of the bulkiness of tin substituents with a small contribution of the metal atom Lewis acidity in the conversion of the primary alcohol, whereas with secondary and tertiary alcohols the steric hindrance of the reagent strongly affects the conversion of the reacting alcohol. The transesterification process takes place at the liquid–solid interface, so that the catalyst grafted to an insoluble solid support can be completely removed by simple filtration. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: triorganotin carboxylate; functionalized resins; transesterification reaction; transesterification catalyst; tin coordination

INTRODUCTION

Organotin compounds have found a large number of applications as catalysts or intermediates in organic synthesis.[1–3] In particular, organotins are known as homogeneous catalysts in transesterification reactions,[4] in which the interaction of the carbonyl oxygen atom with the Lewis acidic metal centre activates the carbonyl carbon atom toward nucleophilic attack of the alcohol.[5]

Despite their versatility, actual applications of these products are hampered by their toxicity, since they are often difficult to remove completely from the reaction mixture, especially when the process is conducted on an industrial scale.[6] This leads to organotin contamination of the final product and to inconvenient losses of catalyst.

In order to overcome these drawbacks, the organotin moiety can be grafted onto an insoluble polymeric support, allowing the catalyst to be recovered by simple filtration and easily recycled after reaction. In this context, several cross-linked polymers bearing organotin moieties in the side chain have been synthesized, generating so-called clean organotin reagents; their syntheses are often complex and multi-stepped, but their final performances as a heterogeneous transesterification catalyst are usually satisfactory.[7,8]

In connection with our interest in triorganotin carboxylates as anion carriers,[9,10] we recently observed that these materials can also be used as transesterification catalysts, likely due to the Lewis acidity of the tin atom, which is affected by the presence of the carboxylic moiety. This finding looks very attractive, since it offers the possibility of easily grafting

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the organotin group onto a polycarboxylic acid by a simple esterification reaction.

The aim of this study, therefore, is to assess the effectiveness of the triorganotin carboxylate moiety as a heterogeneous catalyst in transesterification reactions. For this purpose, a commercially available resin containing free carboxylic acid groups (Fluka Amberlite IRC-86) was functionalized with $SnMe_3$ and $SnBu_3$ moieties. After functionalization, the resins were characterized and screened in the transesterification of ethyl acetate with simple alcohols[8] in order to show the most important features affecting the catalytic activity, with a view to further development of cross-linked systems that are most appropriate to these kinds of applications.

EXPERIMENTAL

Chemicals were supplied by Sigma Aldrich and generally used as received. Solvents were purified using normal purification techniques.[11] Commercially available resin of the Fluka Amberlite IRC-86 type was used as received or after drying overnight at 130 °C.

IR spectra in KBr pellets were recorded on a Perkin Elmer 1750 FT-IR spectrometer. ^{117}Sn NMR spectra in the solid state were recorded using a Bruker Avance 250 NMR spectrometer and tetracyclohexyltin as an external standard. The ^{1}H and ^{119}Sn hr-MAS spectra were recorded on a Bruker AMX500 instrument operating at 500.13 MHz and 186.50 MHz respectively, with an especially dedicated Bruker $^{1}H/^{13}C/^{119}Sn$ hr-MAS probe equipped with gradient coils, by using full rotors containing approximately 20 mg of resin beads, swollen in approximately 100 µl of $CDCl_3$ and magic angle spinning at 4000 Hz. $(CH_3)_4Sn$ was used as internal reference. Thermogravimetric analysis (TGA) was carried out on a TGA-7 Perkin Elmer thermobalance in air.

Functionalization reaction of Amberlite IRC-86 with trimethyltin hydroxide

Working in a dry box, under controlled argon atmosphere, 1.8 g (10 mmol) of trimethyltin hydroxide was added in a 100 ml round-bottomed flask. When the flask was taken out of the dry box, 2.52 g of wet Amberlite IRC-86 resin (containing 9.9 mmol of carboxylic acid) suspended in toluene (30 ml) was added and the flask was equipped with a Dean–Stark apparatus. The reaction mixture was heated at reflux for 24 h, until no more water vaporization was observed. The resin was filtered off from the solvent and unreacted trimethyltin hydroxide and subsequently stirred in chloroform for 2 h in order to allow complete removal of the organotin reagent. The product was finally dried at 130 °C overnight.

