Synthesis and characterization of polystyrenes containing side-chain tributyltin carboxylate moieties linked to the aromatic ring through a 1,2-ethylene spacer

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Abstract

A new triorganotin monomer, tributyltin 3-(*p*-styryl)-propionate (**TBTSP**), has been synthesized and submitted to radical homo- and copolymerization with styrene thus affording the corresponding polymeric derivatives having variable content of triorganotin moieties. The low molecular weight compounds, tributyltin 3-(*p*-ethylphenyl)-propionate and tributyltin 3-(*p*-isopropylphenyl)-propionate, have also been prepared as structural models of the organotin repeating co-units of the polymers. Characterizations in solution and solid state by IR, NMR and thermal techniques of all the polymers and low molecular weight compounds synthesized allow to conclude that the tin atoms are tetra- and/or penta-coordinate depending on structure, physical state and tin content of the polymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Organic–inorganic polystyrenes; Tributyltin polymeric carboxylates; Solid state [117]Sn CP-MAS NMR

1. Introduction

In recent years, organotin derivatives have gained relevant interest both in academic and applied research, because of the ability of tin to afford stable bonds with organic carbon atoms as well as with heteroatoms; this gives rise to a wide range of compounds employed in organic synthesis, catalysis, particularly in esterification and transesterification reactions, in the synthesis of polyesters, polyurethanes and in the crosslinking of silicones [1]. They are also used as PVC heat stabilisers [2,3], as components of aquatic antifouling paints, wood preservatives and biocides in general [4,5]. As a result of their toxicity, however, many organotin derivatives represent a major concern in many applications, particularly when they are released in the environment as hydrolysed pollutants or are present as catalyst residues in pharmaceutical formulations [6]. A potentially promising approach to address this problem consists in the immobilisation of the organotin moieties through chemical bonding to solid inorganic or organic supports, e.g. silica or polystyrene, so as to avoid environmental contamination by toxic organotin residues [7], despite some drawbacks, such as long reaction times

and incomplete conversion of the reactants, connected with the heterogeneous nature of the solid–liquid functionalisation process. For this reason, the chemical anchorage of organotin moieties to soluble organic polymers appears more convenient, as it allows to combine the advantage of performing organic reactions in a homogeneous liquid medium with the possibility offered by polymeric derivatives to be separated by precipitation or other methods based on their high molecular weight, thus allowing a simplified purification of the products. Indeed, this way appears to be well established with a remarkable success in many organic syntheses [8] as well as in combinatorial chemistry [9].

In recent work we have evaluated the possibility of producing polystyrene derivatives bearing side-chain organotin moieties either by functionalisation of suitable polymeric substrates with organometallic reagents or by polymerization of tin containing monomers, thus directly obtaining the desired organotin functionalised polymers [10]. Although the latter route does not allow us to control easily the molecular weight and main chain stereoregularity of the polymer, it appears preferable to the former one, as it yields polymeric derivatives with good chemical purity and well-known composition. The same method has therefore been applied in the present paper to the synthesis of polymeric tributyltin carboxylates, such as the homopolymer

poly(**TBTSP**) and a series of copolymers with styrene [poly(**TBTSP**-*co*-**STY**)] of various compositions, directly obtained from the corresponding organotin monomer tributyltin 3-(*p*-styryl)-propionate (**TBTSP**) by radical homo- and copolymerization with styrene. Low molecular weight model compounds **TBTSP-E** and **TBTSP-I**, resembling the tin containing repeating unit of the polymers, have also been prepared with the aim to compare their properties with those of the polymeric derivatives. The products synthesized and characterized in the present work offer potentials in anion recognition, in particular, as chloride anion carriers. Thus, triorganotin benzoates, phenylacetates and cinnamates have indeed been proved recently to display interesting properties as selective chloride anion sensors when incorporated into plasticized PVC membranes [11]. Triorganotin moieties linked to polymeric polycarboxylates could act as chloride anion sensors with a strong potential to reduce or even suppress the problem of leakage of the organometallic carrier from the membrane into the test solution.
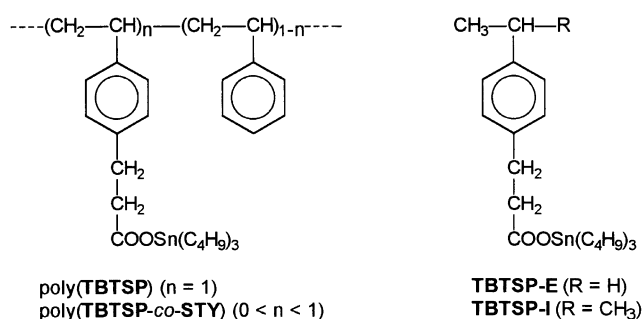

Chart 1.

2. Experimental

2.1. Solvents and chemicals

Styrene was fractionally distilled under reduced pressure (b.p. 45°C at 100 mbar) over a column packed with Raschig rings, then stored under nitrogen in the cold. Anhydrous tetrahydrofuran (THF), benzene, *n*-pentane and carbon disulfide were dried according to the reported procedures [12] and stored over molecular sieves (4 Å) under nitrogen. Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use. Bis(tributyltin) oxide (Aldrich) was used as received.

2.2. Physico-chemical characterizations

^{1}H- and ^{13}C-NMR spectra have been recorded at 300 and 75.5 MHz, respectively, on a Varian NMR Gemini 300 instrument from CDCl$_3$ solutions, unless otherwise stated, using tetramethylsilane (TMS) as internal standard. Chemical shifts are given in ppm from TMS. [117]Sn-NMR spectra were recorded on a Bruker DRX250 spectrometer, operating at 89.15 MHz. [117]Sn chemical shifts were referenced to $\Xi = 35.63229$ MHz [13,14]. Spectra were typically recorded with a pulse angle of 30°, an acquisition time of 0.37 s, a

recycle delay of 0.1 s and a number of scans between 10 000 and 30 000. [117]Sn rather than the more common [119]Sn spectra were recorded in order to overcome local radio interferences around 93.2 MHz [15,16]. Comparing [117]Sn and [119]Sn data is not a problem as primary [117]Sn/[119]Sn isotopic effects are negligible [17].

Solid state ^{13}C and [117]Sn CP-MAS NMR spectra were recorded likewise on a Bruker DRX250 spectrometer at 62.93 and 89.15 MHz, respectively, under the same experimental conditions as described previously [18]. Chemical shift referencing is towards adamantane and tetracyclohexyltin taken as secondary references at 38.3 and −97.4 ppm, respectively, for ^{13}C and [117]Sn. A 90° pulse of 5 μs and a contact time of 2 ms was used in all experiments, with a relaxation delay of 2 s for [117]Sn acquisition and 4 s for ^{13}C acquisition. MAS rates were typically 4000 Hz for ^{13}C and between 4000 and 5000 Hz for [117]Sn. The number of scans was 400–1000 for ^{13}C spectra and between 400 and 30 000 for [117]Sn spectra.

The principal components of the [117]Sn shielding tensors were analysed according to Herzfeld and Berger [19] using WINFIT software [20]. They are reported, following Haeberlen's notation [21], as the isotropic chemical shift $[\delta_{\iota\sigma o} = -\sigma_{\iota\sigma o} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3]$ (ppm), the anisotropy ($\zeta = \sigma_{33} - \sigma_{\iota\sigma o}$), and the asymmetry ($\eta = |\sigma_{22} - \sigma_{11}|/|\sigma_{33} - \sigma_{\iota\sigma o}|$), σ_{11}, σ_{22}, and σ_{33} being the three components of the shielding tensor expressed in its principal axis system with the following rule $|\sigma_{33} - \sigma_{\iota\sigma o}| \geq |\sigma_{11} - \sigma_{\iota\sigma o}| \geq |\sigma_{22} - \sigma_{\iota\sigma o}|$. With this convention, ζ is signed and expressed in ppm.

