Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 691 (2006) 1965–1972

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Triorganotin 4-isopropylbenzoates as model transesterification catalysts for triorganotin carboxylates grafted to cross-linked polystyrene

Luigi Angiolini [a,*], Daniele Caretti [a], Laura Mazzocchetti [a], Elisabetta Salatelli [a], Rudolph Willem [b], Monique Biesemans [b]

[a] Dipartimento di Chimica Industriale e dei Materiali, University of Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy
[b] High Resolution NMR Centre (HNMR), Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium

Received 24 October 2005; received in revised form 29 December 2005; accepted 3 January 2006
Available online 14 February 2006

Abstract

Starting from 4-isopropylbenzoic acid, three new triorganotin carboxylates bearing methyl, butyl and phenyl substituents at tin, respectively, were prepared and fully characterized by spectroscopic and thermal techniques, with particular regard to the coordination number of tin atom, in solution as well as in the solid state. The triorganotin compounds, tested as transesterification catalysts in the reaction between ethyl acetate and primary, secondary or tertiary alcohol, respectively, displayed, as expected, a strong decrease of activity on passing from the primary to the tertiary alcohol reactant. Different activities by the tin carboxylates were also observed in the reaction between primary alcohol and ethyl acetate. The reaction mechanism, as elucidated by Sn NMR, involves coordination of both ester substrate and alcohol reactant to the triorganotin compound, the reaction conversion appearing related not only to the Lewis acidity of the tin atom, but also to the nature of the reactants. Preliminary catalytic tests were also carried out in the reaction between glyceryl tridodecanoate (as a model of natural triglyceride) and ethanol, mimicking the preparation of biodiesel fuel. Although in this case lower conversions were obtained with respect to the reactions on ethyl acetate, the catalytic activity of organotin derivatives appears considerable.

Keywords: Carboxylate ligands; IR spectroscopy; NMR spectroscopy; Organotin; Transesterification

1. Introduction

Since their first biocidal application in the early 1920s [1], the production of organotin compounds [2] has increased for various purposes mainly in the last decades, covering a wide variety of applications, being used in antifouling paints [3–5], PVC stabilization [6], as homogeneous catalysts [7], in antitumour therapy [8] and as ion carriers in electrochemical membranes design [9].

Their actual use remains however limited by their toxicity, particularly when they can be released into the environment, or when they are retained in the final product as catalyst residues [10,11].

The pollution problems raising from the use of organotins can be conveniently addressed by covalently grafting the organometallic moiety to a macromolecular support [12], thus lowering or even preventing tin release into the environment [13], leading to the so-called "clean organotin derivatives" [14–19]. Tin compounds grafted to polymeric carbon chains experience growing interest since alkyltin moieties in polymers or copolymers mimic well the properties of their non-polymeric organotin analogues.

---

[*] Corresponding author. Tel./fax: +39 051 2093687.
E-mail address: luigi.angiolini@unibo.it (L. Angiolini).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.002

In this context, the preparation of non-polymeric model compounds may conveniently parallel the synthesis of related polymeric derivatives when is aimed to reproduce the repeating unit of the polymer, thus allowing to assess the influence of the macromolecular chain on the behaviour of the organometallic moiety.

In particular, when the insolubility of cross-linked polymeric derivatives prevents the application of many common analytical techniques, non-polymeric model compounds, more amenable to full characterization, offer a key support to the assessment of features which would be otherwise undetectable by direct observation.

In the course of our current investigations dealing with the synthesis and characterization of cross-linked systems bearing triorganotin carboxylate residues [20], intended as grafted transesterification catalysts active at the liquid–solid interface, we have prepared the trimethyltin (**2**), the tributyltin (**3**) and the triphenyltin (**4**) esters of 4-isopropylbenzoic acid (**1**, Chart 1) as structural models for the related styrenic repeating unit of stannylated cross-linked polymers possessing the general structure depicted in Chart 2.

The present paper is aimed therefore at investigating structure and catalytic activity of model compounds **2**–**4**, in order to gain a preliminar insight into the properties of the related cross-linked derivatives, which are presently under investigation. Particular attention is focused not only onto the tin atom coordination expansion which is believed to play a key role in the catalytic performances, but also onto the evaluation of the Lewis acidity of the differently substituted organotin derivatives, as an useful indicator of their catalytic potential in transesterifications involving different hindered alcohols. In addition, a model reaction for the *biodiesel* production by transesterification of renewable materials such as vegetable oils [21–23] is presented.

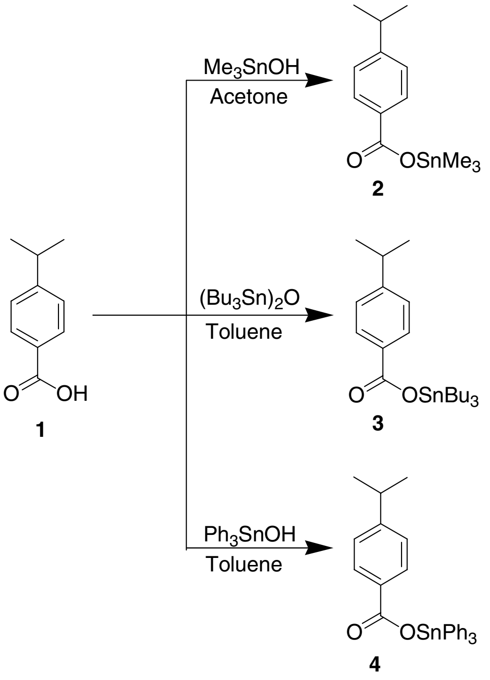

Chart 1. Synthesis of compounds **2**–**4**.

