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Cross-linked polystyrene resins containing triorganotin-4-vinylbenzoates: Assessment of their catalytic activity in transesterification reactions

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

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Abstract

Three new resins are synthesized by radical co-polymerization of triorganotin-4-vinylbenzoates (substituent at tin = Me, Bu or Ph) with styrene and 1,4-divinylbenzene. The products prepared have been characterized by FT-IR and NMR spectroscopy both in the solid state and as swollen samples, showing a predominantly tetracoordinated tin atom. The catalytic activity of the above resins in a transe-sterification reaction has been tested using ethyl acetate and primary, secondary or tertiary alcohol, showing good results with the former, but not with the latter ones. Focussing on the different triorganotin substituents, a comparison between the prepared resins and low molecular weight analogues evidences a lower activity of the resins, due to their inhomogeneous operating conditions. However, the triphenyltin functionalized resin shows a transesterification activity comparable to the corresponding model compound. The reaction mechanism and the effects of Lewis acidity of the different groups linked to tin have been investigated by ¹H and ¹¹⁹Sn hr-MAS NMR. © 2006 Elsevier B.V. All rights reserved.

Keywords: Catalyst; Sn NMR spectroscopy; Organotin; Resins; Transesterification

1. Introduction

Since their first biocidal application in the early 1920s [1], organotin compounds are among the most widely used organometallic chemicals [2]. Their applications cover a wide range of different fields, being used as antifouling paints [3–5], PVC stabilizers [6] and anti-tumour drugs [7] as well as anion carriers in electrochemical membrane design [8] and, last but not least, as homogeneous catalysts [9].

In spite of the well-known homogeneous catalytic activity of organotins in transesterifications, owed to the presence of the Lewis acid metal centre [10], their toxicity, coupled to their difficult removal from the reaction mixture, constitute a serious drawback. Only limited research

* Corresponding author. Tel./fax: +39 051 2093687.

E-mail address: luigi.angiolini@unibo.it (L. Angiolini).

has been dedicated to the separation of the catalyst from the final products, the few reported processes being expensive, due to the use of extraction solvents [11], or leading to loss of catalytic activity because of the drastic conditions needed for its recovery [12].

To address this issue, a useful approach consists of grafting the tin derivative onto a polymeric cross-linked support, since the catalyst obtained in this way at the solid–liquid interface can be easily separated by filtration of the support to which it is grafted, thus reducing, or even completely preventing the presence of toxic organotin residues in solution and giving rise to clean and potentially recyclable organotin reagents.

Several insoluble tri- and dialkyltin grafted polymers have already been synthesized, starting from commercial polystyrene resins cross-linked with 1,4-divinylbenzene [13–18].

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All the synthetic procedures used in previous reports [18] have the common disadvantage to start from an insoluble reactant, which makes the reaction sluggish and difficult to control. Even more hampering is that the organotin functionalization degree cannot always be selected a priori.

In the course of investigations on their potentiometric anion response, tributyltin carboxylates were observed to show interesting properties in transesterification catalysis as well. Since this observation appears likewise related to the Lewis acidity of the tin atom, the natural idea raises that next to grafted dialkyltin dihalides [18], triorganotin carboxylates grafted to the insoluble macromolecular support have the potency to offer an alternative, attractive class of interfacial organotin catalysts.

Stannylating carboxylic acids in cross-linked resins appeared previously to be not achievable quantitatively [19]. Co-polymerization to cross-linked resins involving triorganotin carboxylate monomers is believed to address this issue and is presented in the present paper as an alternative strategy. More particularly, we have addressed the synthesis of cross-linked resins, having a structure closely related to that of Amberlite IRC-86 [19], starting, however, from triorganotin *p*-vinylbenzoates rather than acrylates as suitable monomers, since cross-linked polystyrenes proved previously to be convenient insoluble supports giving rise to satisfactory catalytic activities in other organotin systems [13–18], unlike Amberlite IRC-86, scoring less satisfactorily. In fact, although it is known [20] that organometallic monomers can inhibit the polymerization process, this synthetic route is nevertheless explored since it enables one to skip further functionalization steps, potentially limited by unfavourable diffusion due to the cross-linking, as observed with Amberlite IRC-86 derivatives [19]. In addition, in order to minimise the effect of tin on the chain growth, we designed a monomer having the polymerizable vinyl group and the triorganotin functionality conveniently separated. It is established that inhibition by the organotin moiety strongly depends on the relative position of the polymerizable C=C bond with respect to the organotin moiety in the molecule, the intercalation of polar or polarizable groups such as phenyl or carboxyl ones, leading to a considerably weaker inhibiting action [21,22].

Thus, we have submitted triorganotin derivatives of *p*-vinylbenzoic acid (pVBA) to co-polymerization with styrene and 1,4-divinylbenzene, the carboxylic function of pVBA being functionalized with different R_3Sn organotin residues (R = Me, Bu, Ph). Since the catalytic activity is likely to be affected by the Lewis acidity of the tin atom, the organic substituents were selected in order to investigate their influence on the catalytic performances.

The different tin containing monomeric compounds have been respectively co-polymerized with 1,4-divinylbenzene, as cross-linking bifunctional monomer, and styrene, the latter aiming at limiting the content of stannylated co-units in the final resin.

