Synthesis and characterization of novel organotin carboxylate maleimide monomers and copolymers

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Abstract. Two novel tributyltin carboxylate maleimide monomers, tributyltin(maleimido)acetate and tributyltin(4maleimido)benzoate, were synthesized by condensation reaction of maleimidoacetic acid or 4-maleimidobenzoic acid with bis(tributyltin) oxide. Copolymerization of these monomers with styrene was carried in dioxane at 70°C using asobisisobutyronitrile as free radical initiator. The structures of monomers and copolymers were confirmed by FT-IR (Fourier Transform Infrared), ¹H and ¹³C NMR (nuclear magnetic resonance) spectroscopy and elemental analysis. The copolymers were characterized by solubility and thermal analysis.

Keywords: polymer synthesis, molecular engineering, tributyltin polymeric carboxylate, tin coordination, maleimide copolymer

1. Introduction

Organotin derivatives of a compound containing the bioactive alkyltin groups, attached to organic compound via O-Sn and N-Sn bonds, have considerable interest in several research fields. Apart from academic concern related to fundamental research, tin derivatives are widely used as components for antifouling paints [1–4], as catalysts in organic synthesis of polyesters, polyurethanes and crosslinking silicone [5–7], as well as anti-tumor drugs [8, 9] and ion carriers in electrochemical membrane building [10]. Generally, tin derivatives suffer of some toxicity and applications involving tin leaching should be improved, or even avoided. By minimize this drawback, successful results may be obtained by anchoring organotin functionality to a macromolecular chain [11], which prevents the leaching of the toxic residue and facilitates the recovery of the organo-metallic material after its use. Acrylic copolymers with pendant organotin carboxylate moieties have found wide-spread applications as antifouling agents [12–14] and fungicides [15]. Two types of organotin maleimide derivatives have been prepared and their biological activity was investigated [16, 17].

The present investigation deals with synthesis and characterization of new maleimide monomers containing tributyltin carboxylate units linked to the aromatic ring or aliphatic rest, and their copolymers with styrene.

2. Expermental

2.1. Measurements

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 Instruments equipped with a Golden Gate single reflection ATR (attenuated total reflection) accessory, spectrum range 600–4000 cm⁻¹.

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The proton and carbon nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were recorded on

a Bruker NMR spectrometer, Avance DRX 400 MHz, using DMSO- d_6 (dimethyl sulfoxide) and CDCl₃ as solvents and tetramethylsilane as an internal standard.

Melting and softening points were determined with a Gallenkamp hot-block point apparatus.

Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen.

Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 10°C/min.

Gel permeation chromatographic (GPC) analyses were carried out on a PL-EMD 950 Evaporative light Detect instrument using N,N-dimethylformamide (DMF) as the eluant and standard polystyrene sample for calibration.

2.2. Reagents and materials

Chemicals were supplied by Fluka and Aldrich and used as received. Solvents were purified using standard purification techniques [18]. Maleimidobenzoic acid was prepared according to the method described in the literature [19]. *N*-maleimidoacetic acid was prepared according to Rich method [20], $mp = 112-113^{\circ}$ C.

2.2.1. General procedure for the preparation of tributyltin caboxylate maleimide monomers 2(a-b)

Tributyltin (2,5-dioxo-2,5-dihydro- 1H-pyrrol-1-yl)acetate (2a)

In a 250 ml flask equipped with a Dean Stark apparatus, maleimidoacetic acid (2.5 g, 16.10 mmol), benzene (120 ml) and bis(tributyltin) oxide (8.20 ml, 16.10 mmol) were added. The reaction mixture was heated until no more water evolution was observed and benzene was further distilled under reduced pressure. The monomer **2a** gives stable white crystals by crystallization from dioxane, yield 84%, $mp = 99-100^{\circ}$ C.

Elemental analysis calcd. for $C_{18}H_{31}NO_4Sn$ (444.10): C, 48.68; H, 7.04; N, 3.15; Sn, 26.72%. Found: C, 48.78; H, 7.11; N, 3.23; Sn, 26.90%.

FT-IR spectrum (KBr, cm⁻¹): 3100, 2980, 2920, 2860, 1720, 1605, 1580, 1425, 1390, 1315, 1150, 910, 840, 695, 675, 640.