The functionalization extent of the carboxylic groups is 11%, based upon elemental analysis (all elements), with a 92/8 ratio of acrylic acid/divinylbenzene.

Anal. Found. C: 47.34; H: 5.81; O: 33.89; Sn: 11.11. Calc. C: 48.86; H: 5.78; O: 32.38; Sn: 12.97%. ^{1}H hr-MAS (ppm): 0.00; −0.12; −0.17 (rel. intensity 2; 48; 50): CH_3 singlets. ^{119}Sn hr-MAS (ppm): −1 (narrow); −58 (broad); −69 (broad). FT-IR (cm^{-1}): 3437 (ν_{OH} acid); 2959–2922 (ν_{CH} aliph.); 1701 ($\nu_{C=O}$ acid); 1634 ($\nu_{C=O_{symm}}$ organotin ester); 1465 (δ_{CH_2} main chain); 1384 ($\nu_{C=O_{asymm}}$ organotin ester); 793 ($\delta_{1,4-subst.ring}$ arom.).

Functionalization reaction of Amberlite IRC-86 with bis(tri-*n*-butyltin) oxide

In a 250 ml round-bottomed flask, equipped with a Dean–Stark apparatus, 20 ml (39.3 mmol) of bis-(tri-*n*-butyltin) oxide (BTBTO) was dissolved in toluene (100 ml) and 10 g of wet Amberlite IRC-86 resin (containing 39.3 mmol of carboxylic acid) was added. The reaction mixture was heated at reflux for 6 h, until no more water vaporization was observed. The solvent and the unreacted BTBTO were filtered off and the resin was stirred in chloroform for 2 h to allow the complete removal of the organotin reagent. Finally, the product was dried at 130 °C overnight.

The functionalization extent of the carboxylic groups is 75%, based upon elemental analysis (all elements), with a 92/8 ratio of acrylic acid/divinylbenzene.

Anal. Found. C: 50.22; H: 7.65; O: 9.70; Sn: 29.10. Anal. Calc. C: 51.06; H: 8.42; O: 10.71; Sn: 29.81%. ^{1}H hr-MAS (ppm): 1.6 (CH_2), 1.3 (CH_2), 0.92 (CH_3). ^{119}Sn hr-MAS (ppm): 95. ^{117}Sn CP-MAS (ppm): 90. FT-IR (cm^{-1}): 3401 (ν_{OH} acid); 2957–2851 (ν_{CH} aliph.); 1709 ($\nu_{C=O}$ acid); 1651 ($\nu_{C=O_{symm}}$ organotin ester); 1465 (δ_{CH_2} main chain); 1383 ($\nu_{C=O_{asymm}}$ organotin ester); 694 (δ_{CH_2} butyl).

Assessment of the catalytic activity in transesterification reactions

In a 100 ml round-bottomed flask, ethyl acetate (used simultaneously as a transesterification substrate and solvent) was added to the appropriate high boiling-point alcohol (1-octanol, cyclohexanol, 3-ethyl-3-pentanol) so as to obtain a molar ratio 7/1. A convenient amount of the insoluble catalyst (calculated in order to guarantee 1 mol% of tin-containing units with respect to the alcohol) was added to the reaction mixture heated to reflux; the reaction progress was evaluated after 24 and 48 h. Finally the catalyst was filtered off and washed with diethyl ether and chloroform; the unreacted ethyl acetate was distilled under reduced pressure and the reaction mixture analysed by ^{1}H NMR in order to assess the extent of transesterification.[8]