Fourier-transform infrared spectra (FT-IR) have been obtained from samples prepared as KBr pellets using a Perkin–Elmer 1750 spectrophotometer equipped with an Epson Endeavour II data station. Average molecular weights of the polymers have been determined in THF solution by gel permeation chromatography (GPC) using a HPLC Waters Millipore 590 apparatus equipped with a Waters U6K injector, a Toso Haas G4000HXL column and an UV detector Perkin–Elmer LC-95 operating at 254 nm. Monodisperse polystyrene samples have been used as calibration standards. Thermogravimetric analyses (TGA) have been carried out on a Perkin–Elmer TGA-7 analyser by heating the samples in air at a rate of 20°C/min. Differential scanning calorimetric (DSC) measurements have been performed on a TA Instruments DSC 2920 Modulated apparatus at a heating rate of 10°C/min under nitrogen atmosphere on samples weighing 5–9 mg. Melting points (uncorrected) have been determined in glass capillaries with a Büchi 510 apparatus at a heating rate of 1°C/min. Tin elemental analyses have been carried out by the Service Central d'Analyse of CNRS in Vernaison (France).

2.3. Synthesis of monomer and models

2.3.1. 3-Phenyl propionic acid methyl ester (2)

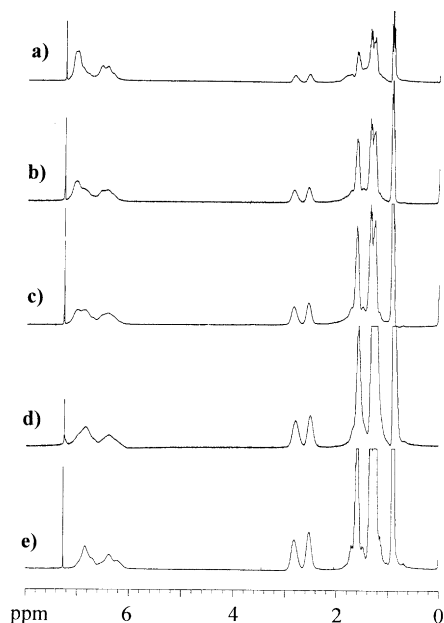This was prepared by esterification of 3-phenyl propionic

Fig. 1. ^{1}H-NMR in CDCl$_3$ of: (a) **copol/20**; (b) **copol/40**; (c) **copol/60**; (d) **copol/80**; and (e) poly(**TBTSP**).

acid **1** (0.2 mol) in 1,2-dichloroethane (60 ml) with methanol (0.6 mol) in the presence of concentrated sulfuric acid (0.6 ml) following a procedure reported for similar derivatives [22]. The mixture was refluxed under stirring for 8 h, the water formed was separated from the organic phase and the organic layer washed with water, aq. NaHCO$_3$ and water again, in that order. After drying (Na$_2$SO$_4$) the solvent was removed under reduced pressure and the crude product fractionally distilled to give the ester (b.p. 116°C at 16 mmHg) in 91% yield.

^{1}H-NMR: 7.30–7.15 (m, 5 H, aromatic), 3.65 (s, 3 H, CH$_3$), 2.95 (t, 2 H, 3-CH$_2$), 2.65 (t, 2 H, 2-CH$_2$).

FT-IR: 3075, 3064, 3029 (ν_{CH} arom.), 2952–2845 (ν_{CH} aliph.), 1741 (ν_{CO} ester), 1605 ($\nu_{C=C}$ arom.), 752 (monosubst. arom.) cm^{-1}.

2.3.2. 3-[(p-Acetyl)phenyl] propionic acid methyl ester (3)

This was prepared by cautious dropwise addition of acetyl chloride (0.240 mol) to an ice-cooled stirred suspension of 3-phenyl propionic acid methyl ester (0.178 mol) in carbon disulfide (120 ml) in the presence of aluminum trichloride (0.440 mol). After the addition, the mixture was refluxed for 4 h, then cooled and poured into aq. 36% HCl (200 ml) and ice (400 g) and the organic layer separated. After thorough washing with water, followed by aq. NaHCO$_3$ and water again, the carbon disulfide solution was dried (Na$_2$SO$_4$), the solvent evaporated under reduced pressure and the residue fractionally distilled to give the acylated product (b.p. 218–220°C at 0.03 mmHg) in 72% yield.

^{1}H-NMR: 7.90–7.30 (m, 4 H, aromatic), 3.65 (s, 3 H,

ester CH$_3$), 3.05 (t, 2 H, 3-CH$_2$), 2.65 (t, 2 H, 2-CH$_2$), 2.60 (s, 3 H, acyl CH$_3$).

FT-IR: 3030, 3003 (ν_{CH} arom.), 2953–2847 (ν_{CH} aliph.), 1738 (ν_{CO} ester), 1682 (ν_{CO} ketone), 1608 ($\nu_{C=C}$ arom.), 841, 671 (p-disubst. arom.) cm^{-1}.

2.3.3. 3-(p-Styryl)-propionic acid methyl ester (5)

Sodium borohydride (0.06 mol) in methanol (10 ml) was dropwise added, under stirring, to the above mentioned acyl intermediate (0.126 mol) in diethyl ether (80 ml). The mixture was kept at room temperature until the ketone carbonyl signal disappeared in the IR spectra of crude reaction samples, thus indicating the progress of the reaction towards alcohol **4**. The mixture was then acidified with aq. 10% HCl and the ether layer washed with water and dried (Na$_2$SO$_4$). After evaporation of the solvent under reduced pressure, the crude product was submitted to distillation, giving directly the dehydrated product (b.p. 115–118°C at 1 mmHg) in 58% yield.

^{1}H-NMR: 7.35–7.15 (m, 4 H, aromatic), 6.70 (dd, 1 H, C*H*=CH$_2$), 5.70 (dd, 1 H, *cis* CH=C*H*$_2$), 5.20 (dd, 1 H, *trans* CH=C*H*$_2$), 3.65 (s, 3 H, CH$_3$), 2.95 (t, 2 H, 3-CH$_2$), 2.62 (t, 2 H, 2-CH$_2$).

FT-IR: 3048, 3005 (ν_{CH} arom.), 2956–2863 (ν_{CH} aliph.), 1734 (ν_{CO} ester), 1630 ($\nu_{C=C}$ vinyl), 1606 ($\nu_{C=C}$ arom.), 904 ($\delta_{CH=CH2}$), 842, 688 (p-disubst. arom.) cm^{-1}.

2.3.4. 3-(p-Styryl)-propionic acid (6)

This was obtained from the methyl ester (0.068 mol) in ethanol (60 ml) by addtion of KOH (0.094 mol) in ethanol (10 ml) under stirring at room temperature for 2 days in the presence of traces of copper powder as polymerization inhibitor. The mixture is then made acidified with aq. 5% H$_2$SO$_4$, the solvent evaporated and the residue extracted with diethyl ether and thoroughly washed with water. After drying (Na$_2$SO$_4$) and solvent evaporation under reduced pressure, the crude product was purified by crystallization from ethanol/water. Yield 78%.

^{1}H-NMR: 11.50 (bs, 1 H, COOH), 7.35–7.15 (m, 4 H, aromatic), 6.70 (dd, 1 H, C*H*=CH$_2$), 5.70 (dd, 1 H, *cis* CH=C*H*$_2$), 5.20 (dd, 1 H, *trans* CH=C*H*$_2$), 2.95 (t, 2 H, 3-CH$_2$), 2.62 (t, 2 H, 2-CH$_2$).