¹H-NMR spectrum (CDCl₃, TMS), δ(ppm): 6.78 (s, 2H, maleimide protons), 4.21 (s, 2H, CH₂ of acetic rest), 1.70 (t, 6H, Sn–C<u>H</u>₂–CH₂–CH₂–CH₂–CH₃), 1.45 (m, 12H, Sn–CH₂–C<u>H</u>₂–CH₂–CH₃) and 0.95 (t, 9H, Sn–CH₂–CH₂–CH₂–C<u>H</u>₃). ¹³C-NMR spectrum (CDCl₃, TMS), δ(ppm): 13.52 (Sn–CH₂–CH₂–CH₂–<u>C</u>H₃), 16.60 (Sn–CH₂–CH₂–CH₂–<u>C</u>H₃), 27 (Sn–CH₂–<u>C</u>H₂–CH₂–CH₃), 27 (Sn–CH₂–<u>C</u>H₂–CH₂–CH₃), 27.58 (Sn–<u>C</u>H₂–CH₂–CH₃), 39.21 (CH₂ of imide rest), 134.28 (CH of maleimide), 170.04 (C=O of maleimide ring),

171.45 (C=O of ester group).

Tributyltin 4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzoate (2b)

The same synthesis system as previously described was used and charged with 4-maleimidobenzoic acid (3.5 g, 16.10 mmol), acetone (50 ml), toluene (80 ml) and bis(tributyltin) oxide (8.20 ml, 16.10 mmol). The reaction mixture was heated at 56°C for 2 hours and then at reflux until no more water evolution was observed and toluene was further distilled under reduced pressure. The monomer **2b** was separated as white crystals by recrystallization from dioxane, mp = 119-123°C, yield 88%.

Elemental analysis calcd. for $C_{23}H_{33}NO_4Sn$ (506.17): C, 54.57; H, 6.57; N, 2.77; Sn, 23.45%. Found: C, 54.61; H, 6.81; N, 2.63; Sn, 23.36%.

FT-IR spectrum (KBr, cm⁻¹): 3110, 2980, 2960, 2860, 1715, 1655, 1605, 1510, 1396, 1340, 1210, 1150, 840, 695, 598, 440.

¹H-NMR spectrum (DMSO-d₆, TMS), δ (ppm): 8.02 (d, 2H, aromatic protons), 7.45 (d, 2H, aromatic protons), 7.20 (s, 2H, maleimide protons), 1.61 (t, 6H, Sn-CH₂-CH₂-CH₂-CH₃), 1.30 (m, 12H, Sn-CH₂-CH₂-CH₂-CH₃) and 0.85 (t, 9H, Sn-CH₂-CH₂-CH₂-CH₃).

¹³C-NMR spectrum (DMSO-d₆, TMS), δ(ppm):

13.64 (Sn-CH₂-CH₂-CH₂-CH₃),

18.59 (Sn–CH₂–CH₂–CH₂–CH₃),

 $26.43 \; (Sn-CH_2-\underline{C}H_2-CH_2-CH_3),$

27.69 (Sn-<u>C</u>H₂-CH₂-CH₂-CH₃),

126.08 (2C, aromatic carbons),

127, 129, 130.40 (aromatic carbons),

134.82 (CH of maleimide),

169.65 (3C, C=O of maleimide and ester groups).

2.2.2. Copolymerization procedure

Copolymerization of monomers 2(a-b) with styrene was carried out in dry dioxane (10 ml) in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN) as radical initiator (2% by weight with respect to the monomer mixtures). The total amount of monomers (2(a-b) and styrene) was 1 g, quantities calculated in order to have molar compositions in the feed of 70, 50, 30 and 20% monomer **2b** and 80, 60, 50 and 30% monomer **2a**.

All solutions were prepared under inert atmosphere into a polymerization vial, and then were degassed by the freeze-thaw technique. The inlet of the ampoule was sealed with gas-oxygen mixture under nitrogen atmosphere at low pressure and then transferred to a thermostated oil bath at 70°C for 24 hours. The copolymer was obtained by precipitation into a large amount of methanol. The precipitated polymer was purified twice by reprecipitation into chloroform/n-pentane mixture for copolymers **3(a-d)** and into chloroform/methanol mixture for copolymers **4(a-d)**.

3. Results and discussion

The tributyltin carboxylate monomers 2(a-b) were synthesized by the condensation reaction of *N*-maleimidoacetic acid (1a) or 4-maleimidobenzoic acid (1b) with bis(tributyltin) oxide in benzene or toluene at reflux (Figure 1).