The knowledge of the features of the related low molecular weight model compounds, namely trimethyl-, tributyland triphenvl-tin *p*-isopropylbenzoate (TMTIB, TBTIB) and TPTIB, respectively), described elsewhere [23], plays a key role for the structural characterization of the crosslinked polymeric derivatives, since their insolubility prevents the application of common analytical techniques. In this respect, the use of proton and tin high-resolution Magic Angle Spinning (hr-MAS) NMR appears of determinant relevance to the characterization of such cross-linked materials [15] (see Section 3). Moreover, the comparison with the catalytic performances of low molecular weight models allows a rough evaluation of the activity changes associated with the use of an insoluble cross-linked macromolecular structure, a feature which is believed to affect the accessibility to the catalytic sites.

2. Results and discussion

2.1. Synthesis and characterization of monomers

As reported in Scheme 1, the first step of the synthesis of p-vinylbenzoic acid (pVBA) implies the formation of a Grignard derivative of p-chlorostyrene which is quenched with CO₂ in order to achieve the carboxylic moiety, after treatment with aqueous H₂SO₄.

pVBA was characterized by FT-IR and ¹H and ¹³C NMR spectroscopy. The conversion of *p*-vinylbenzoic acid into the desired triorganotin *p*-vinylbenzoate monomers was then achieved by direct triorganostannylation with the suitable triorganotin derivative (Scheme 2) in the presence of a small amount of hydroquinone as a polymerization inhibitor.

Direct triorganostannylation of a carboxylic acid with a bis(triorganotin) oxide is one of the most common methods [24] to synthesize triorganotin carboxylates. As an alternative, the reaction of the carboxylic acid with a suitable triorganotin hydroxide can likewise be used [25]. The water, produced as co-product in both cases, can be conveniently removed from the reaction mixture by azeotropic distillation in toluene, in order to conduct the reaction to completion.

As represented in Scheme 2, we applied this synthetic pathway to the production of both the tributyltin (TBTVB) and triphenyltin (TPTVB) *p*-vinylbenzoates, starting from pVBA and bis(tributyltin)oxide or triphenyltin hydroxide, respectively.



pVBA

Scheme 1.



Scheme 2.

The synthesis of the trimethyltin *p*-vinylbenzoate (TMTVB) was also achieved by direct trimethylstannylation of pVBA with the corresponding trimethyltin hydroxide, using in this case acetone as solvent. Since trimethyltin hydroxide sublimates at 80 °C, the solvent was chosen so as to enable a sufficiently low refluxing temperature in order to prevent sublimation of the reactant. The water obtained as a by-product was removed by using 5 Å molecular sieves added to the reaction mixture. In this case the purification from the organometallic reagent in excess was simply achieved by gentle heating under reduced pressure in order to sublimate any unreacted trimethyltin hydroxide.

Whereas the final purification of TMTVB and TPTVB was easily achieved by crystallization of the product from ethanol/water, this was not possible with the tributyltin derivative, the final crude product appearing as a viscous oil. Purification of TBTVB from the corresponding unreacted tin oxide was thus achieved by treatment of the reaction mixture with a weak ionic exchange resin (Fluka Amberlite IRC-86) consisting of poly(acrylic acid) cross-linked with 1,4-divinylbenzene, which is able to react with the organometallic reagent in excess, as previously reported [25], thus leading to pure TBTVB after filtration of the resin from the reaction mixture and solvent evaporation.

All the reactions were monitored by FT-IR spectroscopy and kept under reflux until no more absorption bands related to the carboxylic acid carbonyl stretching at 1678 cm^{-1} could be detected.

The asymmetric stretching vibration of the triorganotin carboxylate displays an absorption band in the range $1620-1635 \text{ cm}^{-1}$ for both TBTVB and TPTVB, while the symmetric one lies around 1330 cm^{-1} . As previously stated, these bands refer to a carbonyl moiety free from any interaction with the metal atom [26], indicating the presence of tetracoordinated tin atom in the solid state. This behaviour

is well established for low molecular weight compounds bearing the triphenyltin carboxylate moiety, and also the tributyltin analogue, although two examples of pentacoordinated tributyltin carboxylates were recently ascertained by the X-ray crystal structure of tributyltin *p*-ethyl and *p*isopropyl phenylacetate [27].

The tin pentacoordination in TMTVB is evidenced by its FT-IR spectrum, displaying asymmetric and symmetric stretching bands at 1587 and 1378 cm^{-1} , respectively, in agreement with a trigonal bipyramidal structure with a diaxial configuration of the carboxylic oxygen of one ligand and the carbonyl oxygen of a neighbouring triorganotin carboxylate molecule [28].

The FT-IR absorptions of the monomers (Table 1) are in good agreement with those of the related *p*-isopropyl tin benzoate models [23], reflecting the same behaviour as regards the coordination at tin. The presence of the absorption at 1629 cm⁻¹ related to the carbonyl stretching of TPTIB (Fig. 1), allows also to assign the band at 1620 cm⁻¹ of TPTVB to the same vibration, as the extension of conjugation of a carbonyl moiety with the aromatic system lowers the frequency of the stretching absorption [29]. As a consequence, the absorption at 1635 cm⁻¹ in TPTVB is assigned to the vinyl stretching vibration. It can also be noticed that the absorption frequency of the

Table 1 Carbonyl stretching frequencies of triorganotin *p*-vinyl and *p*-isopropyl benzoates

Tin substituent	$v(C=0) (cm^{-1})$		
	p-Vinyl benzoate	p-Isopropyl benzoate ^a	
Me	1587	1595	
Bu	1630	1636	
Ph	1620	1629	

^a From Ref. [23].