RESULTS AND DISCUSSION

Synthesis and characterization of the functionalized resin

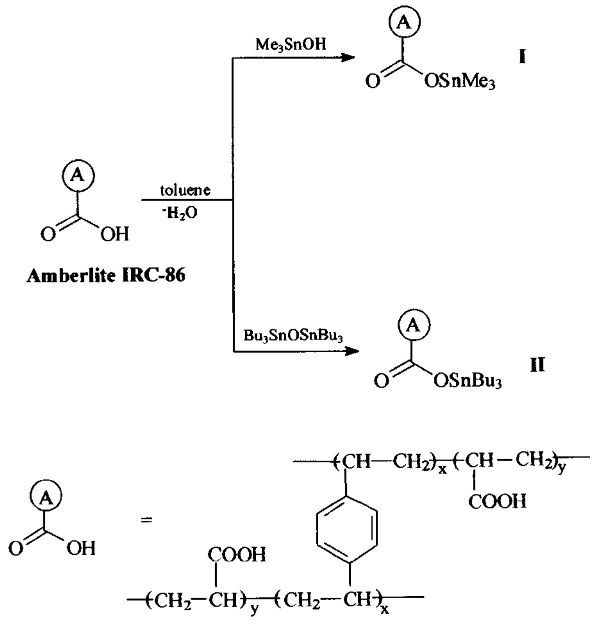
A preliminary assessment of the activity of the triorganotin carboxylate used as a heterogeneous transesterification catalyst requires an insoluble polymeric support that is easy to functionalize and not too expensive in order to afford a first, low-cost evaluation of its properties. The ideal cross-linked matrix should contain free carboxylic groups that are reasonably easy to quantify, since their insolubility hampers their characterization to a large extent. For all these reasons, the macromolecular support selected was Fluka Amberlite IRC-86, a commercial cation exchange gel-type resin, which is a divinylbenzene–acrylic acid copolymer containing no actual porosity, so that the access to the internal functional groups is driven by diffusional processes. Despite this potential limitation, this material is not brittle and generally reacts quickly in functionalization reactions.

The water content of the commercially available Amberlite IRC-86 resin, evaluated by gravimetric analysis, was 51%. The elemental analysis data of the starting Amberlite, after thorough drying for 48 h were 54.19% carbon, 6.17% hydrogen and 38.04% oxygen. According to these data, the content of acrylic acid is 92%.

The present preliminary work focused on the trimethyl- and the tri-*n*-butyl-tin derivatives, which are characterized by similar Lewis acidities, the latter displaying a somewhat larger steric hindrance on the metal site.

The Amberlite IRC-86 functionalization was carried out by direct esterification of carboxylic moieties with trimethyltin hydroxide (**I**) and bis(tri-*n*-butyltin) oxide (**II**), as depicted in Scheme 1. The water obtained as a side-product was azeotropically distilled using a Dean–Stark apparatus in order to shift the equilibrium towards the desired organotin carboxylates.

The synthesis of the trimethyltin carboxylate (**I**) derivative was first attempted through the formation of a polycarboxylate salt by treatment of the resin with NaOH solution, followed by reaction with trimethyltin chloride.[12] However, this synthetic route was discarded, since the highest functionalization extent of the carboxylic groups was 0.04%, as determined by tin elemental analysis.



Scheme 1.

Attempts were also made to synthesize the triphenyltin carboxylate derivative, which would be very interesting from the catalytic point of view, since in this case the tin atom possess a stronger Lewis acidity, when compared with the trialkyltin analogues. Unfortunately, no functionalization at all was ever obtained, probably due to the lower nucleophilicity of the oxygen atom in the triphenyltin hydroxide; moreover, the very high steric hindrance of the triphenyltin moiety and the poor accessibility of the acrylic carboxylic residue strongly affected by the presence of the cross-linked polymer backbone could have been an additional limiting factor.