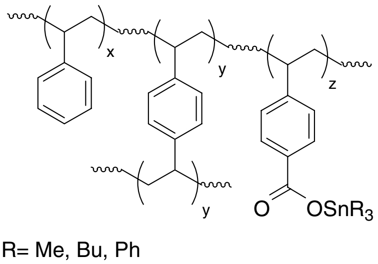

Chart 2. General structure of cross-linked polymers.

2. Results and discussion

2.1. Synthesis and structural characterization

Direct triorganostannylation of a carboxylic acid with the appropriate bis(triorganotin) oxide is one of the most commonly used methods [24] to obtain triorganotin carboxylates, along with reaction of the carboxylic acid with the suitable triorganotin hydroxide [25]. The water produced in both cases as a by-product can be conveniently removed from the reaction mixture by azeotropic distillation with toluene, in order to push the reaction to completion.

As represented in Chart 1, we have applied this well established synthetic pathway to synthesize both the tributyltin (**3**) and triphenyltin (**4**) carboxylic esters, starting from commercial 4-isopropylbenzoic acid (**1**), which was allowed to react with bis(tributyltin)oxide and triphenyltin hydroxide, respectively. While in the latter case separation of the reaction product from unreacted stannylating reagent was straightforward, the isolation of **3** from unreacted tin hydroxide required the treatment of the crude reaction mixture with a weak ionic exchange resin (Fluka Amberlite IRC-86), which is able to entrap the organometallic reagent present in excess [26], thus allowing to obtain pure **3**.

The synthesis of the trimethyltin ester **2** from 4-isopropylbenzoic acid (**1**) was achieved by direct esterification with trimethyl tin hydroxide, but using in this case acetone as the reaction solvent in order to operate at a refluxing temperature low enough to prevent undesired sublimation of the reacting trimethyltin hydroxide during the reaction. The water produced was separated in this case by 5A molecular sieves added to the reaction mixture and the final elimination of unreacted reagent was simply achieved by sublimation under reduced pressure and gentle heating.

Model compounds **2**–**4** were all characterized by FT-IR as well as NMR spectroscopy.

The infrared asymmetric stretching vibration of the newly formed triorganotin carboxylate group appears in the range 1630–1635 cm^{-1} for both **3** and **4**, while the sym-

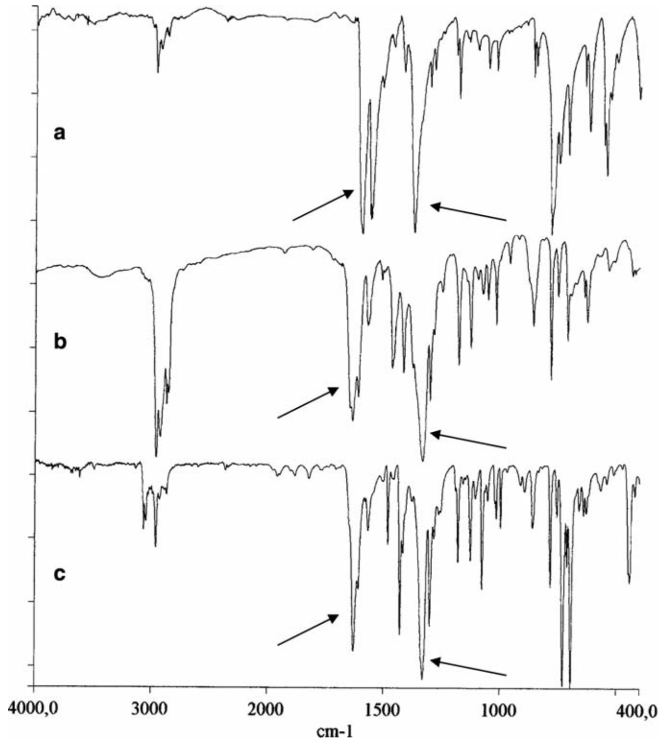

Fig. 1. FT-IR spectra of **2** (a), **3** (b) and **4** (c).

metric one lies around 1330 cm^{-1} (Fig. 1b and c), these bands being related to a carbonyl moiety free from any interaction with the metal atom [27], therefore evidencing tetracoordinated tin in **3** and **4** in the bulk.

This behaviour, well established for analogue non-polymeric compounds bearing the triphenyltin carboxylate moiety, is uncommon for tributyltin derivatives. These last compounds are in fact usually pentacoordinated [28,29], at least when not hindered by the presence of a macromolecular backbone, as demonstrated by X-ray crystallography [30].

The unusual non-coordinated arrangement of the tin atom in **3** can tentatively be attributed to the concomitant contribution of both the conformational rigidity of the molecule due to π conjugation, inducing restricted rotation around the phenyl ring–carboxylate bond, and the steric hindrance of the butyl groups, apparently preventing the carbonyl oxygen from interaction with tin. The steric hindrance of the Me_3Sn moiety in **2** being lower, such a restriction to tin coordination by the carbonyl oxygen atom is no longer holding, as demonstrated by the carbonyl absorptions in the FT-IR spectrum of **2** (Fig. 1-a), with asymmetric and symmetric stretching bands at 1595 and 1371 cm^{-1}, respectively, indicative of pentacoordination [30] at tin. The frequency values found for the triorganotin derivatives **2**–**4** parallel those of the related triorganotin *p*-vinyl benzoate monomeric derivatives [21], displaying a strictly similar coordination behaviour at tin.

With the aim of assessing their structure, products **2**–**4** have been investigated by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, using in particular two-dimensional correlation techniques.

The ^{1}H NMR resonances were fully assigned on the basis of COSY and HSQC experiments, since straightforward assignment of the aromatic proton resonances, based solely on standard ^{1}H NMR, failed. This was particularly the case for **4**, due to the presence of overlapping signals of the protons belonging to different aromatic rings.