Fig. 1. FT-IR spectra of model compound TPTIB (a) and of triphenyltin*p*-vinyl benzoate monomer TPTVB (b).

carbonyl moiety in the triphenyltin derivatives is lower than in the analogous non-coordinated tributyltin ones both in the monomers and the models, as reported in Table 1.

The monomeric triorganotin *p*-vinylbenzoates were also characterized by ¹H and ¹³C NMR spectroscopy, using two-dimensional COSY and HSOC experiments where necessary, in particular for the proton resonances of TPTVB, due to the presence of two overlapping aromatic spin systems. All the investigated triorganotin carboxylate monomers clearly display the expected multiplet pattern of vinyl protons analogously to the pVBA precursor, confirming that the vinyl group remained unaltered after the triorganostannylation of the starting carboxylic acid. The ¹¹⁹Sn NMR spectra of TMTVB, TBTVB and TPTVB in non-coordinating CDCl₃ display a single resonance with chemical shift values typical for tetracoordinated tin [30] (Table 2). This allows to conclude that the monomeric triorganotin *p*-vinylbenzoates are exempt from any unreacted organotin reagent after the triorganostannylation reaction.

2.2. Synthesis and characterization of cross-linked polymers

A first unsuccessful attempt to polymerize the synthesized monomers with 1,4-divinylbenzene and styrene was performed by radical polymerization in emulsion. This procedure allows to operate at short reaction times, in addition, at least in principle, to a better control over the final resin particle size, therefore leading to a product sufficiently easy to handle. The polymerization was carried out in aqueous medium, in the presence of dodecylsulphate sodium salt as surfactant, and sodium persulphate as the radical initiator. The reaction mixture was allowed to react for 24 h at 80 °C under vigorous stirring and the obtained polymers were recovered from the emulsion by filtration, after coagulation with a concentrated aqueous $Al_2(SO_4)_3$ solution.

The occurrence of polymerization involving the vinyl functionality was proved by infrared spectra, showing the disappearance of the typical CH_2 bending band of the vinyl group around 1400 cm⁻¹. However, the presence of an absorption band around 1690 cm⁻¹, a value typical for the carbonyl vibration of carboxylic acids for the tributyl and trimethyl derivatives, suggested the occurrence of a partial hydrolysis of triorganotin carboxylate during the polymerization. The thermogravimetric analysis, coupled to elemental analysis, confirmed indeed the occurrence of hydrolysis for all the ter-polymers, since abnormally low

Table 2	
¹¹⁹ Sn NMR chemical shifts o	f triorganotin monomers in CDCl ₃

Compound	δ^{119} Sn (ppm)
TMTVB	137
TBTVB	112
TPTVB	-112

tin and high oxygen contents (deviations from expected up to 50%) were found. Consequently, this synthetic procedure was abandoned.

An alternative route to cross-linked derivatives was then applied by performing the radical polymerization of the monomers in dry THF, using AIBN as a thermal radical initiator, and keeping the reaction mixture sealed under vacuum for 5 days at 60 °C (Scheme 3).

The obtained cross-linked triorganotin ter-polymers, labelled as S-ter-X (Table 3), where S refers to solution and X to the substituent at tin, were recovered by simple



Table 3					
Polymerization	data for	cross-linked	terpoly	ymers	S-ter-X

Polymer	Styrene (% mole)	Divinylbenzene (% mole)	Organotin monomer (% mole)	Yield ^a (%)	Functiona- lization degree ^b (% mole)
S-ter-Me	85	10	5	52	5.7
S-ter-Bu	85	10	5	62	7.1
S-ter-Ph	85	10	5	54	7.7

^a Determined as (g of polymer/g of feeding monomers) \times 100.

^b Determined by a statistical processing method of elemental data analysis of C, H, Sn, and O, as described elsewhere [18]. The functionalization degree is defined as the percent molar content of triorganotin carboxylate monomeric units present in the final polymeric products. filtration and purified from unreacted monomers and soluble oligomers by swelling the mixture in different solvents followed by filtration. As reported in Table 3, the content of triorganotin carboxylate units in the products results higher than expected on the basis of the corresponding monomer feeds. This would indicate a significantly higher reactivity of the tin functionalized monomer with respect to the other co-monomers, at least for the tributyl- and the triphenyltin derivatives, in contrast with results obtained for similar derivatives where the organotin functionality was connected to the styrenic residue through a dimethylene spacer [31]. The rather low polymerization vields obtained, however, suggest that an abundant fraction of soluble product, probably constituted by styrene moieties, was lost in the manipulation of the crude material, thus increasing the relative content of organotin counits. Indeed, DSC investigations on the resins obtained allowed to exclude the presence of polystyrene homopolymer in the purified material, no glass transition being observed in the thermograms.