Structures of these monomers were confirmed by FT-IR and ¹H and ¹³C NMR spectroscopy and elemental analysis. FT-IR spectra of monomers showed absorption bands characteristic to: imide ring at 3100 cm⁻¹ (=CH stretching), 1725 cm⁻¹ (asymmetric C=O stretching), 1385 and 1150 cm⁻¹ (maleimide C–N–C stretching symmetric and



Figure 1. The synthesis of monomers 2(a-b)

asymmetric), 839 cm⁻¹ (maleimide symmetric C–H out-of-plane bending) and 697 cm⁻¹ (deformation of maleimide ring in plane), tributyltin carboxylate groups at 2980–2880 cm⁻¹ (CH stretching of aliphatic butyl groups) and 1697 cm⁻¹ (asymmetric stretching COO of carboxylate group). In addition, the spectrum of monomer **2b** shows absorption bands for *p*-substituted aromatic ring.

The ¹H-NMR spectra of monomers 2(a-b) showed the signals for all types of protons. The spectrum of monomer 2a presents a singlet at 6.78 ppm attributed to maleimide protons, a singlet at 4.21 ppm for >N-CH2-COO- protons and three multiple signals at 1.70, 1.45 and 0.95 ppm corresponding to butyl group protons. In addition, the spectrum of monomer **2b** shows aromatic protons as two doublets at 7.45 and 8.02 ppm. The butyl group protons of monomer 2b appear upfield shifted due to the solvent (DMSO). The ¹³C-NMR spectra of monomers 2(a-b) (Figures 2 and 3) show signals for aliphatic carbon atoms at 13.52, 16.60, 27 and 27.58 ppm for butyl group carbons and at 39.21 ppm for $-\underline{C}H_2$ from acetyl group. HC= carbons of maleimide appear at 134.30 or 134.82 ppm respectively, C=O carbons of maleimide appear at 170 ppm and COO



Figure 2. The ¹³C-NMR spectra of monomer 2a



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Figure 3. The ¹³C-NMR spectra of monomer 2b

carbon at 171.447 ppm. The aromatic carbons from monomer **2b** appear in the range 126.077–129.849 ppm.

The copolymerization of monomers 2(a-b) was carried out in the presence of significant amount of thermal initiator (2% AIBN). The general structure of the copolymers is illustrated in Figure 4. The experimental copolymerization conditions results and copolymer compositions determined by ele-



Figure 4. The synthesis of copolymers 3(a-d) and 4(a-d)



Figure 5. The FT-IR spectra of copolymers 3a and 4c

mental analysis data are shown in Table 1. The copolymers were insoluble in water, methanol and soluble in chloroform, acetone and dimethylsulfoxide (DMSO). The yield was lower than 83% for all the copolymerization reactions and there was not an important effect of the monomer feed composition on the yield. The average molecular weight ranged between 34 800 and 129 000 g/mol and the polydispersity varied in the range of 1.36–2.35.

The chemical structures of the copolymers were confirmed by FT-IR and ¹H-NMR spectroscopy and elemental analysis. The FT-IR spectra of copolymers as shown in Figure 5, revealed the absorption bands at 1778, 1720 cm⁻¹ (corresponding to symmetrical and asymmetrical C=O stretching of the imide ring), 1377, 1172 cm⁻¹ (maleimide C–N–C stretching symmetric and asymmetric), 695 cm⁻¹ (imide ring), 3060, 1600, 820 cm-1(aromatic rings), 2958-2853 cm⁻¹ (vibration of aliphatic rest) and new absorption bands at 1570, 1455, 1418 cm⁻¹ for copolymers **3(a–d)** and at 1647, 1463, 1474, 1407 cm⁻¹ for copolymers **4(a–d)**



Figure 6. The possible structures for non-polymeric tributyltin carboxylates in the solid state

Copolymer	Monomer feed		Conversion	Copolymer composition		$\overline{\mathbf{M}}_{n}$ (×10 ⁻⁴) ^c	$\overline{\mathbf{M}}$ $(\overline{\mathbf{M}})^{d}$
	M1 [mol%]	M ₂ [mol%]	[wt%]	N ^b [mol%]	M ₁ [mol%]	[g/mol]	IVIW/ IVIn
3a	80	20	53.0	2.65	55.5	4.52	1.36
3b	60	40	71.7	2.57	53.5	3.48	1.77
3c	50	50	72.0	2.43	44.0	4.27	1.57
3d	30	70	63.0	2.40	43.0	6.23	1.89
4a	70	30	83.0	2.26	48.0	5.20	1.87
4b	50	50	80.0	1.79	27.0	12.90	2.98
4c	30	70	75.0	1.95	33.0	4.37	2.35
4d	20	80	68.0	1.48	19.0	7.22	1.42

Table 1. Copolymerization of monomers 2(a-b) (M_1) with styrene (M_2) in dioxane at 70°C, in the presence of AIBN^a

^aAIBN concentration = 2% by weight with respect to the monomer mixtures; total monomer concentration = 10%.