The ^{119}Sn NMR spectra of **2**–**4** in dilute $CDCl_3$ solution (Table 1) show the same trend as the related styryl monomers [21], the actual chemical shift values of model compounds **2**–**4** being only slightly higher than those of the monomers, probably due to lower π conjugation. As expected in solution, all the observed resonances are typical of tetracoordinated tin atom [31].

Solid-state ^{117}Sn MAS NMR spectra could be obtained only for **2** and **4** (Table 1), given the oily state of the tributyltin derivative **3**. The observed resonances are in line with the FT-IR data, displaying $\delta(^{117}Sn) = -110$ ppm for **4**, a value typical of tetracoordinated triphenyltin moiety, similar to the value reported in solution [32]. By contrast, the trimethyltin derivative **2** shows a single isotropic chemical shift at 26 ppm, which can be assigned to pentacoordinated tin when the coordination with the carbonyl oxygen occurs intramolecularly [31].

The model compounds **2**–**4** were also investigated by DSC in order to get a deeper insight into their thermal properties, given the unusual tin tetracoordination in **3** in the solid state, as revealed by FT-IR.

When submitted to heating/cooling cycles in the temperature range 0–160 °C (Table 2), **2** shows an endothermic peak in the first heating, the enthalpy of which is similar to the one of the related exothermic process occurring during the cooling step. These thermal transitions can be referred to melting and subsequent crystallization of crystalline domains induced by pentacoordinated tin, as previously reported [26,33]. The same pattern is present in a second heating cycle, with melting enthalpy close to the values found in the first one, evidencing the complete reversibility of the transition.

By contrast, the triphenyltin derivative **4** does not display any thermal transition after the melting observed in the first heating step, thus confirming the absence of relevant crystalline domains formation, at least in the time scale of the DSC measurements.

The tributyltin derivative **3** when submitted to the same heating/cooling cycles in the range 0–160 °C as **2** and **4**, does not display any thermal transitions at all. However,

Table 1
^{119}Sn and ^{117}Sn NMR chemical shifts (ppm) of **2**–**4** in dilute (1%) $CDCl_3$ solution and in the solid state, respectively

Sample	Solution	Solid state
2	133	26
3	109	–
4	−115	−110

Table 2
Thermal behaviour of **2**–**4**

Sample	First heating step		First cooling step		Second heating step	
	T_m[a] (°C)	ΔH_m (kJ mol^{-1})	T_c[b] (°C)	ΔH_c (kJ mol^{-1})	T_m[a] (°C)	ΔH_m (kJ mol^{-1})
2	147	32.6	108	26.7	143	26.0
3[c]	–	–	−24	16.6	25	18.2
4	109	23.5	–	–	–	–

[a] Melting temperature at maximum endothermic peak height.
[b] Crystallization temperature at maximum exothermic peak height.
[c] Temperature range from −60 to 160 °C.

when the sample is cooled to −60 °C (starting temperature of the second cycle), an exothermic peak appears at −24 °C, the enthalpy of which is similar to that one measured for the endothermic transition at around 25 °C observed in the subsequent heating step. This observation explains the oily state of the product at room temperature, in addition to confirm its scarce tendency to give crystalline aggregates.

2.2. Assessment of the catalytic activity in transesterification reactions

The catalytic activity of the triorganotin carboxylates **2**–**4** was investigated in a transesterification reaction on ethyl acetate with differently hindered alcohols, namely 1-octanol, cyclohexanol and 3-ethyl-3-pentanol, in order to assess the influence on the catalytic performance of the accessibility to tin by the alcohol and ester carbonyl functions [19]. The amount of added catalyst was measured so as to achieve a 1% tin-to-alcohol molar ratio in all experiments. No attempt was made to remove the added catalyst from the reaction mixture, the reaction being performed in homogeneous phase for 48 h. All the reactions were also carried out in the absence of catalyst, no transesterification at all being detected, as required.

The alcohol conversion in each catalysed transesterification reaction (Table 3) was determined by GC after evaluation of the response factor of each species present.

The most effective catalyst appears to be **4**, giving the highest conversion after 24 h reaction of ethyl acetate with 1-octanol. The conversion is only slightly lower with **3**, and markedly lower with **2**.

Table 3
Alcohol conversions obtained in the catalysed transesterification of ethyl acetate

Catalyst	Alcohol conversion (%)					
	1-Octanol		Cyclohexanol		3-Ethyl-3-pentanol	
	24 h	48 h	24 h	48 h	24 h	48 h
2	19	43	5	6	–	Trace
3	76	95	7	9	–	Trace
4	95	100	10	17	–	Trace

The question raises as to whether, and, if so, how, the observed increase of catalytic activity from compounds **2** to **4** can be correlated to their Lewis acidity.

In order to address this issue, ^{119}Sn NMR spectra were recorded for compounds **2**–**4** in the presence of the actual reagents ethyl acetate and 1-octanol. For the sake of comparison in the assessment of the degree of tin complexation, acetone-d_6, likewise containing a carbonyl but no alkoxy function as in the ester, was first used as a reference solvent, so as to enable us to find out whether complexation occurs in the ester predominantly by its carbonyl or alkoxy function. As seen in Table 4, the ^{119}Sn resonances of **2**–**4** in acetone-d_6 are shifted to lower frequency, as expected for such a coordinating solvent. The trimethyltin derivative **2** displays the highest low frequency shift, and **4** the smallest one, which suggests a complexation stability toward tin by acetone decreasing from **2** to **4**. The smallest low frequency shift observed for the triphenyltin derivative **4** is somewhat surprising since the latter compound is generally assumed to have higher Lewis acidity [9,32,34].