In contrast with the derivatives prepared by emulsion polymerization, the FT-IR spectra of S-*ter*-X did not exhibit any absorption at 1690 cm⁻¹ related to free carboxylic acid, indicating the absence of triorganotin carboxylate hydrolysis when the procedure in organic solution is adopted.

The carbonyl absorption frequency of S-*ter*-Me moved with respect to monomer TMTVB from 1587 cm⁻¹ (Table 1) to 1639 cm⁻¹, a value typical for non-coordinated triorganotin carboxylate [27]. It appears therefore that the presence of a stiff cross-linked polymeric structure prevents the interactions between organotin carboxylate groups, which are anyhow highly unlikely due to the low content of tin containing units in the material.

To confirm the result of IR spectra, tin NMR experiments were also performed on the cross-linked derivatives, in the solid state, by CP-MAS (Cross Polarization-Magic Angle Spinning), as well as in heterogeneous medium at the solid–liquid interface, with the derivatives swollen in CDCl₃, using tin hr-MAS NMR spectroscopy (Table 4) [15]. The ¹¹⁹Sn hr-MAS spectra show, in agreement with the behaviour of the model compounds in solution, only resonances typical for tetracoordinated tin [30] (Table 4). Similarly, for both the tributyl and the triphenyltin derivatives, the ¹¹⁷Sn CP-MAS NMR spectra in the solid state reveal the presence of fully tetracoordinated tin atom, in

Table 4

 119 Sn NMR chemical shifts (ppm) of S-*ter*-X cross-linked polymers swollen in CDCl₃ and in the solid state

Polymer	δ (Sn) (ppm)			
	¹¹⁹ Sn hr-MAS	¹¹⁷ Sn solid state		
S-ter-Me	132	$121(92); -57(8)^{a}$		
S-ter-Bu	101	97		
S-ter-Ph	-121	-114		

^a Values in brackets refer to the percentage of each integrated resonance.

line with the FT-IR data. By contrast, S-ter-Me displays only a major ¹¹⁷Sn resonance at 121 ppm, typical for tetracoordinated tin, and a second minor resonance at -57 ppm. The latter is notably different from that observed for the corresponding trimethyltin *p*-isopropylbenzoate model in the solid state, showing a chemical shift of +26 ppm [23], attributed to pentacoordinated tin originated by intermolecular interaction with the neighbouring carbonyl moieties [30]. The higher level of shielding indicated by the value of -57 ppm for the minor tin species suggests an even stronger pentacoordination than in the model, the exact structural nature of which remains unclear. Integration of these signals supplies a rough evaluation of the relative amounts of the two differently coordinated tin species, the pentacoordinated form being estimated as 8% of the total, a content which reasonably explains why the related carbonyl stretching could not be detected by FT-IR, and which is too low to enable further investigations regarding the nature of this type of pentacoordination at tin.

In order to assess the thermal stability of these materials in view of possible applications, the thermogravimetric analysis (TGA) was performed both on the polymeric and model compounds, with the aim of evaluating the influence of the macromolecular cross-linked chains on the thermal behaviour. As reported in Fig. 2 and Table 5, all the cross-linked materials display a notably higher initial degradation temperature with respect to the monomeric models, a contribution to the increase of T_{d} values deriving also from the low concentration of tin containing units in the resins when compared to the triorganotin *p*-isopropylbenzoate model compounds. As previously established [32], the thermal stability of polystyrenic macromolecules increases upon lowering the triorganotin co-unit content, as the triorganotin carboxylate group substantially favours the decomposition process.

2.3. Assessment of catalytic activity in transesterification reactions

In order to investigate the catalytic performance, the activity of S-*ter*-X resins has been assessed in a transesterification reaction of ethyl acetate with differently hindered alcohols, similarly to the previously described Amberlite derivatives [19]. A comparison with the catalytic performances of the related low molecular weight models [23] under the same conditions has also been carried out. The amount of catalyst in each experimental run was calculated so as to have a 1% mole ratio of tin containing units with respect to the selected alcohol, 1-octanol, cyclohexanol or 3-ethyl-3-pentanol. All the reactions, when carried out in the absence of catalyst gave, as expected, no conversion at all of ethyl acetate.

The alcohol conversion in each catalytic run was assessed by gas chromatography (Table 6), determining the relative amounts of transesterified product and unreacted starting alcohol after 24 and 48 h.



Fig. 2. TGA curves of S-ter-Me (a), S-ter-Bu (b), S-ter-Ph (c) and the related models TMTIB (d), TBTIB (e) and TPTIB (f).

Table 5 Initial decomposition temperature of the S-*ter*-X resins and the related low molecular weight compounds

Polymer	$T_{\rm d}^{\rm a}$ (°C)	Model	$T_{\rm d}$ (°C)
S-ter-Me	361	TMTIB	150
S-ter-Bu	350	TBTIB	169
S-ter-Ph	370	TPTIB	183

^a Temperature of the first weight loss.