FT-IR: 3437 (ν_{OH} acid), 3085, 3005 (ν_{CH} arom.), 2906–2853 (ν_{CH} aliph.), 1703 (ν_{CO} acid), 1630 ($\nu_{C=C}$ vinyl), 1606 ($\nu_{C=C}$ arom.), 902 ($\delta_{CH=CH2}$), 839, 670 (p-disubst. arom.) cm^{-1}.

2.3.5. Tributyltin 3-(p-styryl)-propionate (TBTSP)

This was prepared from the acid (0.028 mol) and bis(tributyltin) oxide (0.014 mmol) in benzene (100 ml) under reflux in a Dean Stark apparatus by azeotropically removing the water produced in the reaction. The benzene solution was evaporated to dryness under reduced pressure and the **TBTSP** monomer purified by crystallization from ethanol/water. Yield 89%.

^{1}H-NMR: 7.35–7.15 (m, 4 H, aromatic), 6.70 (dd, 1 H,

Table 1
Polymerization data for **TBTSP** and copolymers **TBTSP/STY** (polymerizations carried out in benzene at 60°C for one week)

Feed		Conversion[a]	Polymeric product			
TBTSP (mol%)	**STY** (mol%)		**TBTSP** (mol%)[b]	**TBTSP** (weight%)[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
100	–	73	100	100 (97.2)	8400	1.4
80	20	70	83.6	95.8 (94.7)	7700	1.4
60	40	50	59.9	87.0 (85.4)	10 000	1.4
40	60	48	40.7	75.4 (73.2)	10 700	1.2
20	80	25	19.7	52.3 (50.5)	15 000	1.1

[a] Calculated as (gram of polymer/gram of monomers) 100.

[b] Determined by ^{1}H-NMR in CDCl$_3$ solution.

[c] Calculated from molar composition, as determined by^{1}H NMR. Values in parenthesis are derived from elemental analysis of tin.

[d] Determined by GPC in THF at 25°C.

C*H*=CH$_2$), 5.70 (dd, 1 H, *cis* CH=C*H$_2$*), 5.20 (dd, 1 H, *trans* CH=C*H$_2$*), 2.95 (t, 2 H, 3-CH$_2$), 2.62 (t, 2 H, 2-CH$_2$), 1.55 (m, 6 H, SnCH$_2$C*H$_2$*), 1.35 (m, 6 H, C*H$_2$*CH$_3$), 1.15 (t, 6 H, SnC*H$_2$*), 0.90 (t, 9 H, CH$_3$).

^{13}C-NMR: 178.2 (C=O), 141.1 (*p*-arom.), 136.7 (*i*-arom.), 135.4 (*C*H=CH$_2$), 128.5 (*o*-arom.), 126.2 (*m*-arom.), 112.9 (CH=*C*H$_2$), 36.3 (3-CH$_2$), 31.6 (2-CH$_2$), 27.8 (SnCH$_2$*C*H$_2$) ^{2}J(^{13}C$-^{119/117}$Sn) = 20 Hz], 27.0 (SnCH$_2$CH$_2$*C*H$_2$) [^{3}J(^{13}C$-^{119/117}$Sn) = 65 Hz], 16.4 (Sn*C*H$_2$) [^{1}J(^{13}C$-^{119/117}$Sn) = 358/342 Hz], 13.6 (Sn(CH$_2$)$_3$ *C*H$_3$).

^{117}Sn-NMR: 107.

FT-IR: 3085, 3003 (ν_{CH} arom.), 2956–2853 (ν_{CH} aliph.), 1631 ($\nu_{C=C}$ vinyl), 1556 (ν_{CO} ester), 906 ($\delta_{CH=CH2}$), 840, 670 (*p*-disubst. arom.) cm^{-1}.

2.3.6. Tributyltin 3-(p-ethylphenyl)-propionate (**TBTSP-E**)

This was prepared by H$_2$ hydrogenation of **TBTSP** (4 mmol) in dry THF (50 ml) in the presence of palladium 10% on activated carbon (0.1 g) as catalyst, at room temperature for 1 h. After evaporation of the solvent under reduced pressure, the crude product was purified by crystallization from ethanol/water. M.p. 61°C, yield 55%.

^{1}H-NMR: 7.12 (m, 4 H, aromatic), 2.95 (t, 2 H, 3-CH$_2$), 2.65 (m, 4 H, 2-CH$_2$ and ArC*H$_2$*CH$_3$), 1.60 (m, 6 H, SnCH$_2$C*H$_2$*), 1.35 (m, 6 H, C*H$_2$*CH$_3$), 1.30–1.20 (m, 9 H, SnC*H$_2$* and ArCH$_2$C*H$_3$*), 0.90 (t, 9 H, CH$_3$).

^{13}C-NMR: 178.5 (C=O), 141.8 (*p*-arom.), 138.5 (*i*-arom.), 128.2 (*o*-arom.), 127.8 (*m*-arom.), 36.5 (3-CH$_2$), 31.5 (2-CH$_2$), 28.4 (*C*H$_2$CH$_3$), 27.8 (SnCH$_2$*C*H$_2$) [^{2}J(^{13}C$-^{119/117}$Sn) = 20 Hz], 27.0 (SnCH$_2$CH$_2$*C*H$_2$) [^{3}J(^{13}C$-^{119/117}$Sn) = 65 Hz], 16.4 (Sn*C*H$_2$) [^{1}J(^{13}C$-^{119/117}$Sn) = 360/344 Hz], 15.6 (CH$_2$*C*H$_3$), 13.6 (Sn(CH$_2$)$_3$ *C*H$_3$).

^{117}Sn-NMR: 106.

FT-IR: 3086, 3019 (ν_{CH} arom.), 2957–2854 (ν_{CH} aliph.), 1556 (ν_{CO} ester), 824, 669 (*p*-disubst. arom.) cm^{-1}.

2.3.7. Tributyltin 3-(p-isopropylphenyl)-propionate (**TBTSP-I**)

This was prepared by hydrogenation of *p*-isopropyl tributyltin cinnamate in the presence of palladium 10% on

activated carbon, following the same method described above. The product, m.p. 66°C, was obtained in 75% yield.

^{1}H-NMR: 7.14 (s, 4 H, aromatic), 2.91 (t, 2 H, 3-CH$_2$), 2.89 (m, 1 H, C*H*–CH$_3$), 2.61 (t, 2 H, 2-CH$_2$), 1.59 (m, 6 H, SnCH$_2$C*H$_2$*), 1.34 (m, 6 H, C*H$_2$*CH$_3$), 1.26–1.20 (m, 12 H, SnC*H$_2$* and CHC*H$_3$*), 0.90 (t, 9 H, CH$_2$C*H$_3$*).

^{13}C-NMR: 178.4 (C=O), 146.4 (*p*-arom.), 138.6 (*i*-arom.), 128.2 (*o*-arom.), 126.3 (*m*-arom.), 36.5 (3-CH$_2$), 33.7 (*C*H(CH$_3$)$_2$), 31.5 (2-CH$_2$), 27.8 (SnCH$_2$*C*H$_2$) [^{2}J(^{13}C$-^{117}$Sn) = 21 Hz], 27.0 (SnCH$_2$CH$_2$*C*H$_2$) [^{3}J(^{13}C$-^{119/117}$Sn) = 64 Hz], 24.0 (CH(*C*H$_3$)$_2$), 16.4 (Sn*C*H$_2$) [^{1}J(^{13}C$-^{119/117}$Sn) = 358/342 Hz], 13.6 (Sn(CH$_2$)$_3$ *C*H$_3$).