The ^{117}Sn NMR spectra of compounds **2**–**4** in the presence of the transesterification reagents, either ethyl acetate or 1-octanol or mixtures of both (with a small amount of $CDCl_3$ as a deuterated lock solvent), shed some light into these observations (Table 5). In the presence of ethyl acetate alone, the low frequency shifts are only slightly smaller than in acetone-d_6, indicating that complex formation with an ester gives rise to only a slightly smaller shielding at the tin nucleus than acetone, in line with the well-known lower nucleophilicity of the oxygen atom of an ester carbonyl function with respect to that of a ketone; however the presence of $CDCl_3$ in ethyl acetate, by contrast with pure acetone-d_6, can also contribute to the lower shielding at the ^{117}Sn nucleus. Upon addition of pure 1-octanol a more pronounced low frequency shift is observed, thus suggesting a stronger complex formation with the alcohol than with the ester.

This is in contrast with earlier results on ring opening polymerisation of ε-caprolactone, initiated by *n*-propanol and catalysed by dibutyltindichloride, where ε-caprolactone displays stronger complexation toward tin than *n*-propanol [35]. No straightforward explanation of this finding can be presently proposed, except the observation that both the catalyst and the reactants in the transesterification here reported are notably different from those investigated in that report. In all cases, adding an amount of *n*-octanol to the triorganotin carboxylates **2**–**4** in ethyl acetate, induces an additional low frequency shift, implying that

Table 4
^{119}Sn NMR chemical shifts (ppm) in $CDCl_3$ and acetone-d_6 for compounds **2**–**4**

Sample	$\delta(^{119}Sn)$		$\Delta\ \delta(^{119}Sn)$
	$CDCl_3$	Acetone-d_6	Acetone-d_6 vs. $CDCl_3$
2	133	90	−43
3	109	84	−25
4	−115	−134	−19

Table 5
^{117}Sn Chemical shifts in solution of compounds **2**–**4** in the presence of the transesterification reactants, ethyl acetate (EtOAc) and 1-octanol (OctOH)

Solvent	**2** [Sn(Me)$_3$]		**3** [Sn(Bu)$_3$]		**4** [Sn(Ph)$_3$]	
	$\delta(^{117}Sn)$	$\Delta\delta$[a]	$\delta(^{117}Sn)$	$\Delta\delta$[a]	$\delta(^{117}Sn)$	$\Delta\delta$[a]
CDCl$_3$	133.0		109.3		−114.9	
100 μl CDCl$_3$ + 400 μl EtOAc	94.9	−38.1	87.5	−21.8	−126.6	−11.7
100 μl CDCl$_3$ + 400 μl EtOAc + 100 μl OctOH	77.7	−17.2	81.7	−5.8	−130.4	−3.8
100 μl CDCl$_3$ + 400 μl EtOAc + 200 μl OctOH	65.6	−12.1	76.9	−4.8	−133.7	−3.3
100 μl CDCl$_3$ + 400 μl EtOAc + 300 μl OctOH	57.9	−7.7	72.8	−4.1	−136.2	−2.5
100 μl CDCl$_3$ + 400 μl EtOAc + 400 μl OctOH	52.4	−5.5	69.6	−3.2	−138.7	−2.5
100 μl CDCl$_3$ + 400 μl EtOAc + 400 μl OctOH[b]	49.2	−45.7[c]	66.9	−20.6[c]	−139.3	−12.7[c]
100 μl CDCl$_3$ + 400 μl OctOH	34.8	−98.2	73.2	−36.1	−145.2	−30.3
100 μl CDCl$_3$ + 400 μl OctOH + 100 μl EtOAc	36.3	+1.5	66.5	−6.7	−149.3	−4.1
100 μl CDCl$_3$ + 400 μl OctOH + 200 μl EtOAc	40.8	+4.5	66.1	−0.4	−147.3	+2.0
100 μl CDCl$_3$ + 400 μl OctOH + 300 μl EtOAc	43.9	+3.1	66.5	+0.4	−145.7	+1.6
100 μl CDCl$_3$ + 400 μl OctOH + 400 μl EtOAc	46.6	+2.7	67.8	+1.3	−143.5	+2.2
100 μl CDCl$_3$ + 400 μl OctOH + 400 μl EtOAc[b]	46.7	+11.9[c]	67.4	−5.8[c]	−143.1	+2.1[c]

[a] Difference in chemical shift relative to previous situation.
[b] After two weeks.
[c] $\Delta\delta$ induced by total amount (400 μl) of OctOH or EtOAc.