The catalytic performances offered by the cross-linked derivatives are significantly more promising than the previously described organotin modified Amberlite IRC-86 [19]. In the case of S-*ter*-Ph in particular, the conversion of primary alcohol compares remarkably well with the corresponding model compound TPTIB [23], the grafted catalyst at the liquid–solid interface displaying a catalytic activity very close to that of the model counterpart in homogeneous solution. The presence of the macromolecular cross-linked backbone, expected to hamper to some

extent the accessibility to the tin atom, actually does not affect the transesterification rate. By contrast, the trialkyltin substituted resins S-ter-Me and S-ter-Bu display a remarkable decrease of the transesterification conversion with respect to corresponding model compounds, the obtained values being in good agreement with those obtained with the Amberlite IRC86 organotin derivatives [19]. It is not yet clear why this effect does not have relevant consequences for the phenyl derivative, S-ter-Ph having quite hindering sustituents at tin. Presumably, this indicates that a balance between Lewis acidity, as outlined previously for the model compounds [23], and steric hindrance of the cross-linked backbone is operative.

In order to obtain a better insight in factors governing the catalysis, ¹¹⁹Sn hr-MAS spectra of the catalysts were recorded in the actual reaction mixture. The ¹¹⁹Sn chemical shifts of the cross-linked polymers in the presence of transesterification reagents, either ethyl acetate or a mixture of ethyl acetate and *n*-octanol, summarized in Table 7, reveal a low frequency shift with respect to the chemical

Table 6

Conversions obtained in catalysed transesterification reaction of ethyl acetate with differently hindered alcohols, as determined by gas chromatography

Catalyst	Alcohol conversion (%)						
	1-Octanol		Cyclohexanol		3-Ethyl-3-pentanol		
	24 h	48 h	24 h	48 h	24 h	48 h	
TMTIB	19	43	5	6	_	Trace	
TBTIB	76	95	7	9	_	Trace	
TPTIB	95	100	10	17	_	Trace	
S-ter-Me	10	18	3	3	_	Trace	
S-ter-Bu	8	28	2.5	7	_	Trace	
S-ter-Ph	90	96	3	4.5	_	Trace	

sin chemical sinits (ppin) of the model compounds and the corresponding cross-inited polymers in various solvents						
Compound	CDCl ₃	EtOAc	$\Delta\delta$ (EtOAc vs. CDCl ₃)	EtOAc/octanol ^b	$\Delta\delta$ (EtOAc/oct. vs. EtOAc)	
TMTIB	133 ^c	95	-38	78	-17	
TBTIB	109 ^c	88	-21	82	-6	
TPTIB	-115 ^c	-127	-12	-130	-3	
S-ter-Me	132	90	-42	78	-12	
S-ter-Bu	101	84	-17	81	-3	
S-ter-Ph	-121	-128	-7	-131	-3	

Table 7 hr-MAS ¹¹⁹Sn chemical shifts (ppm) of the model compounds and the corresponding cross-linked polymers in various solvents⁸

^a Pure octanol does not swell the polymers and consequently no ¹¹⁹Sn spectrum is obtained in this solvent.

^b EtOAc/octanol is 4/1 for the model compounds and 7/1 for the polymers.

^c From Ref. [23].

shifts in CDCl₃, similar to the effects observed for the model compounds. Although no spectra could be obtained in pure n-octanol as a result of insufficient swelling, the more pronounced low frequency shift observed with a mixture octanol/ethyl acetate than with the ester alone, implies that both reagents coordinate the tin atom. As for the model compounds, the explanation for the transesterification proceeding better with the triphenyltin polymer, where coordination of both the ester and alcohol is obviously weaker, is that although complex formation is necessary, the complex has to be sufficiently labile in order to achieve fast exchange between incoming reactants and outgoing products. Compared to the model compounds, a difference in behaviour is noticed for the tributyltin compound. Whereas the model compound TBTIB scores rather well, only little conversion is observed for the cross-linked polymer S-ter-Bu (Table 6). Careful inspection of the ¹¹⁹Sn hr-MAS chemical shift data reveals that the relative increase in ¹¹⁹Sn chemical shift difference $(\Delta \delta)$ in chloroform and ethyl acetate between S-ter-Bu and S-ter-Ph (-17 compared to -7 ppm, i.e., 24 times) is somewhat stronger than between the corresponding model compounds (-21 compared to)-12 ppm, i.e., 1.8 times), suggesting that ethyl acetate coordinates somewhat stronger the tin atom in the polymer than in the corresponding model compound. The addition of n-octanol results in the same relative increase (-3 ppm) for both polymers, while a significantly more pronounced effect (2 times) is noticed for the related model compound TBTIB, suggesting n-octanol coordinates somewhat less the tin atom in S-ter-Bu than in the model compound (Table 7). These subtle changes in coordination, may lay at the basis of the change in catalysis kinetics, but no further evidence can be provided to this.

When the secondary alcohol cyclohexanol is used in the transesterification reaction, a low final conversion is found even with S-*ter*-Ph, which now scores similarly to the trial-kyltin substituted resins. This suggests that the steric hindrance of incoming alcohol becomes the determinant factor, since also in homogeneous solution the conversions are very low, even after 48 h, being at most 17% with TPTIB. The transesterification of ethyl acetate with 3-ethyl-3-pentanol practically does not proceed at all, there-

fore confirming the data obtained both with the low molecular weight model compounds and the Amberlite IRC86 derivatives [19].