^bThe average nitrogen content in the copolymer which was determined by elemental analysis.

^cNumber-average molecular weight by GPC measurement.

^dPolydispersities by GPC measurement.



7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

Figure 7. ¹H-NMR spectra of copolymer 3a



Figure 8. TGA curve of copolymer 3c

Table 2. TGA data for copolymers 3(a-d) and 4(a-d)

attributed to the nonpolymeric trialkyltin carboxylate in the solid state (Figure 6) [11, 21–23]. A similar behaviour was found in other tin functionalized copolymers [24]. The ¹H-NMR spectra of copolymers displayed the expected resonance at 7.06 ppm (aromatic protons), 3.91 ppm ($-COO-CH_2-N<$), 3.15 ppm (C<u>H</u> of succinimide ring units), 2.42 ppm (C<u>H</u> of styrene units), 1.70 (C<u>H</u>₂ of styrene units), 1.58, 1.33 and 0.91 ppm (butyl rest) (Figure 7). Additionally, copolymers **4(a–d)** exhibited resonances in the range of 7.8–7.2 ppm attributed to psubstituted aromatic protons.

3.1. Thermal characterization

By processing TGA curves, thermal data presented in Table 2 resulted. The thermogravimetric curves of the copolymers showed three stages of decomposition. The first stage corresponding to the decomposition of tributyltin carboxylate groups range between 285–350°C for copolymers 3(a-d) and $267-350^{\circ}$ C for copolymers **4(a-d)**, and the weight loss varied with the content of tributyltin units in copolymer. The second stage of decomposition varied in the range of 335-415°C for copolymers 3(a-d) and 345–440°C for copolymers 4(a-d) and corresponded to the decomposition of polystyrene. The third stage of decomposition ranged between 375–750°C for copolymers 3(a-d) and 415–750°C for copolymers 4(a-d). A representative TGA curve for copolymer 3 is presented in Figure 8. The inorganic residue left after heating at 750°C in air constituted by SnO₂, has a lower mass than that calculated for the copolymer structure which is clearly attributed to the sample volatility. DSC measurements have been performed on the as prepared products, without any preliminary thermal conditioning, in order to avoid alterations of the materials and to obtain results directly comparable

Copolymer	IDT	Weight loss	ses [%]/decompos	Inorganic residue [%]			
	[°C]	Global [%]	Step I	Step II	Step III	Calcd	Found
3 a	303	80	38/303-355	23/355-415	19/415–750	23.6	20
3b	300	77	36/300-350	22/350-410	19/410–750	29.9	23
3c	298	78	32/298-350	18/350-410	28/410-750	26.1	22
3d	285	79	30/285-335	19/335–375	30/375-750	25.9	21
4a	267	79	28/267-345	12/345-440	39/440–750	24.4	21
4b	286	82	29/286-350	13/350-420	35/420-750	19.2	18
4c	295	80	28/295-345	12/345-415	30/415-750	21.0	20
4d	308	86	27/308-345	25/345-415	34/415-750	15.9	14



Figure 9. DSC scans of copolymers 3(a, c, d) and 4(a, c, d)

to the data afforded by the other solid state measurements. The copolymers 4(a-d) showed broad endothermic peaks in the range of 55–75°C (Figure 9), whereas the copolymers 3(a-d) displayed a sharp signal around 70–72°C, due to the crystalline domains in the materials, and a small endothermic peak around 100°C only for copolymers 3(c, d)attributed to atactic polystyrene [11]. The crystalline domains in the materials can be attributed to oligomeric or polymeric tin moiety aggregation of variable extent, generating pentacoordinated tin atoms of the type depicted in Figure 6, structure A, connecting pendant triorganotin carboxylates bound to the polystyrene side-chains with one other [11].

4. Conclusions

New functional tributyltin carboxylate maleimide monomers were synthesized, characterized and copolymerized. The copolymerization with styrene under radical conditions affords in good yields the corresponding polymers having tributyltin carboxylate moiety covalently linked to the side chain of polystyrene backbone.

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