^{117}Sn-NMR: 106.

FT-IR: 3088, 3021, 3005 (ν_{CH} arom.), 2956–2854 (ν_{CH} aliph.), 1556 (ν_{CO} ester), 818, 668 (*p*-disubst. arom.) cm^{-1}.

2.3.8. p-Isopropyl cinnamic acid

This was prepared by a Knoevenagel-type reaction [23] by dropwise addition, under strong stirring, of *p*-isopropyl benzaldehyde (30 mmol) to malonic acid (30 mmol) in pyridine (20 ml) in the presence of piperidine (1 ml) and hydroquinone (0.01 g). The mixture was then kept at 90°C for 4 h, cooled and treated with ice-cooled diluted HCl. The product was extracted with diethyl ether and the ether solution washed with water and dried (Na$_2$SO$_4$). Evaporation under reduced pressure of the solvent gave the crude product, which was purified by crystallization from ethanol/water. M.p. 160°C (lit. [24] 157–8°C), yield 83%.

^{1}H-NMR: 7.78 (d, 1 H, ArCH=), 7.50–7.25 (dd, 4 H, aromatic), 6.42 (d, 1 H, =CHCOO), 2.92 (m, 1 H, C*H*–CH$_3$), 1.25 (d, 6 H, CH$_3$).

FT-IR: 3300–3200 (ν_{OH} acid), 2953–2589 (ν_{CH} aliph.), 1683 (ν_{CO} acid), 1626 ($\nu_{C=C}$ aliph.), 1608 ($\nu_{C=C}$ arom.), 980 ($\delta_{CH=CH}$), 823, 678 (*p*-disubst. arom.) cm^{-1}.

2.3.9. Tributyltin p-isopropyl cinnamate

This was prepared from the acid (0.024 mol) and bis(tributyltin) oxide (0.012 mmol) in benzene (120 ml) as described above for the esterification of 3-(*p*-styryl)-propionic

acid. The product was purified by crystallization from ethanol/water. M.p. 83°C, yield 88%.

^{1}H-NMR: 7.61 (d, 1 H, ArCH=), 7.45–7.25 (m, 4 H, aromatic), 6.45 (d, 1 H, =CHCOO), 2.90 (m, 1 H, CHCH$_3$), 1.70 (m, 6 H, SnCH$_2$CH$_2$), 1.35 (m, 18 H, CH$_2$CH$_3$, SnCH$_2$ and CHCH$_3$), 0.90 (t, 9 H, CH$_2$CH$_3$).

FT-IR: 3082, 3022, 3007 (ν_{CH} arom.), 2958–2860 (ν_{CH} aliph.), 1639 ($\nu_{C=C}$ aliph.), 1604 ($\nu_{C=C}$ arom.), 1543 (ν_{CO} ester), 982 ($\delta_{CH=CH}$), 828, 673 (*p*-disubst. arom.) cm^{-1}.

2.3.10. Polymerizations: general procedure

The homo- and copolymerizations with styrene of **TBTSP** were carried out in dry benzene (10 ml) in the presence of AIBN as radical initiator (2% by weight with respect to the monomer, or monomer mixtures). The total amount of 1 g of monomer(s) was used, with **TBTSP** and styrene quantities calculated in order to have molar compositions in the feed of 100, 80, 60, 40 and 20% of **TBTSP** [poly(**TBTSP**) and **copol/80**, **/60**, **/40** and **/20**, respectively]. All solutions, prepared under inert atmosphere into a polymerization vial, were submitted to several freeze–thaw cycles in order to remove every trace of oxygen. The vials were then kept at 60°C for one week and the reaction product precipitated by dropwise addition into excess (150 ml) of *n*-pentane. The polymers were purified by repeated dissolution in chloroform and reprecipitation in

Fig. 2. FT-IR spectra of (a) **copol/20**; (b) **copol/40**; (c) **copol/60**; (d) **copol/80**; and (e) poly(**TBTSP**). Arrows indicate the absorption bands at 1650 and 1560 cm^{-1}.

n-pentane, then thoroughly dried under vacuum to constant weight. All polymers were readily soluble in THF, chloroform and dimethylsulfoxide. Copolymers composition was determined by ^{1}H-NMR spectra, based on the ratios of the integrated signals of the aromatic to aliphatic protons according to the following expression:

$$\text{Aromatic }^1\text{H/Aliphatic}^1\text{H} = 4n + 5(1-n)/34n + 3(1-n)$$

where *n* represents the molar fraction of organotin co-units. Based on tests on samples of known composition, the error in the obtained data resulted around the 2% of the value found. The composition values obtained from elemental analysis of tin were in excellent agreement with the data calculated from ^{1}H-NMR spectra.

Polymerization yields and compositions of the copolymers are reported in Table 1. ^{1}H-NMR and FT-IR spectra of homo- and copolymers are reported in Figs. 1 and 2, respectively.

3. Results and discussion

3.1. Syntheses

The synthesis of monomer **TBTSP** has been carried out starting from 3-phenyl propionic acid (**1**), through methanol esterification to ester **2**, followed by subsequent Friedel–Crafts acylation to the *p*-acetyl derivative **3**, hydride reduction of the ketone to the alcohol **4**, and alcohol dehydration to the styrene derivative **5**. The intermediate alcohol **4** was actually not isolated in the pure form, as the crude product gave directly the subsequent derivative **5**, due to thermal dehydration during distillation. Finally, hydrolysis of the methyl ester **5** gave 3-(*p*-styryl)-propionic acid **6** (Scheme 1). Steps from **2** to **6** have been performed according to procedures reported for the synthesis of *p*-vinyl phenylacetic acid [25], the acid 6 being only mentioned in a patent [26] as a byproduct obtained through a different route.

Monomer **TBTSP** was finally obtained by esterification of **6** with bis(tributyltin) oxide according to standard procedures [5]. All products reported in Scheme 1 were characterized by IR and NMR techniques (see Section 2). Monomer **TBTSP** was also used to prepare the model compound **TBTSP-E** by double bond hydrogenation. Model **TBTSP-I** was similarly prepared by hydrogenation of *p*-isopropyl tributyltin cinnamate, prepared by known methods (see Section 2).