The reaction progress was monitored by FT-IR spectroscopy: observation of the decrease of the intensity of the band centred at 1718 cm^{-1} (related to the carbonyl stretching of the carboxylic acid), and a new absorption attributed to the organometallic ester formation appears at around 1630–1650 cm^{-1}, depending on the nature of the tin substituent.[13] Since complete functionalization could not be achieved, all the functionalized resins' spectra show the band of the free carboxylic acid at about 1715 cm^{-1}. Moreover, the relative intensities of the two different carbonyl stretching vibrations of each stannylated polymer show a significant difference when changing the tin substituent, as depicted in Fig. 1. In fact, for the tri-*n*-butyltin ester containing polymer

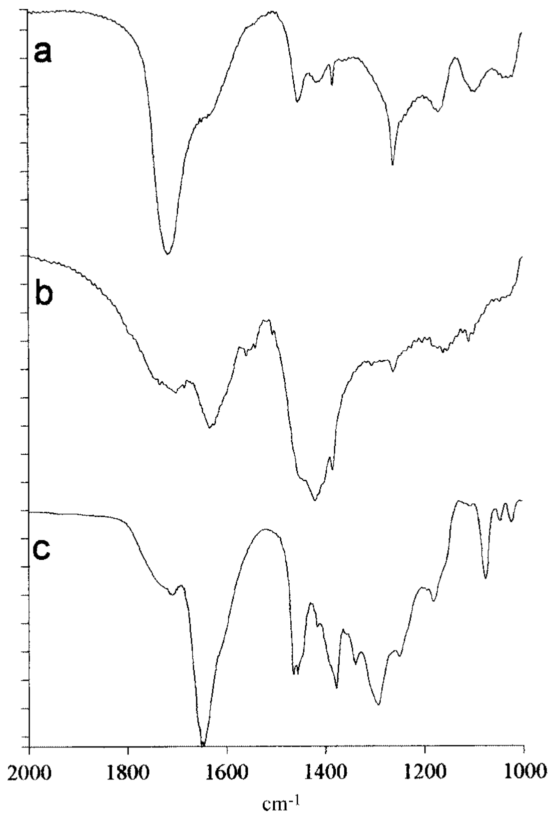


Figure 1. FT-IR spectra of Amberlite IRC-86 (a), trimethyltin ester derivative **I** (b) and tributyltin ester derivative **II** (c).

(**II**) the absorption ascribed to the acidic carbonyl is almost negligible, whereas for the trimethyltin derivative (**I**) the two bands are of similar intensity. These observations account for different degrees of functionalization, depending on the tin reactant used.

All of the above products show the absorption band at around 1630–1650 cm^{-1}, typical of a carbonyl function not interacting with tin, so that no expansion of the coordination number from 4 to 5 occurs,[14] at least for compound **II**; in fact, in the latter case, the expected absorption at around 1560–1580 cm^{-1} is not present. This observation can be explained on the basis of chain stiffness due to highly cross-linked resin, thus preventing a significant interaction between the carbonyl oxygen atom and neighbouring tributyltin moieties. Compound **I**, however, shows a small absorption at around 1570 cm^{-1} that could be tentatively attributed to pentacoordinated tin.[13]

In order to assess quantitatively the functionalization extent of the carbonyl moieties in the starting Amberlite IRC-86, and then the actual amount of tin in each compound synthesized, the latter being a critical parameter in the catalyst activity, elemental analysis of all elements was performed on the starting Amberlite IRC-86 and both the stannylated samples. The data were treated using a home-made computer program based on the mathematical MATLAB package, as explained elsewhere.[8] In brief, the method consists of determining the functionalization extent by a non-linear least-squares analysis of all elemental mass fractions, making use of calibration curves giving the functionalization degree as a function of the mass fraction for each element as calculated for all target compounds. The elemental analysis data of dried Amberlite IRC-86 (C: 54.19; H: 6.17; O: 38.04%) thus reveal that the resin contains 92% acrylic acid residues and 8% divinyl benzene. Taking this ratio (92/8) into account, the amount of stannylated carboxylic acid functions amount to 11% and 75% for **I** and **II** respectively. These data are in agreement with the FT-IR spectra trends, confirming a remarkable difference in the final extent of carboxyl group functionalization (Table 1). Only the esterification using BTBTO, leading to the tributylstannyl compound **II**, could be achieved without any problem, and the final functionalization extent was the highest possible reached (75%).