the tin atom coordinates both reagents, and that ethyl acetate does not bind strongly enough to tin to prevent *n*-octanol from complexing likewise to tin, both reagents being brought in this way into a favourable position for the transesterification by a straightforward proximity effect. Table 5 indicates indeed not only that 1-octanol displays a stronger ^{117}Sn low frequency shift than ethyl acetate for all three triorganotin carboxylates **2**–**4**, but also that addition of further aliquots of 1-octanol to the ethyl acetate solution of the triorganotin carboxylate enhances the low frequency shift. This happens however to an increasingly limited extent, as evidenced by the increasingly smaller low frequency shift increments upon increasing the number of added 1-octanol aliquots. By contrast, the stronger complexation ability of 1-octanol is in turn supported by the finding that progressive additions of increasing aliquots of ethyl acetate to the 1-octanol solution does not enhance the shielding at the ^{117}Sn nucleus to a significant extent, deshielding tending even to take place in the case of **2**, while for **3** and **4** an approximately break even situation is obtained. This now suggests not only that 1-octanol is interacting sufficiently strongly with tin to be able to prevent significant further complexation of the tin atom by ethyl acetate, but also, somewhat paradoxically, that the latter, possibly, slightly destabilizes the 1-octanol–tin interaction. Overall, these findings strongly suggest that the Lewis acidity of the tin atom toward both ethyl acetate and 1-octanol decreases also in that order from **2** to **4**. In turn this means that, while the joined interaction of both the alcohol and ester with tin is a necessary condition for the catalytic activity, too strong a thermodynamic stability in this interaction, as observed for **2**, obviously disfavours the catalysis kinetics, compound **2** being precisely the one with the significantly lowest catalytic activity. Stated in other terms, the explanation for the transesterification proceeding better with the triphenyltin compound, where coordination of both the ester and alcohol is obviously weaker, is that although complex formation is indeed necessary, the complex has to be sufficiently labile in order to achieve fast exchange between incoming reactants and outgoing products. This conclusion was also reached in a study relating electrochemical chloride anion response to the structure of different tributyltin and triphenyltin carboxylates [9]. In this study, it was shown, by combining potentiometric anionic response data with ^{119}Sn NMR titrations and AM1 calculations, that the observed potentiometric response is related to the binding constant, but that carriers with too high binding constants show lower potentiometric response. In contrast to the present investigation, the triphenyltin carboxylates in the electrochemical response investigation showed a much higher affinity for the chloride anion than the corresponding tributyltin compounds, which was explained by their higher Lewis acidity. Thus Lewis acidity is not an intrinsic property, but also depends on the nature of the Lewis base with which the tin atom interacts, as well as on the chemical conditions, e.g., the solvent. In conclusion, toward 1-octanol as well as to ethyl acetate, the Lewis acidity of the tin atom decreases from **2** to **4**, a more labile Lewis base–acid interaction obviously favouring the catalysis kinetics.

Upon increasing the steric hindrance of the alcohol, switching to cyclohexanol, the achieved final conversion of the reactant (Table 3) is dramatically reduced, probably because of the lower reactivity of the alcohol due to the higher steric demand of the intermediate, the molecular mobility of which is lowered by the stiffness of the carboxylic residue, as already outlined for Amberlite derivatives [20]. Although differences in catalytic performances are small, an increasing trend is again observed from **2** to **4**. In the case of the tertiary alcohol, only traces of the desired products can be observed, confirming the determinant influence of steric hindrance.

Compounds **2**–**4** were also applied as catalysts in a model reaction mimicking *biodiesel* production by transesterification of vegetable oils with methanol. Vegetable oils are a renewable and potentially inexhaustible source of

Table 6
Triglyceride conversion obtained in the catalytic transesterification of glyceryl tridodecanoate with ethanol

Catalyst	Conversion (%)	
	24 h	48 h
2	27	30
3	20	25
4	43	49

energy with an energetic content similar to diesel fuel [36], and their transesterification with both methanol and ethanol leads readily to a product that can be directly combusted in unmodified diesel engines [36–38].

Our model reaction involves glyceryl tridodecanoate, a simplified triglyceride model, which is converted with an excess of ethanol into the corresponding fatty acid ethyl ester, the *biodiesel* fuel. The catalyst is added in 1% molar amount with respect to the triglyceride.

The glyceryl tridodecanoate conversion to ethyl dodecanoate in each catalytic run was assessed (Table 6) by ^{1}H NMR directly on the reaction mixture, after evaporation of unreacted ethanol.

The catalytic performances of the triorganotin catalysts in the triglyceride transesterification to produce *biodiesel* are lower for **3** and **4** but of similar efficiency for **2**, when compared to the transesterification of ethyl acetate with 1-octanol, which is ascribed to the low accessibility of the bulky reactants to the triorganotin carboxylate moiety directly linked to the aromatic ring. However, similarly to the reaction between ethyl acetate and 1-octanol, the activity of the trimethyl- and tributyltin derivatives **2** and **3** remains lower than that of the triphenyltin one **4**. The better score of **2** with respect to **3** is attributed to the superior accessibility to tin atom by the sterically demanding triglyceride with the trimethyltin carboxylate. Beyond the reaction time of 24 h it clearly appears that no further significant conversion takes place, indicating that the reaction with the glyceride cannot go to completion.

3. Conclusions

New catalytic systems containing various triorganotin carboxylate moieties were prepared by direct triorganostannylation of 4-isopropylbenzoic acid. The trimethyltin derivative exhibits tetracoordinated and pentacoordinated tin in solution and in the solid state, respectively. By contrast, both the tributyltin and triphenyltin esters display only tetracoordinated tin, regardless of their aggregation state.

The products displayed catalytic activity in the transesterification of ethyl acetate with decreasing efficiency on going from primary to secondary and tertiary alcohol. Interestingly, a significant reverse dependence on Lewis acidity is displayed in the transesterification with 1-octanol, the triphenyltin derivative being the most active, which is explained by the need of weak Lewis acid–base interaction between tin atom and both the transesterification reactants to obtain favourable kinetic features [39]. In the *biodiesel* model reaction between glyceryl tridodecanoate and ethanol, the catalytic performance of the system is lowered, confirming the limiting effect of the reactants bulkiness, however the triphenyltin catalyst displays again the best performance.

In spite of only moderate catalytic activities, the present investigation on model triorganotin carboxylates can serve as a basis, not only to a better understanding of the role of the Lewis acidity of the tin atom, in competition with steric demand, but also to the investigation on related triorganotin carboxylates grafted to cross-linked polymeric systems. It can also be hypothesized that improved performances as transesterification catalysts can be obtained by properly varying the substituents at tin as well as by optimally tuning the length of the spacer between the triorganotin carboxylate moiety and the aromatic ring of the cross-linked support, thus favouring a better, but still kinetically labile, accessibility by the reactants to the metal atom.