3. Experimental

3.1. Materials

Chemicals were supplied by Sigma-Aldrich and generally used as received. Solvents were purified using standard techniques [33] and stored under nitrogen. Commercial styrene was treated with 5% aq. NaOH solution, washed with water, dried for 24 h on anhydrous MgSO₄ and distilled at 16 mmHg (b.p. = $35 \circ C$). The obtained monomer was stored under nitrogen at 0 °C. Commercial tetrahydrofuran (THF) was kept in contact with KOH for 8 h, refluxed with metallic K and Na in the presence of benzophenone and then distilled (b.p. = $65 \,^{\circ}$ C) under nitrogen atmosphere; the dried solvent was freshly distilled every time, immediately prior to synthetic use. α, α' -azobisisobutyronitrile (AIBN) was purified by crystallization from absolute ethanol before use. Commercial 1,4-divinylbenzene was treated with 5% ag. NaOH solution, washed with water, dried for 24 h on anhydrous MgSO₄ and distilled at 4 mmHg (b.p. = 40 °C). The monomer obtained was stored under nitrogen at 0 °C.

3.2. Measurements

Infrared spectra in KBr pellets or in chloroform solution were recorded on a Perkin–Elmer 1750 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded both on a Varian Gemini 300 NMR and Varian Mercury 400 NMR using CDCl₃ solutions and tetramethylsilane as internal standard. Notations in NMR spectra: $C_i = ipso$ carbon of the functionalized phenyl group, bound to the variable triorganotin carboxylate; $C_o = ortho$; $C_m = meta$; $C_p = para$. Solid state ¹¹⁷Sn NMR spectra were recorded at 89.15 MHz using a Bruker Avance 250 NMR spectrometer, equipped with a 7 or 4 mm MAS broad-band probe using tetracyclohexyltin (-97.4 ppm relative to (CH₃)₄Sn), as an external standard. The ¹H and ¹¹⁹Sn hr-MAS NMR spectra of heterogeneous samples, consisting of cross-linked resins to which organotin compounds are covalently grafted and swollen up with an appropriate solvent [15], were recorded on a Bruker AMX500 NMR spectrometer equipped with three channels and gradient pulse hardware, using a Bruker triple ¹H-¹³C-¹¹⁹Sn TXI probe especially dedicated for NMR measurements at the liquid-solid interface of organotin moieties grafted to a macromolecular support. Thermogravimetric analyses were carried out on a TGA-7 Perkin-Elmer thermobalance in air. Oxygen elemental analyses were performed by REDOX s.n.c. (Milano). Carbon, Hydrogen and Tin elemental analyses were performed by Centre National de la Recherche Scientifique (CNRS), Service Central d'Analyse, Vernaison (France). Conversion assessments in catalytic tests were made by gas chromatography using an Agilent 6890 instrument equipped with a capillary methylsilicone column and an Agilent 5973 M mass detector.

3.3. Synthesis of monomers

3.3.1. p-Vinylbenzoic acid (pVBA)

In a nitrogen flushed 250 mL three-necked, round-bottomed flask, equipped with a magnetic stirrer and a dropping funnel, pure magnesium (1.78 g, 71.3 mmol) is added to freshly distilled THF (20 mL); subsequently, a solution of *p*-chlorostyrene (5.0 mL, 41.7 mmol) in THF (10 mL) is slowly dropped in. The mixture is heated at 35 °C and allowed to react for 2 h. Carbon dioxide is then bubbled in the solution for 3 h, aqueous H_2SO_4 2 M (20 mL) is added, and the solution extracted with diethyl ether (2 × 20 mL). The organic phase is dried with Na₂SO₄. The organic solvent is distilled off and the product is purified by crystallization with petroleum ether. Yield: 3.81 g (62%).

¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): $\delta = 5.4$ (d, ³ $J(H_{cis},H) = 11$ Hz, 1H; =CH_{trans} H_{cis}), 5.9 (d, ³ $J(H_{trans},H) =$ 18 Hz, 1H; =CH_{trans} H_{cis}), 6.8 (dd, ³ $J(H,H_{cis}) = 11$ Hz, ³ $J(H,H_{trans}) = 18$ Hz, 1H; =CH), 7.5 (d, ³J(H,H) = 8 Hz, 2H; CH_m), 8.1 (d, ³J(H,H) = 8 Hz, 2H; CH_o) ppm.

¹³C NMR (300 MHz, CDCl₃, 20 °C, TMS): $\delta = 117.7$ (=CH₂), 126.7 (C_m), 129.0 (C_i), 131.3 (C_o), 136.4 (=CH), 143.5 (C_o), 172.4 (COOH) ppm.

IR (KBr): 3006–2960 (v_{CH} arom.), 1682 (v_{CO} acid), 1627 ($v_{C=C}$ vinyl), 1408 ($\delta_{=CH2}$), 990, 904 ($\delta_{CH=CH2}$), 827 ($\gamma_{1,4-\text{subst. ring}}$ arom.) cm⁻¹.