The polymerization of **TBTSP** was carried out in the presence of a significant amount (2%) of radical thermal initiator (AIBN) and adopting a long polymerization time in order to favour the conversion of the organotin monomer. It is in fact established that vinyl monomers bearing the tin atom directly linked to the reactive moiety exhibit an inhibiting effect by the metal towards the growing radical chain, [27] although the presence of phenyl or carboxy groups interposed between tin and the polymerizing center renders
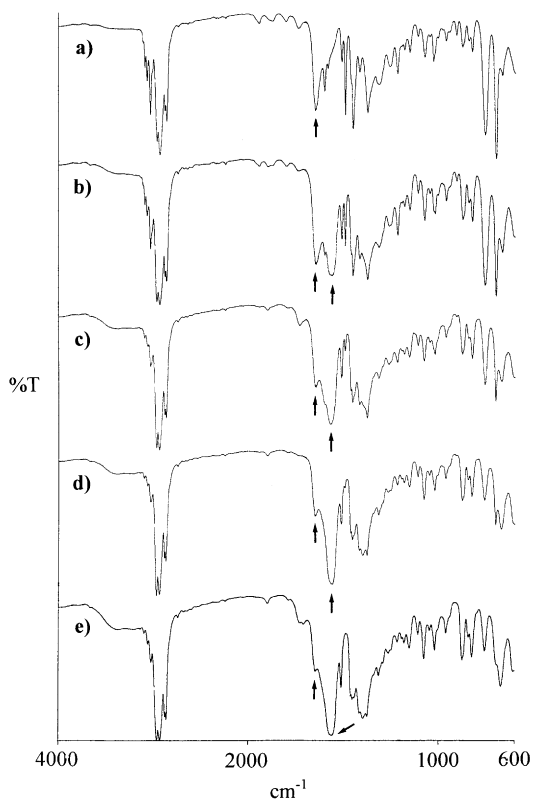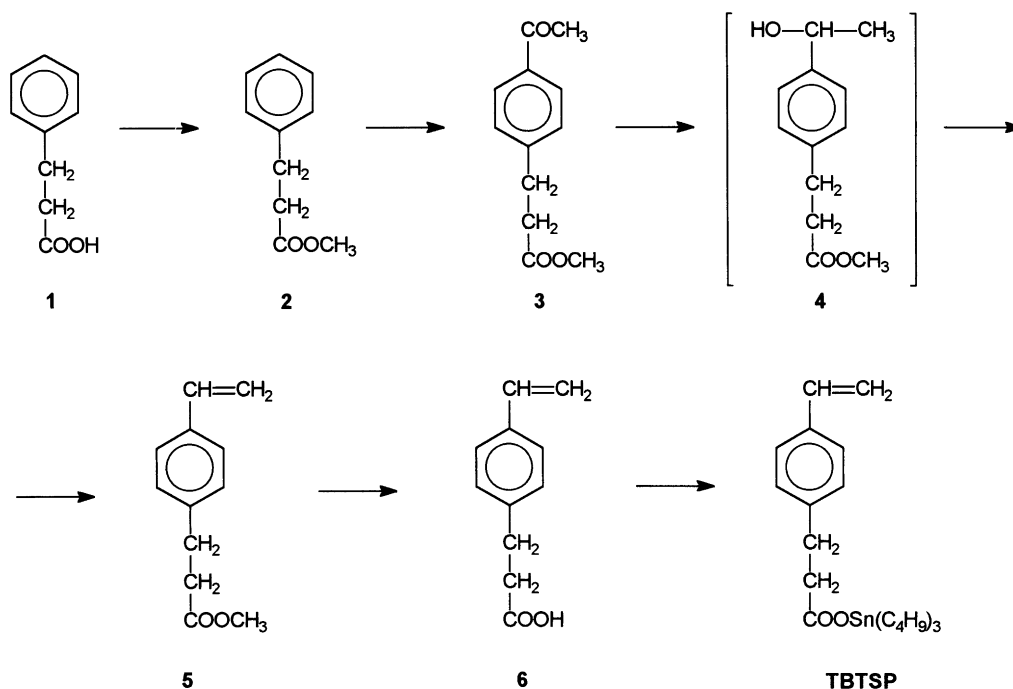
Scheme 1.

the above effect much less relevant [28,29]. For instance, 3-tributyltin styrene [30] and tributyltin methacrylate [31] can be readily homo- and copolymerized with styrene in acceptable yields under radical conditions. Tributyltin cinnamates do not homopolymerize, but give copolymers with styrene [32]. Under the adopted conditions, the radical homopolymerization of **TBTSP** (Table 1) indeed affords in appreciably good yield the corresponding polymeric derivative having rather low average molecular weight, as expected on the basis of steric hindrance of the bulky tributyltin group. The possibility of degradative chain transfer by the organotin moiety could also be taken into consideration as a factor favouring low values of molecular weight. Accordingly, a trend in average molecular weight increase with increasing content of styrene co-units is observed in the copolymers. A reduction of conversion is found upon increasing the amount of styrene comonomer in the feed, which can be attributed to increased solubility and reduced aggregation capability of the macromolecules in the precipitating solvent when the organotin containing co-units are dispersed between progressively longer chain sections constituted by styrene sequences. The polydispersity index values, particularly observed at higher contents of styrene co-monomer, appear quite low for a radical polymerization (Table 1). This could be likewise attributed to the progressive fractionation of the material occurring upon repeated dissolution and reprecipitation of the macromolecules.

As a result of the long reaction time adopted and the high monomer conversions, the compositions of copolymers strictly resemble the feed compositions, thus preventing any evaluation of monomers reactivity ratios, however it is reasonable to hypothesize a substantially similar reactivity of the comonomers.

The ^{1}H-NMR analysis is in agreement with the proposed structures, the resonances of vinyl protons at 5.70 and 5.20 ppm being absent in the spectra of the polymers (Fig. 1) and new signals related to the saturated methylene and methine protons located in the main chain appearing in the 1–2 ppm region.

3.2. FT-IR characterization

The FT-IR spectra, in addition to confirming the disappearance of the vinyl group in the polymers, exhibit (Fig. 2) the expected patterns related to the different compositions. In particular, the absorptions above 3000 cm^{-1}, connected to the aromatic CH stretchings, as well as the bands at 760 and 700 cm^{-1}, related to the monosubstituted aromatic ring of the styrene co-units, appear progressively decreasing in intensity as the content of triorganotin carboxylate co-units increases. Moreover, one can observe, in the spectral region related to the triorganotin carboxylate carbonyl stretching frequency, a progressive increase of the band close to 1560 cm^{-1} with a concomitant decrease of the absorption located around 1650 cm^{-1}, upon increasing the content of the triorganotin carboxylate co-units. It is well established [33] that trialkyltin carboxylates can exhibit in the solid state a symmetrical structure with trigonal bipyramidal geometry where the trialkyltin group assumes a planar configuration, thus generating polymeric structures of the type depicted in Chart 2, involving penta-coordinated tin atoms.

Table 2
IR carbonyl stretching frequencies of model and polymers (in the solid state (KBr disc))

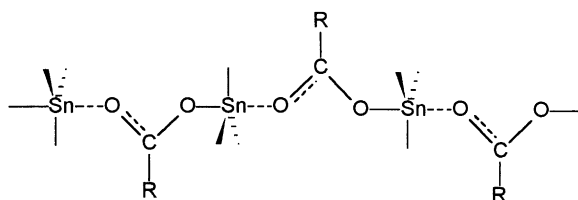| Sample	CO stretch. frequency (cm^{-1})				$\Delta\nu_{as-s}$ (cm^{-1})
	ν_{as}	ν_s	ν_{as}	ν_s	
TBTSP-MI	1556	1406	–	–	150
Poly(**TBTSP**)	1562	1418	1651	1317	144, 334
copol/80	1567	1417	1651	1317	150, 334
copol/60	1567	1417	1646	1317	150, 329
copol/40	1562	1418	1646	1317	144, 329
copol/20	–	–	1651	1315	336

Chart 2.