All the products synthesized were analysed by TGA, in order to assess their maximum working temperature, and the results compared with those of Amberlite IRC-86. Degradation temperatures T_d were determined as the temperature where the first massive weight loss occurs (Table 2). As displayed in Fig. 2, the presence of tin-functionalized moieties lowers dramatically the thermal stability of the resins: in fact, even the 11% organotin carboxylate groups present in **I** causes a dramatic temperature drop of about 70 °C in the first significant weight loss. However, a further increase of the tin-containing units does not seem to affect this parameter anymore. Previous studies[14] on soluble systems containing triorganotin carboxylate moieties outlined two opposite effects of the organometallic group: the first enhances T_d through tin interactions with electron-withdrawing groups, such as the neighbouring carbonyl functionalities, and leads to a pentacoordinated tin-based supramolecular structure that stabilizes the whole system; the second accounts for the organotin carboxylate favouring the polymer degradation process, mainly in the presence of oxygen. In the present case, the cross-linked structure (8% of divinylbenzene co-units) prevents the generation of the supramolecular structure between the tin and carbonyl functionalities, particularly when the organometallic units are diluted in the bulk, thus leading to an overall destabilizing contribution to the degradation temperature.

Both the stannylated products, heated at 20 °C min^{-1} from room temperature to 900 °C in air, reach a constant weight at about 600–630 °C, the residue consisting of SnO_2, while the Amberlite IRC-86 affords a complete weight loss at about the same temperature (Fig. 2), as expected on the basis of the resin composition. For the tin-functionalized compounds, the amount of inorganic residue is sometimes significantly different than expected on the basis of tin elemental analysis (Table 2). For this reason, TGA was unsuitable for assessing the actual metal content in these products, in order to determine the polymer composition.

Table 2. Degradation temperature and tin content of the polymeric derivatives

		Tin content (% w/w)	
	T_d[a] (°C)	Elemental analysis	TGA residue
Amberlite IRC-86	298	—	—
I	222	11.85	0.42
II	222	28.25	29.9

[a] Determined as the temperature of the first weight loss.

Table 1. Functionalization data of Amberlite IRC-86 with different triorganotin residues

Reactant	Reactant feed (mmol)	COOH content in Amberlite IRC-86 feed (mmol)	Reaction time (h)	Extent of COOH functionalization[a] (%)
Me_3SnOH	10	9.9	24	11
$Bu_3SnOSnBu_3$	39.3	39.3	6	75

[a] Determined by elemental analysis.