3.3.2. Trimethyltin p-vinylbenzoate (TMTVB)

In a 100 mL flask pVBA (0.40 g, 2.70 mmol), trimethyltin hydroxide (0.50 g, 2.76 mmol) and hydroquinone (0.12 g) are dissolved in dry acetone (70 mL). Molecular sieves 5A are added to remove the water formed as byproduct. The mixture is heated to reflux, the reaction progress being monitored likewise by FT-IR spectroscopy. The cloudy reaction mixture was finally filtrated over a Celite path to remove traces of molecular sieves, then the solvent was evaporated under reduced pressure to leave an oily residue. This was pumped at high vacuum, leading to a white solid, further purified by crystallization in ethanol/water mixture. Yield: 0.39 g (46%).

Elemental analysis calcd (%) for C₁₂H₁₆O₂Sn (310.95): C 46.35, H 5.19, O 10.29; found: C 46.21, H 5.17, O 10.32.

¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = 0.7$ (s, 9H, CH₃), [²*J*(H–^{119/117}Sn) = 58/56 Hz]; 5.35 (dd, ³*J*(H_{cis}, H) = 11 Hz, ³*J*(H_{cis}, H_{trans}) = 0.8 Hz, 1H; =CH_{trans}H_{cis}), 5.85 (dd, ³*J*(H_{trans}, H) = 18 Hz, ³*J*(H_{trans}, H_{cis}) = 0.8 Hz, 1H; =CH_{trans}H_{cis}), 6.75 (dd, ³*J*(H,H_{cis}) = 11 Hz, ³*J*(H,H_{trans}) = 18 Hz 1H; =CH), 7.45 (d, ³*J*(H,H) = 8 Hz, 2H; CH_m), 8.0 (d, ³*J*(H,H) = 8 Hz, 2H; CH_o) ppm.

¹³CNMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = -2.1$ (CH₃, ¹*J*(¹³C–^{119/117}Sn) = 397/380 Hz), 116.3 (=CH₂), 126.2 (C_m), 126.4 (C_i), 130.7 (C_o), 136.4 (=CH), 141.6 (C_p), 171.9 (COO) ppm.

IR (KBr): 3077–3003 (v_{CH} arom.), 2915 (v_{CH} aliph.), 1587 ($v_{as COOSn}$), 1606 ($v_{C-C ring}$), 1399 ($\delta_{=CH2}$), 991, 916 ($\delta_{CH=CH2}$), 863 (γ_{CH} 1,4-subst. ring) cm⁻¹.

3.3.3. Tributyltin p-vinylbenzoate (TBTVB)

In a 100 mL flask equipped with a Dean-Stark apparatus pVBA (0.40 g, 2.70 mmol) and hydroquinone (0.12 g) are dissolved in toluene (20 mL) and bis(tributyltin) oxide (BTBO) (0.7 mL, 1.35 mmol) is added. The mixture is heated until no more water evolution is observed, the reaction progress being monitored likewise by FT-IR spectroscopy. The crude product appearing as a viscous liquid, its purification from the unreacted BTBTO was achieved through reaction in heterogeneous phase with dried Amberlite IRC-86 for 24 h. The resin was filtered off and washed with chloroform (3×20 mL), the combined solutions were evaporated under reduced pressure to give a yellowish oil which could not be crystallized. Yield: 0.63 g (53%).

Elemental analysis calcd (%) for $C_{21}H_{34}O_2Sn$ (437.19): C 57.69, H 7.84, O 7.32; found: C 57.81, H 7.81, O 7.34.

¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = 0.9$ (t, ³*J*(H,H) = 8 Hz, 9H; CH_{3Bu}), 1.4–1.2 (m, 12H, CH_{2ασ} _{Bu} + CH_{2γBu}), 1.6 (m, ³*J*(¹H^{-119/117}Sn) = 65 Hz, 6H; CH_{2βBu}), 5.35 (d, ³*J*(H_{cis},H) = 11 Hz, 1H; =CH_{trans}H_{cis}), 5.85 (d, ³*J*(H_{trans},H) = 17 Hz, 1H; =CH_{trans}H_{cis}), 6.75 (dd, ³*J*(H,H_{cis}) = 11 Hz, ³*J*(H,H_{trans}) = 17 Hz, 1H; =CH), 7.45 (d, ³*J*(H,H) = 8 Hz, 2H; CH_m), 8.0 (d, ³*J*(H,H) = 8 Hz, 2H; CH_o) ppm.

¹³C NMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = 14.0$ (CH_{3Bu}), 16.9 (CH_{2 α Bu}, ¹*J*(¹³C^{-119/117}Sn) = 359/342 Hz), 27.4 (CH_{2 γ Bu}, ³*J*(¹³C^{-119/117}Sn) = 64 Hz), 28.2 (CH_{2 β Bu}, ²*J*(¹³C^{-119/117}Sn) = 20 Hz), 116.0 (=CH₂), 126.2 (C_m), 130.8 (C_o), 131.7 (C_i), 136.7 (=CH), 141.4 (C_p), 171.6 (COO) ppm.

IR (neat): 3085–3037 (v_{CH} arom.), 2956–2854 (v_{CH} aliph.), 1630 ($v_{as COOSn}$), 1606 ($v_{C-C ring}$), 1401 ($\delta_{=CH2}$), 988, 912 ($\delta_{CH}=_{CH2}$), 863 (γ_{CH} 1,4-subst. ring) cm⁻¹.