4. Experimental

All chemicals were supplied by Sigma–Aldrich, with the exception of trimethyltin hydroxide (Strem Chemicals), and generally used as received. Solvents were purified using usual purification techniques.

Elemental analyses were performed by REDOX s.n.c.(Milano).

^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded at room temperature on a Varian Gemini 300, a Varian Mercury 400, a Bruker AMX 500 or a Varian Inova 600 spectrometer using $CDCl_3$ solutions, unless otherwise stated, and tetramethylsilane as internal standard. ^{117}Sn NMR spectra in the solid state were recorded on a Bruker Avance 250 NMR spectrometer and tetracyclohexyltin as external standard. Notations: C_i = *ipso* carbon of the phenyl ring linked to triorganotin carboxylate; C_o (H_o) = *ortho*; C_m (H_m) = *meta*; C_p (H_p) = *para* carbon (hydrogen) atom with respect to carboxylate substituent.

Infrared spectra were recorded on a Perkin–Elmer 1750 FT-IR spectrometer on KBr pellets.

Melting points and ΔH_m values of stannylated compounds have been determined by differential scanning calorimetry (DSC) using a TA Instruments DSC 2920 modulated calorimeter operating under nitrogen at a heating/cooling rate of 10 °C/min; m.p. values are given as the temperature at the maximum of the endothermic peak.

4.1. *Trimethyltin(4-isopropylbenzoate)* (**2**)

In a 250 mL flask 4-isopropylbenzoic acid (1.00 g, 6.09 mmol) and trimethyltin hydroxide (1.10 g, 6.09 mmol) are dissolved in dry acetone (150 mL). Molecular sieves 5A are added to remove the water formed as by-product. The reaction mixture is heated at reflux, the reaction progress being monitored by FT-IR spectroscopy. The cloudy reaction mixture is finally filtered over a Celite path, in order to remove traces of molecular sieves, and the solvent evaporated under reduced pressure to leave an oily residue, which is kept under high vacuum, leading to a white solid. Yield 1.39 g (70%); m.p. 147 °C; $\Delta H_m = 32.6$ kJ mol^{-1}.

Elemental analysis (%): calc. for $C_{13}H_{20}O_2Sn$ (326.99) C 47.75, H 6.16, O 9.79; found: C 47.61, H 6.18, O 9.82.

^{1}H NMR (300 MHz): $\delta = 0.6$ (s, $^2J(^1H,^{119/117}Sn) = 58/56$ Hz, 9H; $SnCH_3$), 1.3 (d, 6H; CH_3CH), 2.9 (hept, 1H; CH_3CH), 7.3 (dd, 2H; H_m), 8.0 (dd, 2H; H_o) ppm.

^{13}C NMR (400 MHz): $\delta = -2.1$ ($^1J(^{13}C-^{119/117}Sn) = 381/399$ Hz; $SnCH_3$), 24.0 (CH_3CH), 34.4 (CH_3CH), 126.4 (C_m), 129.3 (C_i), 130.5 (C_o), 153.2 (C_p), 171.8 (COO) ppm.

FT-IR: 2963–2868 (ν_{CH} aliph.), 1595 ($\nu_{a\,COOSn}$), 1555, 1508 ($\nu_{C-C\,ring}$), 1371 ($\nu_{s\,COOSn}$), 1179, 1099; 1018 (δ_{CH} arom.), 860 (γ_{CH} 1,4-subst. ring) cm^{-1}.

4.2. *Tri-n-butyltin(4-isopropylbenzoate) (**3**)*

In a 100 mL flask equipped with a Dean-Stark apparatus, 4-isopropylbenzoic acid (1.00 g, 6.09 mmol) and bis(tributyltin) oxide (BTBTO) (1.55 mL, 3.05 mmol) are dissolved in toluene (20 mL). The reaction mixture is heated until no more water evolution is observed, the reaction progress being monitored by FT-IR spectroscopy. The oily crude product is separated from unreacted BTBTO by treatment in heterogeneous phase with dry Amberlite IRC-86 under stirring for 24 h. The resin is filtered off and washed with chloroform (3 × 20 mL), the combined chloroform extracts are evaporated under reduced pressure to give a yellowish oil. Yield 2.45 g (76%).

Elemental analysis (%): calc. for $C_{22}H_{38}O_2Sn$ (453.23) C 58.30, H 8.45, O 7.06; found: C 58.42, H 8.48, O 7.04.

^{1}H NMR (300 MHz): $\delta = 0.9$ (t, 9H; CH_3CH_2), 1.2 (d, 6H; CH_3CH), 1.4–1.2 (m, 12H; CH_2Sn and CH_3CH_2), 1.6 (m, 6H; $CH_2CH_2CH_2$), 2.9 (hept, 1H; CH_3CH), 7.3 (dd, 2H; H_m), 8.0 (dd, 2H; H_o) ppm.

^{13}C NMR (400 MHz): $\delta = 13.9$ (CH_3CH_2), 16.8 ($^1J(^{13}C-^{119/117}Sn) = 359/342$ Hz; CH_2Sn), 24.0 (CH_3CH), 27.2 ($^3J(^{13}C-^{119/117}Sn) = 63$ Hz; CH_3CH_2), 28.1 ($^2J(^{13}C-$119/117Sn) = 20 Hz; $CH_2CH_2CH_2$), 34.4 (CH_3CH), 126.4 (C_m), 130.0 (C_i), 130.5 (C_o), 153.5 (C_p), 171.8 (COO) ppm.