In this situation, as observed for instance in tributyltin acetate, two absorptions at 1572 and 1410 cm^{-1}, respectively, related to asymmetrical and symmetrical carbonyl stretching frequencies with a $\Delta\nu$ value of 162 cm^{-1}, close to the value (153 cm^{-1}) for the corresponding sodium salt [34], are present in the solid state IR spectrum. Similarly, tributyltin phenylacetate exhibits bands at 1565 and 1400 cm^{-1} ($\Delta\nu = 165$ cm^{-1}) [35]. In solution of a noncoordinating solvent, or in the liquid (molten) state, the above depicted symmetrical structure is broken, the tin
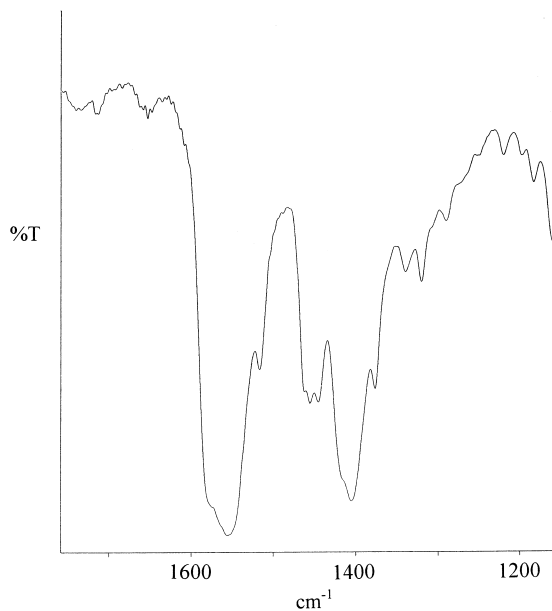

Fig. 3. FT-IR spectrum of **TBTSP-I** in the 1200–1700 cm^{-1} spectral region.

atom assumes a tetra-coordinated structure resembling the one of normal organic esters, and the IR spectra display carbonyl stretching frequencies located at 1650 and 1300 cm^{-1} with $\Delta\nu$ values around 350 cm^{-1}, corresponding to free, monodentate carboxylic groups [35]. $\Delta\nu$ values of about 170 and 330 cm^{-1} in the solid state and in solution, respectively, have also been observed for a series of tributyltin phenoxyacetates [36].

As shown in Table 2, all polymeric products, with the exception of **copol/20**, evidence the presence in the solid state of both penta- and tetra-coordinated tin atoms in ratios gradually decreasing upon decrease of the content in organotin co-units. This is clearly the consequence of a decreased ability of trialkyltin carboxylates to be involved in inter- and/or intrachain interactions. In these products, therefore, the macromolecules are characterized, to a more or lesser extent, by the presence of both inter- and intramolecular bridges generating penta-coordinated tin, and tetra-coordinated (isolated) trialkyltin carboxylates. In the case of **copol/20**, only the absorptions related to tetra-coordinated tin are actually present, due to the increased dilution of the trialkyltin carboxylate moieties in the macromolecular coils, which prevents the possibility of mutual interactions, in a manner similar to the liquid state. On the contrary, the lack of structural restraints arising from the macromolecular coil, allows the low molecular weight model compound **TBTSP-I** to assume a structure involving exclusively penta-coordinated tin moieties, as indicated by the absence of significant absorption signals at 1650 cm^{-1} (Fig. 3).

3.3. ^{13}C- and ^{117}Sn-NMR characterization

The solution state ^{13}C-NMR data of the monomer and model compounds display (see Section 2) $^1J(^{13}C-^{119/117}Sn)$ coupling constants unambiguously characteristic for tetra-coordinated tin atoms [37–39]. The ^{13}C spectra of the polymers look very similar, displaying rather broad resonances for the backbone carbons and narrower resonances for the butyl carbon atoms, the latter varying in intensity according to the **TBTSP** content. The $^1J(^{13}C-^{119/117}Sn)$ coupling constants are exactly the same (358/342 Hz) as in the monomer or model compounds, indicating the tin atoms are tetra-coordinated in all the CDCl$_3$ dissolved (co)polymers.

All CP-MAS ^{13}C spectra of the solid polymers display resonances with comparable chemical shifts, again reflecting, by the varying intensities of the butyl resonances relative to the aromatic carbons, the varying content in **TBTSP**. Attempts to determine the compositions of the copolymers by integration of the aromatic and aliphatic carbons were unsuccessful due to the different cross polarization behaviour of these carbon atoms. Also, the overlap and the intensity of the aliphatic resonances mask the $^{119/117}$Sn satellites, thus preventing measurement of the $^1J(^{13}C-^{119/117}Sn)$ coupling constants in the solid state. Table 3 provides an overview of the solution and solid state ^{117}Sn-NMR data.

The chemical shift data of the solution state are

Table 3
^{117}Sn-NMR data for model compounds and polymers (see Section 2 for definitions)

Sample	$\delta_{sol.}$ [a]	δ_{iso} [b]	ζ [c]	η [d]	σ_{11} [e]	σ_{22} [e]	σ_{33} [e]
TBTSP-E	106	−53	−259	0.05	190	177	−206
TBTSP-I	106	−47	−275	0.01	177	175	−210
TBTSP	107	−51	−258	0.10	193	167	−207
		−61	−275	0.00	199	198	−214
poly(**TBTSP**)	103	93, −45 (65)[f]					
copol/80	104	92, −45 (59)[f]					
copol/60	105	92, −45 (57)[f]					
copol/40	105	92, −45 (53)[f]					
copol/20	106	95[f]					

[a] Solution ^{117}Sn chemical shift in ppm at 303°K in CDCl$_3$ (ca 100 mg/0.5 mL); no concentration dependency was detected upon tenfold dilution.

[b] Isotropic solid-state ^{117}Sn chemical shift.

[c] The anisotropy parameter.

[d] The asymmetry parameter.

[e] σ_{11}, σ_{22} and σ_{33} represent the three components of the shielding tensor.

[f] The ^{117}Sn resonances of the polymers are very broad, typically 20–30 ppm; values between brackets indicate the percentage of penta-coordinated tin atoms.
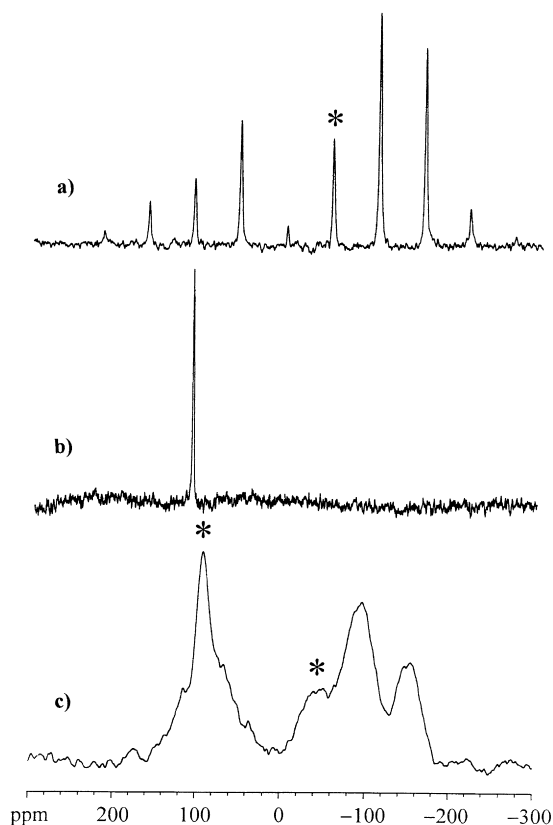

Fig. 5. TGA curves of: (a) **TBTSP-E**; (b) **copol/20**; (c) **copol/40**; (d) **copol/60**; (e) **copol/80**; and (f) poly(**TBTSP**).

Fig. 4. ^{117}Sn CP-MAS NMR spectrum of: (a) **TBTSP-I**; (b) ^{117}Sn-NMR spectrum of **copol/60** in CDCl$_3$ solution; and (c) in the solid state. Resonances marked with asterisk in spectra (a) and (c) correspond to isotropic chemical shifts, all other signals representing spinning side bands.
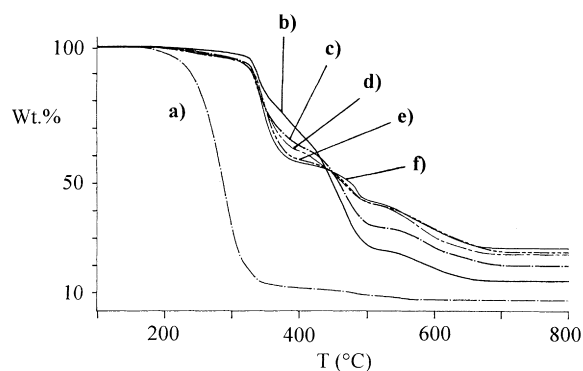
characteristic for tetra-coordinated tin atoms in tributyltin-carboxylates [40–42].