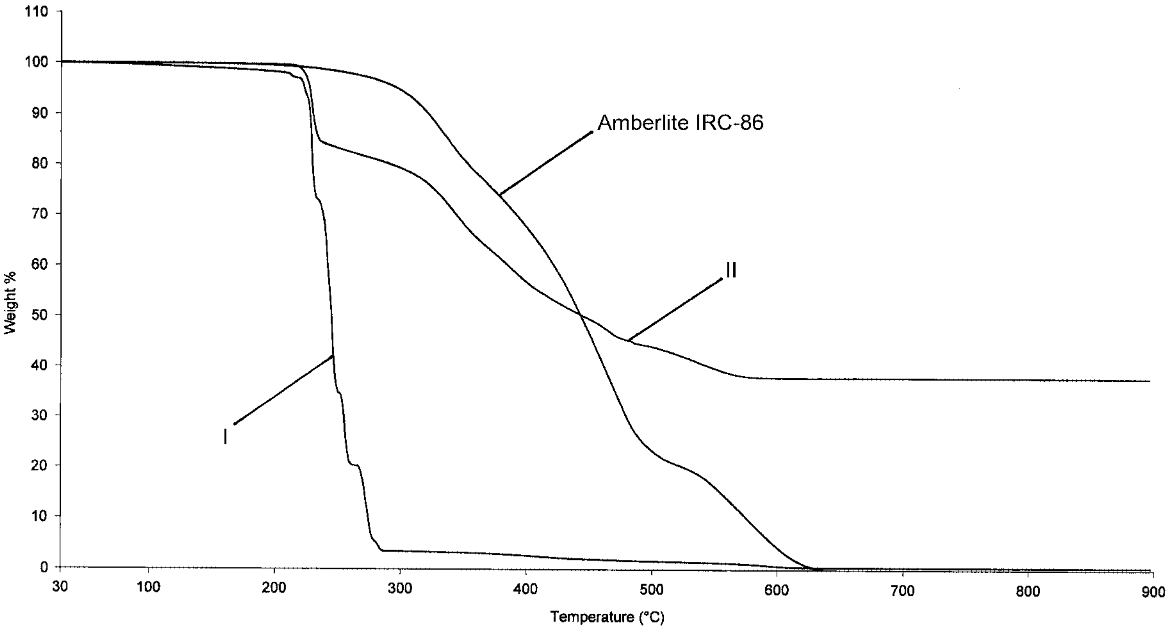


Figure 2. TGA patterns of Amberlite IRC-86, trimethyltin ester derivative **I** and tributyltin ester derivative **II**.

With the aim of assessing the coordination degree of the tin atom, $^{117/119}$Sn NMR spectra of the polymers were recorded both in the solid state and on $CDCl_3$-swollen resins, the coordination number of tin appearing as a key factor affecting the catalytic performances of the transesterification reactants.

The ^{117}Sn-CPMAS-NMR spectrum of the tributyltin derivative (**II**) shows one resonance, with the isotropic chemical shift at 90 ppm attributed to tetracoordinated tributyltin carboxylate. In contrast to earlier observations on polymers grafted with a tributyltin carboxylate functionality, no resonance for pentacoordinated species (ca −40 ppm) is found.[9,10] The absence of pentacoordination is confirmed by FT-IR spectra lacking the typical absorption in the region 1560–1580 cm^{-1} (Fig. 1c). Also, in the ^{119}Sn hr-MAS spectrum of this compound only one resonance at 95 ppm is observed.

The trimethyltin derivative **I** displays a narrow tin resonance at −1 ppm and two broader resonances at −58 and −69 ppm in the ^{119}Sn hr-MAS spectrum of the solvent-swollen resin. The ^{119}Sn chemical shift for a tetracoordinated trimethyltin carboxylate is expected at ca 130 ppm,[15] suggesting that the trimethyltin derivative has undergone coordination expansion. Coordination expansion implies that the tin atom coordinates either 'intramolecularly' with the second oxygen atom of the carboxylate moiety or with a carboxylate oxygen atom of a neighbouring acrylate subunit. In the FT-IR spectrum, a small absorption in the region 1560–1580 cm^{-1} is visible, confirming the existence of a tin atom, coordinating with a free carboxylic acid.

The ^{1}H hr-MAS spectrum of the trimethyl derivative contains two intense tin methyl resonances and a third smaller one. The ^{1}H–^{119}Sn HMQC spectrum under MAS conditions[16,17] gives three correlation peaks, i.e. the small CH_3 resonance correlates with a tin resonance at −1 ppm, and the two intense methyl resonances at −0.12 ppm and −0.17 ppm correlate with the tin resonances at −58 ppm and −69 ppm respectively. These chemical shifts are in the region of the chemical shift of (solid) polymeric trimethyltin formate[18] and trimethyltin carbonate,[19] compounds that contain trigonal-bipyramidal trans Me_3SnO_2 units connected via bridging formate or carbonate anions respectively. This implies that the trimethyl derivative contains mostly associated tin carboxylate species, with two different chemical environments. This is not surprising, since it is a copolymer containing two different units. These observations in **I** are in strong contrast to the tributyltin derivative **II**, which only contains monomeric tetracoordinated tin atoms.