FT-IR: 2958–2871 (ν_{CH} aliph.), 1636 ($\nu_{a\,COOSn}$), 1611, 1571, 1509, 1416 ($\nu_{C-C\,ring}$), 1332 ($\nu_{s\,COOSn}$), 1178, 1127, 1018 (δ_{CH} arom.), 858 (γ_{CH} 1,4-subst. ring) cm^{-1}.

4.3. *Triphenyltin(4-isopropylbenzoate) (**4**)*

In a 100 mL flask equipped with a Dean-Stark apparatus, 4-(isopropyl)-benzoic acid (1.46 g, 8.89 mmol) and triphenyltin hydroxide (3.59 g, 9.78 mmol) are dissolved in toluene (50 mL). The reaction mixture is heated until no more water evolution is observed, the reaction progress being monitored by FT-IR spectroscopy. The solvent is evaporated under reduced pressure and the solid residue purified by crystallization from ethanol/water. Yield 3.65 g (80%); m.p. 109 °C; $\Delta H_m = 23.5$ kJ mol^{-1}.

Elemental analysis (%): calc. for $C_{28}H_{26}O_2Sn$ (513.20) C 65.53, H 5.11, O 6.24; found: C 65.39, H 5.09, O 6.26.

^{1}H NMR (300 MHz): $\delta = 1.2$ (d, 6H; CH_3CH), 2.9 (hept, 1H; CH_3CH), 7.3 (dd, 2H; H_m), 7.4–7.5 (m, 9H; $H_{m(SnPh)}$ and $H_{p(SnPh)}$), 7.8 (bs, 6H; $H_{o(SnPh)}$), 8.1 (dd, 2H; H_o) ppm.

^{13}C NMR (400 MHz): $\delta = 24.0$ (CH_3CH), 34.5 (CH_3CH), 126.5 (C_m), 129.1 ($^3J(^{13}C-^{119/117}Sn) = 63$ Hz; $C_{m\text{-}SnPh}$), 130.3 ($C_{p\text{-}SnPh}$), 131.0 (C_o), 131.2 (C_i), 137.1 ($^2J(^{13}C-^{119/117}Sn) = 47$ Hz; $C_{o\text{-}SnPh}$), 138.8 ($C_{i\text{-}SnPh}$), 154.4 (C_p), 173.1 (COO) ppm.

FT-IR: 3065–3046 (ν_{CH} arom), 2960–2867 (ν_{CH} aliph.), 1629 ($\nu_{a\,COOSn}$), 1608, 1566, 1508 ($\nu_{C-C\,ring}$), 1331 ($\nu_{s\,COOSn}$), 1180, 1126, 1077, 1052, 1016 (δ_{CH} arom.), 860 (γ_{CH} 1,4-subst. ring), 731 (γ_{CH} monosubst. ring), 696 (γ_{C-C} monosubst. ring) cm^{-1}.

4.4. *Assessment of the catalytic activity in ethyl acetate transesterification reactions [19]*

In a 100 mL round-bottomed flask, ethyl acetate (15 mL) used simultaneously as a transesterification substrate and solvent was added to the appropriate alcohol (1-octanol, cyclohexanol, 3-ethyl-3-pentanol) so as to obtain a molar ratio ester/alcohol 7/1. The reaction mixture was heated to reflux, in the presence of 1 mol% of catalyst with respect to the alcohol, the alcohol conversion being determined after 24 and 48 h by gas chromatography using an Agilent 6890 instrument equipped with a capillary methylsilicone column and an Agilent 5973 M mass detector.

4.5. *Assessment of the catalytic activity in glyceryl tridodecanoate transesterification reactions*

In a 100 mL round-bottomed flask, glyceryl tridodecanoate (1.0 g, 1.56 mmol) was added to an excess of absolute ethanol (50 mL). The reaction mixture was heated to reflux in the presence of 1 mol% of catalyst with respect to the ester, the reaction progress being determined after 24 and 48 h by integration of two selected resonances at 0.85 and 1.15 ppm in the ^{1}H NMR (600 MHz) spectra in DMSO-d_6 solution of the reaction mixture, after evaporation under reduced pressure of any unreacted ethanol.

Acknowledgements

This work was financially supported by the University of Bologna (*Progetti Pluriennali di Ricerca and Ricerca Finalizzata Orientata*) and Polo Scientifico-Didattico di Rimini (*Catalizzatori polimerici a basso impatto ambientale per reazioni di transesterificazione*).

M.B. and R.W. are indebted to the Fund for Scientific Research–Flanders (Belgium) (FWO) (Grant G.0016.02) and to the Research Council of the VUB (Grants GOA31, OZR362, OZR875) for financial support.

References

[1] J.A. Thompson, M.G. Sheffer, R.C. Pierce, Y.K. Chau, J.J. Cooney, W.P. Cullen, R.J. Maguire, Organotin Compounds in the Aquatic Environment: Scientific Criteria for Assessing their Effects on Environmental Quality, National Research Council Canada, Ottawa, 1985, p. 284.

[2] A.G. Davies, Organotin Chemistry, VCH, Weinheim, 2004.

[3] D. Seyferth, T.C. Masterman, Appl. Organomet. Chem. 8 (1994) 335–349.

[4] A.A. Mahmoud, A.F. Shaaban, M.M. Azab, N.N. Messia, Eur. Polym. J. 28 (1992) 555–559.

[5] J.R. Dharia, C.P. Pathak, G.N. Babu, S.K. Gupta, J. Polym. Sci. 26 (1988) 595–599.

[6] R. Gächter, H. Müller, in: R. Gächter, H. Müller (Eds.), Plastics Additives Handbook, Hanser Publisher, Munich, 1990, pp. 281–287.

[7] J. Otera, Chem. Rev. 93 (1993) 1449–1470.

[8] M. Gielen, Chim. Nouvelle 19 (2001) 3333–3346.