3.3.4. Triphenyltin p-vinylbenzoate (TPTVB)

In a 250 mL flask equipped with a Dean-Stark apparatus pVBA (1.80 g, 11.2 mmol), hydroquinone (0.12 g) and triphenyltin hydroxide (4.5 g, 12.2 mmol) are dissolved in toluene (150 mL). The mixture is heated until no more water evolution is observed, the reaction progress being monitored likewise by FT-IR spectroscopy. The solvent was evaporated under reduced pressure and the solid residue purified by crystallization from ethanol/water. Yield: 3.64 g (64%).

Elemental analysis calcd (%) for $C_{27}H_{22}O_2Sn$ (497.16): C 65.23, H 4.46, O 6.44; found: C 65.11, H 4.47, O 6.46.

¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = 5.3$ (d, ³ $J(H_{cis},H) = 11$ Hz, 1H; =CH_{trans} H_{cis}), 5.8 (d, ³ $J(H_{trans},H)$ = 17 Hz, 1H; =CH_{trans} H_{cis}), 6.7 (dd, ³ $J(H,H_{cis}) = 11$ Hz, ³ $J(H,H_{trans}) = 17$ Hz, 1H; =CH), 7.4 (m, 11H; CH_m + CH_{m-SnPh} + CH_{p-SnPh}), 7.9 (bs, 8H, CH_o + CH_{o-SnPh}) ppm.

¹³C NMR (400 MHz, CDCl₃, 20 °C, TMS): $\delta = 115.0$ (=CH₂), 125.2 (C_m), 127.8 (C_{m-SnPh}, ${}^{3}J({}^{13}C-{}^{119/117}Sn) = 68$ Hz), 128.6 (C_{p-SnPh}), 129.6 (C_o), 132.9 (C_i), 135.7 (=CH), 136.1 (C_{o-SnPh}, ${}^{2}J({}^{13}C-{}^{119/117}Sn) = 46$ Hz), 139.7 (C_p), 132.1 (C_{i-SnPh}), 169.6 (COO) ppm.

IR (KBr): 3065–2997 (v_{CH} arom), 1635 ($v_{C=C}$ vinyl), 1620 ($v_{as COOSn}$), 1606 ($v_{C-C ring}$), 1401 ($\delta_{=CH2}$), 1331 ($v_{a COOSn}$), 861 (γ_{CH1} ,4-subst. ring) cm⁻¹.

3.4. Polymeric compounds

All polymeric derivatives listed in Table 3 were prepared following the same procedure reported here for S-*ter*-Me. To TMTVB (0.32 g, 1.03 mmol), 1,4-divinylbenzene (0.3 mL, 2.09 mmol) and styrene (2.0 mL, 17.4 mmol) dissolved in anhydrous THF (20 mL), AIBN (33.8 mg, 1% w/w) is added in a vial kept under nitrogen atmosphere and submitted to several freeze – thaw cycles in order to remove any oxygen trace. The vials were left at 60 °C for 5 days and the polymeric products purified by stirring in diethyl ether and subsequently in pentane, followed by drying under vacuum till constant weight. Data related to polymers synthesis are summarized in Table 3.

3.5. Elemental analysis

S-*ter*-Me: found: C 85.04, H 7.34, Sn 5.01, O 1.96; calculated according to the functionalization degree (Table 3) as described in Ref. [18]: C 85.20, H 7.39, Sn 5.87, O 1.58.

S-*ter*-Bu: found: C 83.69; H 7.80; Sn 5.82; O 1.65; calculated according to the functionalization degree (Table 3) as described in Ref. [18]: C 83.85; H 7.77; Sn 6.60; O 1.78.

S-*ter*-Ph: found: C 84.46; H 6.91; Sn 6.19; O 2.18; calculated according to the functionalization degree (Table 3) as described in Ref. [18]: C 84.60; H 6.81; Sn 6.77; O 1.82.

4. Conclusions

New catalytic systems derived from convenient *p*-vinyl triorganotin benzoate monomers, cross-linked by co-polymerization with 1,4-divinylbenzene and styrene, were prepared. This synthetic pathway enables one to obtain non-coordinated trimethyltin, tributyltin and triphenyltin cross-linked polymeric benzoates and allows a better control of the final composition in triorganotin carboxylate moieties. Another advantage is that the synthesized resins do not require any further functionalization, thus avoiding the potentially unfavourable need of heterogeneous reaction on cross-linked substrates.

The assessment of their catalytic properties in the reaction of ethyl acetate with differently hindered alcohols indicates an influence of the Lewis acidity of the metal, confirming the trend outlined previously for the model compounds [23]. The triphenvltin derivatives having lower Lewis acidity result the most active, close to the related soluble model compound, the methyltin catalyst with the highest Lewis acidity [23], displaying a lower activity. This confirms that although the Lewis acidity of the metal centre is a prerequisite for catalytic activity, the interactions between the tin atom and the incoming transesterification reagents must not be too strong, because this would disfavour a fast addition-release mechanism of the reagents at the tin atom. The weak activity of the trimethyltin derivatives can be related to higher affinity of the tin atom for the carbonyl oxygen, which leads to a more stable tin complex, thus slowing down the exchange kinetic associated with the catalytic process.

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