Assessment of catalytic activity in transesterification reaction

The catalytic activity of the synthesized products was assessed in a transesterification reaction using ethyl acetate and differently hindered alcohols, in order to investigate the role of the accessibility of the hydroxyl and ester carbonyl groups to tin on the overall catalytic performance.[8] The weight of catalyst added was calculated in order to have 1 mol% of the tin-containing units with respect to the selected high boiling-point alcohols, i.e. 1-octanol, cyclohexanol and 3-ethyl-3-pentanol.

All the reactions were also examined either in the absence of the catalyst or with the unfunctionalized Amberlite IRC-86, with the aim of assessing the possible influence of any possible additional contributions to the reaction other than those involving the organotin carboxylate moiety; no conversion at all was detected in any of these reactions without tin.

Table 3. Conversions obtained in catalytic transesterification reaction of ethyl acetate with sterically hindered alcohols

	Conversion[a] (%)					
	1-Octanol		Cyclohexanol		3-Ethyl-3-pentanol	
Catalyst	24 h	48 h	24 h	48 h	24 h	48 h
I	10	23	4.8	5.2	0	0.3
II	14	33	3.0	5.6	0	0.7

[a] Determined on the basis of the starting alcohol.

The results obtained for the reaction of ethyl acetate with the less sterically hindered alcohol 1-octanol (Table 3) show the presence of some catalytic activity, not strongly influenced by the bulkiness of the tin substituents. Upon increasing the steric hindrance of the alcoholic reactant, passing to cyclohexanol, the conversions are lowered to about 5% regardless of the tin substituents (Table 3); besides the intrinsically lower reactivity of a secondary alcohol with respect to a primary alcohol, this may be due to the higher steric demand of the intermediate being formed during the activation process, as a consequence of the grafting. Accordingly, the transesterification of ethyl acetate with 3-ethyl-3-pentanol leads only to traces of the desired products (Table 3) even after the longest reaction time addressed. Anyway, in the last two cases, the poor accessibility to the tin atom does not appear to depend on the tin substituents, since the trimethyltin derivative **I** shows the same feature as the more hindered analogue **II**. Such a behaviour could thus be ascribed to the low accessibility to the carboxylic moiety, which is directly linked to the main chain of the insoluble macromolecular support with a high steric hindrance.

Though NMR and IR do not qualify optimally as techniques to assess the absence of trace amounts of tin, no organometallic derivative could be observed by any one of these techniques when the transesterification solution was checked. This is a relevant point, since this observation implies that the organometallic ester would remain unmodified in the transesterification conditions, without any leaching from the solid support. However, analysis for possible trace amounts of tin, undetectable by IR and NMR spectroscopy, remains to be done.

An approach to this kind of problem is suggested in the literature, where the release of active species from a heterogeneous support is hypothesized and defined as 'Greek warriors from the Trojan Horse'.[20] In order to exclude this possibility, we have carried out a simple experiment where the catalyst is thoroughly filtered off from the mixture after 24 h reaction and the clear solution allowed to react for a further 24 h. Indeed, we have verified that no further transesterification reaction occurred in the absence of solid catalyst.

Table 4. Elemental analysis data for compounds **I** and **II** before and after use as catalyst in a transesterification reaction

	C (%)	H (%)	O (%)	Sn (%)
I before catalysis	47.34	5.81	33.89	11.11
I after catalysis	47.28	5.80	33.34	10.89
II before catalysis	50.22	7.65	9.70	29.10
II after catalysis	50.61	8.14	11.10	27.97

The filtered catalysts, after washing with diethyl ether and chloroform, were analysed in order to assess their stability when submitted to the reaction conditions. The analysis data relevant to all elements (Table 4) show no significant change in the catalyst after one transesterification run for **I**, whereas the slightly stronger changes observed for **II** in tin and oxygen contents nevertheless remain within an acceptable experimental uncertainty margin for these elements, which are more difficult to quantify accurately. Moreover, the FT-IR spectra of the recovered products **I** and **II**, after the transesterification reactions, look similar to the starting ones, as shown in Fig. 3 for product **II**. Indeed, not only the carboxylic ester appears to be unchanged, but also no esterification occurred on the unfunctionalized carboxylic moieties deriving from incomplete organometallic esterification. In fact, no evident signal of organic ester formation on the graft appears at ca 1740 cm^{-1} after the transesterification reaction. Moreover, the ^{1}H and ^{119}Sn hr-MAS spectra of the catalysts used are identical within experimental error to those before use. In view of all the above-mentioned arguments, we can safely rule out significant tin leaching from the graft into the reaction medium. This behaviour can be attributed to the high steric demand and stiffness of the cross-linked support, which prevents the polymer's free carboxylic groups from access by the organometallic sites to form an activated adduct, since both are firmly anchored to the polymer main chain.