[9] J.K. Tsagatakis, N.A. Chaniotakis, K. Jurkschat, S. Damoun, P. Geerlings, A. Bouhdid, M. Gielen, I. Verbruggen, M. Biesemans, J.C. Martins, R. Willem, Helv. Chim. Acta 82 (1999) 531–542.

[10] E. Merian, Metals and Their Compounds in the Environment, VCH, Weinheim, 1991.

[11] M.A. Champ, P.F. Seligman, Organotins, Environmental Fate and Effects, Chapman and Hall, London, 1996.

[12] L. Angiolini, M. Biesemans, D. Caretti, E. Salatelli, R. Willem, Polymer 41 (2000) 3913–3924.

[13] M. Hoch, Appl. Geochem. 16 (2001) 719–743.

[14] B. Delmond, G. Dumartin, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), Physical Organometallic Chemistry. Solid State Organometallic Chemistry. Methods and Applications, John Wiley & Sons, Chichester, 1999, p. 445.

[15] M. Biesemans, F.A.G. Mercier, M. Van Poeck, J.C. Martins, G. Dumartin, R. Willem, Eur. J. Inorg. Chem. 14 (2004) 2908–2913.

[16] J.C. Martins, F.A.G. Mercier, A. Vandervelden, M. Biesemans, J.-M. Wieruszeski, E. Humpfer, R. Willem, G. Lippens, Chem. Eur. J. 8 (2002) 3431–3441.

[17] G. Deshayes, K. Poelmans, I. Verbruggen, C. Camacho-Camacho, P. Degée, V. Pinoie, J.C. Martins, M. Piotto, M. Biesemans, R. Willem, P. Dubois, Chem. Eur. J. 11 (2005) 4552–4561.

[18] C. Camacho-Camacho, M. Biesemans, M. Van Poeck, F.A.G. Mercier, R. Willem, K. Darriet-Jambert, B. Jousseaume, T. Toupance, U. Schneider, U. Gerigk, Chem. Eur. J. 11 (2005) 2455–2461.

[19] F.A.G. Mercier, M. Biesemans, R. Altmann, R. Willem, R. Pintelon, R. Schoukens, B. Delmond, G. Dumartin, Organometallics 20 (2001) 958–962.

[20] L. Angiolini, D. Caretti, L. Mazzocchetti, E. Salatelli, M. Biesemans, R. Willem, Appl. Organomet. Chem. 19 (2005) 841–847.

[21] L. Mazzocchetti, Hybrid organic inorganic polymeric materials bearing the triorganotin carboxylate moieties, Ph.D. Thesis, University of Bologna, 2005.

[22] U. Schuchardt, R. Sercheli, R.M. Vargas, J. Braz. Chem. Soc. 9 (1998) 199–210.

[23] H.E. Hoydonckx, D.E. De Vos, S.A. Chavan, P.A. Jacobs, Top. Catal. 27 (2004) 83–96.

[24] R.K. Ingham, S.D. Rosenberg, H. Gilman, Chem. Rev. 60 (1960) 459–539.

[25] K.C. Molloy, K. Quill, S.J. Blunden, R. Hill, Polyhedron 5 (1986) 959–965.

[26] L. Angiolini, D. Caretti, L. Mazzocchetti, E. Salatelli, M. Biesemans, R. Willem, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 3091–3104.

[27] J. Holeček, K. Handlíř, A. Lyčka, T.K. Chattopadhyay, B. Majee, A.K. Kumar, Collect. Czech. Chem. Commun. 51 (1986) 1100–1111.

[28] L. Angiolini, E. Salatelli, D. Caretti, M. Biesemans, H. Dalil, R. Willem, N.A. Chaniotakis, E. Gouliaditi, K. Perdikaki, Macromol. Chem. Phys. 203 (2002) 219–229.

[29] R. Willem, A. Bouhdid, B. Mahieu, L. Ghys, M. Biesemans, E.R.T. Tiekink, M. Gielen, J. Organomet. Chem. 531 (1997) 151–158.

[30] L. Angiolini, D. Caretti, L. Mazzocchetti, E. Salatelli, C. Femoni, J. Organomet. Chem. 689 (2004) 3301–3307.

[31] B. Wrackmeyer, Ann. Rep. NMR Spectrosc. 16 (1985) 73–186.

[32] J. Holeček, K. Handlíř, M. Nàdvorník, A. Lyčka, J. Organomet. Chem. 258 (1983) 147–153.

[33] L. Angiolini, D. Caretti, L. Mazzocchetti, E. Salatelli, M. Biesemans, R. Willem, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 5372–5383.

[34] J.T.B.H. Jastrzebski, G. Van Koten, Advances in Organomet. Chem. 35 (1993) 241–294.

[35] G. Deshayes, F.A.G. Mercier, P. Degée, I. Verbruggen, M. Biesemans, R. Willem, P. Dubois, Chem. Eur. J. 9 (2003) 4346–4352.

[36] F.A. Zaher, Grasas Aceites 41 (1990) 82–91.

[37] M. Mittelbach, P. Tritthard, J. Am. Oil Chem. Soc. 65 (1988) 1185–1187.

[38] F. Staat, G. Vermeersch, Rev. Fr. Corps Gras 40 (1993) 167–174.

[39] The possibility of formation of an alkoxide intermediate by reaction of tin carboxylate with the alcohol reactant, as suggested by one reviewer, can be excluded for these derivatives by the observed lack of tin leakage from triorganotin carboxylates grafted to cross-linked resins of similar structure as in Chart 2, in the experiments reported in Refs. [20] and [21]. Alcoholysis would have in fact produced detachment of the triorganotin moiety from the matrix and a variation of the properties of the catalyst.