The isotropic ^{117}Sn chemical shifts of the monomer **TBTSP** and the model compounds **TBTSP-E** and **TBTSP-I** in the solid state, shifted by some 150 ppm to lower frequency, when compared to the solution state, reflect penta-coordination (Fig. 4a), which is strongly indicative of a polymeric structure lost in solution towards a tetrahedral configuration. It is also indeed well established, by Sn-NMR studies, that polymeric or oligomeric organotin structures, present in the solid state and/or in concentrated solutions, can decompose into their monomers upon dilution [43,44]. These penta-coordinated tin compounds display (nearly) axially symmetric shielding tensors and a shielding anisotropy of the order of −260 ppm. This is in good agreement with literature data on a variety of polymeric tin compounds, including carboxylates, displaying the polymeric zig-zag chains with tin in a trigonal-bipyramidal $trans$-R$_3$SnO$_2$ geometry [45,46]. Accordingly, this structure is proposed likewise for the monomer and model compounds of the present work. Note that **TBTSP** (Table 3) displays two slightly different molecular environments in the solid state, in comparable amounts, as assessed by the observation of two different sets of chemical shift anisotropy parameters.

The solid state ^{117}Sn spectra of the polymers show very broad resonances (20–30 ppm) with few spinning side bands. The spectrum of **copol/20** displays only one isotropic shift at 95 ppm, evidencing only tetra-coordinated tin atoms are present in this copolymer. This finding confirms the conclusions from the IR data discussed above.

The other copolymers and the homopolymer exhibit two isotropic resonances (Fig. 4c), the first one at −45 ppm, with an anisotropy pattern very similar to the penta-coordinated model compound (Fig. 4a), which likewise displays spinning side bands of very low intensity at the high frequency side of the isotropic resonance, indicative of penta-coordinated tin atom. By contrast, a single ^{117}Sn resonance is present in the CDCl$_3$ solution (Fig. 4b) with a chemical shift value of 105 ppm, in the tetra-coordination range, as also established by the ^{1}J(^{13}C–$^{119/117}$Sn) coupling

Table 4
TGA data for model and polymers (performed in the air at 20°C/min heating rate)

Sample	T_d (°C)[a]	First step of weight loss (%)		Inorganic residue (%)		
		Found	Calc.[b]	Found	Calc.[c]	Found/calc. (%)
TBTSP-E	185	n.d.	37	6.9	32.2	21.4
Poly(**TBTS**)	216	40	37	26.1	32.4	80.5
copol/80	215	40	35	24.7	31.0	79.7
copol/60	215	35	32	23.9	28.2	84.7
copol/40	230	30	28	19.7	24.4	80.1
copol/20	252	20	19	14.1	16.9	83.4

[a] Initial decomposition temperature measured after 1% weight loss.

[b] Calculated weight loss due to butyl groups release, based on structural formula or copolymer composition as determined by ^{1}H-NMR.

[c] Calculated values of SnO_2 residue, based on structural formula or copolymer composition as determined by ^{1}H-NMR.

constants (see Section 2), thus revealing release of penta-coordination at tin in solution. The second resonance is located at 93 ppm, very close to the chemical shift value in solution (Fig. 4b) and attributed to tetrahedral tin. The relative amounts of these tetra- and penta-coordinated sites can be estimated by the integration of corresponding resonances. It was demonstrated before that quantitative data obtained from [117]Sn CP-MAS NMR analysis is reliable to within ±10%, provided relaxation and cross polarization properties are comparable for the different tin sites within the molecule [47]. The amount of penta-coordinated tin,

mentioned between brackets in Table 3, is slightly decreasing from 65% in poly(**TBTSP**) to 53% in **copol/40**.

These data also are in complete agreement with the FT-IR analysis, both in solution and in the solid state and are discussed further in the context of thermal analysis results.

3.4. Thermal characterization

The thermogravimetric analysis of the polymers shows, as expected, improved thermal stability with respect to the low molecular weight model (Fig. 5 and Table 4), with initial decomposition temperature values in the air above 200°C. The stability appears significantly higher for the copolymers containing lower amounts of triorganotin moieties; hence it is related to the lowered presence of the tributyltin carboxylate groups, which appear to initiate the polymer decomposition, the extent of resulting weight loss being very close to the content in tributyltin groups of each material sample.

The inorganic residue left after heating at 800°C in the air, constituted by SnO_2, has a remarkably lower mass than calculated for the model compound, which is clearly attributable to sample volatility. However, the non-volatile polymeric samples also afford a residual amount of inorganic material in all cases lower by 15–20% than the expected values, as calculated on the basis of copolymer composition determined by ^{1}H-NMR (Table 4). This finding, which appears to be originated by incomplete tin oxidation taking place under the conditions adopted, regardless the amount of organotin present in the sample, makes therefore the TGA method rather inaccurate for assessing the metal content in this type of products. This can be due to the formation of volatile, low molecular weight, organotin compounds, a proposal which looks reasonable since thermolysis occurs in the contact of air, and, e.g. tributyltin hydroxide can be easily formed.

DSC determinations have been performed on the as-prepared products, without any preliminary thermal conditioning, in order to avoid alterations of the materials and to
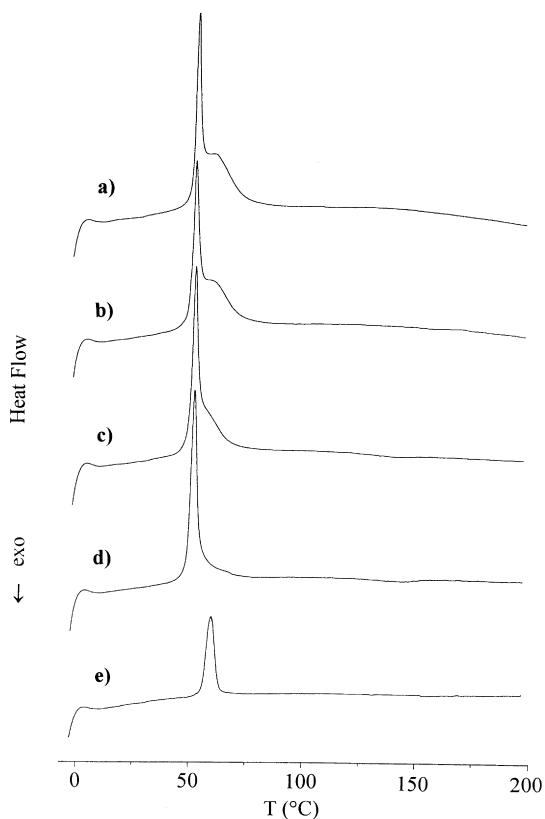

Fig. 6. DSC curves of: (a) poly(**TBTSP**); (b) **copol/80**; (c) **copol/60**; (d) **copol/40**; and (e) **copol/20**.