CONCLUSIONS

Functionalization of Amberlite IRC-86 with two different organotin residues was achieved, albeit to very different extents of carboxyl conversion, depending on the starting reactant. Products were characterized by FT-IR and $^{117/119}$Sn NMR spectroscopy, showing the presence of tin in its tetracoordinated form for the tributyl derivative, whereas the trimethyl derivative seems to be pentacoordinated, according to hr-MAS measurements. The thermal characterization outlines the degrading effect of the tin-containing units on the functionalized resins; anyway, the initial degradation temperature is above 200 °C, thus allowing a possible industrial application for all the stannylated samples prepared.

The grafting of triorganotin carboxylate moieties onto an insoluble resin leads to a material featuring some interesting catalytic properties that could be conveniently improved by

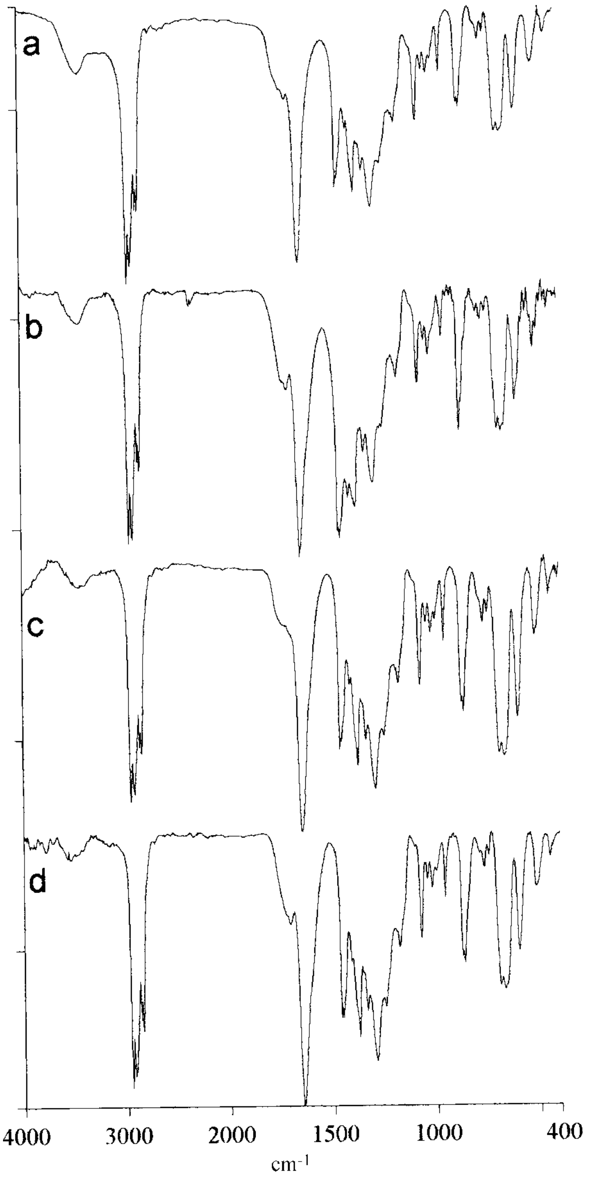


Figure 3. FT-IR of native **II** (a) and after transesterification test with primary (b), secondary (c) and tertiary (d) alcohols.

modification of the polymeric support and increasing of the metal centre's Lewis acidity.

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