Table 5
DSC data from the first heating/cooling cycle of model and polymers (performed under nitrogen at 10°C/min heating/cooling rate)

Sample	T_m (°C)[a]	ΔH_m (J/g)	T_c (°C)[b]	5-coord. Sn (wt%)[c]	5-coord./4-coord. Sn[d]	5-coord./4-coord. Sn[e]
TBTSP-E	61.4	65.8	42.1 (47.7)	100	100/0	100/0
Poly(**TBTSP**)	51.1	11.1	55.0 (29.0)	64	64/36	65/35
	58.9	30.9				
copol/80	51.1	11.5	51.5 (24.2)	59	61/39	59/41
	58.6	27.3				
copol/60	50.1	13.0	47.9 (20.6)	51	58/42	57/43
	56.6	20.4				
copol/40	50.3	28.7	42.2 (10.4)	44	58/42	53/47
copol/20	59.6	13.7	–	n.d.	n.d.	0/100

[a] Melting temperature at maximum endothermic peak height.
[b] Crystallization temperature at maximum exothermic peak height. Values in parenthesis refer to the amount of heat (J/g) exchanged in the transition.
[c] Calculated as $(\Delta H_m/65.8) \times 100$.
[d] Calculated on the basis of polymers composition values as determined by ^{1}H-NMR and expressed as wt% (Table 1).
[e] Determined by solid state ^{117}Sn-NMR (Table 3).

obtain results directly comparable to the data afforded by the other solid state measurements. All polymeric samples have been submitted to heating under inert atmosphere from 0 to 200°C at a 10°C/min rate, then cooled at the same rate and submitted to a second heating/cooling cycle. As far as the first heating is concerned, all samples exhibit (Fig. 6) endothermic melting peaks in the 50–60°C interval, close to the melting temperature of **TBTSP-E**, attributable to the presence of crystalline domains in the material (Table 5). Upon cooling, the samples recrystallize, displaying an exothermic peak at temperatures (42–55°C) close to [poly(**TBTSP**) and **copol/80**] or lower than (**copol/60** and **copol/40**) the melting values, with enthalpy values lower than those observed in the heating, thus confirming the occurrence of a reversible transition with partial recrystallization of the material. The only exception to this behaviour is given by **copol/20**, which does not produce any exothermic signal upon cooling. Two overlapping thermal transitions are observed for poly(**TBTSP**) and the copolymers having higher tin content, the broad signal at higher temperature progressively disappearing as the amount of organotin co-units in the copolymers is lowered. Similarly, the amount of heat involved in the transition decreases upon lowering the tin content, thus clearly suggesting a correlation between exchanged heat and content of trialkyltin moieties. No transitions around 100°C, the glass transition temperature of atactic polystyrene, are observed in the copolymers, which is indicative of the absence, to any significant extent, of polystyrene homopolymer contaminating the samples.

Multiple melting endotherms are frequently observed in the DSC curves of semicrystalline polymers. In the case of isotactic polystyrene, the presence of two or more groups of crystals with different morphologies, namely chain-folded crystals and extended-chain crystals, was earlier proposed [48]. Later studies, however, taking into account the effect of heating rate, suggested that multiple peaks are due to a recrystallization process occurring during the scan, wherein the sample partially melts, then recrystallizes and melts a second time [49,50]. In the case of poly(**TBTSP**) and the copolymer series, that have been obtained by radical polymerization, the microstructure of the main chain is atactic and the presence of crystallinity in the material has to be ascribed to the tributyltin carboxylate moieties giving rise to inter- and intrachain interactions due to additional coordination from carboxylate groups to tin atoms, as indicated by IR and ^{117}Sn-NMR spectra. Consequently, the broad peaks at higher temperature, which are more evident in the samples having higher amounts of triorganotin carboxylate moieties, can be attributed to oligomeric or polymeric tin moiety aggregation of variable extent, generating penta-coordinated tin atoms of the type depicted in Chart 2, connecting pendant triorganotin carboxylates bound to the polystyrene side-chains with one another. The narrow peaks at lower temperature, contributing to a lesser extent to the amount of heat absorbed by the sample (Table 5), could be consequently attributed to very short sequences of penta-coordinated tin moieties or, tentatively, to the presence of cyclic dimers of the type depicted in Chart 3, which may be more present when the tin containing co-units become more diluted in the polymeric chain.
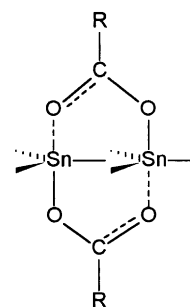

Chart 3.

The above view, which attributes the occurrence of thermal transitions only to the melting of penta-coordinated tin moieties, with no thermal contribution from tetra-coordinated

tin groups or from main chain motions, is supported by the following considerations. If it is considered that the enthalpy change involved in the melting of **TBTSP-E** is due to the melting of completely penta-coordinated tin, as indicated by solid state IR and Sn-NMR spectra, the weight amount of this species can be calculated for all the polymers, except for **copol/20** (see below), by making use of the total heat exchanged in the melting transitions of the samples (Table 5). Thus, on the basis of the known weight content of tin moieties (Table 1), the percent ratio between penta- and tetra-coordinated tin in each sample can be easily determined. Indeed, the values calculated according to this procedure appear in very nice agreement with those independently obtained by solid state ^{117}Sn-NMR (Table 3), thus confirming the above made hypothesis.

A particular comment has to be dedicated to the DSC behaviour of **copol/20**. This compound, differently from all the other products synthesized, possesses only tetra-coordinated tin atoms, hence no inter or intramolecular interactions giving rise to crystallinity are present. However, it exhibits a melting peak with a maximum at 59.6°C, very close to the value found for **TBTSP-E**, having completely penta-coordinated tin atoms. This transition cannot be attributed to the melting of tetra-coordinated tin moieties, as it should have also been present in the other polymeric samples to a decreasing extent upon increasing the content of organometal co-units. It could be proposed that the observed melting is due to crystalline regions constituted by sequences of styrene co-units, as observed [32] for the copolymer poly(tributyltin cinnamate-*co*-styrene) of similar composition (17.3 mol% of organotin co-units), for which a sequence length of at least three styrene co-units for crystallization to occur was calculated. Taking into account that in **copol/20** the mean styrene co-units sequence should be around four, the above hypothesis appears reasonable. As mentioned above, cooling of this sample does not produce any exothermic peak, as expected for molten atactic polystyrene co-units submitted to insufficiently slow cooling for allowing the crystallization to occur. Indeed, when **copol/20** is submitted to a second heating cycle, only a glass transition around 39–40°C is displayed, and no melting peak. This confirms that the thermal behaviour of this sample is not related to tin coordination, but rather to the possibility for polystyrene chain sections to crystallize when cooled at a sufficiently low rate. It is worth observing that, due to the macromolecular structure, the organotin moieties are prevented to interact with one another, hence giving rise to an example of tri-alkyltin carboxylate existing exclusively in the tetra-coordinated form in the solid state. This is a rather uncommon feature, although examples with such a tetra-coordination are known when either the organic moiety of the carboxylate residue or the triorganotin moiety on the latter are sterically bulky [40,51–53]. In the case of the present **copol/20** a sterical constraint is again responsible for the presence of tetra-coordination at tin solely.

4. Conclusions

The homo and copolymerization with styrene of monomer **TBTSP** under radical conditions affords in good yields the corresponding polymers having the tributyltin carboxylate moiety covalently linked to the side chain of a polystyrenic backbone. The independent techniques applied to the characterization of the synthesized polymeric products univocally indicate that when these derivatives are in the solid state the tin atoms are both penta- and tetra-coordinated, with the content of penta-coordinated form gradually decreasing upon decreasing the content of triorganotin moieties. When the triorganotin carboxylate groups are sufficiently diluted in the polymeric matrix, such as in the copolymer constituted of about 20 mol% of **TBTSP** monomer, only the tetra-coordinated form of tin is present in the material. By contrast, all products display in CDCl$_3$ solution only the tetra-coordinated form of tin, due to the rupture operated by the solvent of any inter- and/or intramolecular interaction generating the penta-coordinated form.

These findings appear to be of substantial interest to the research currently in progress aimed at evaluating the properties of these polymeric organotin derivatives as selective anion sensors incorporated into plasticized PVC membranes.

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