

Synthesis and characterization of di- and triorganotin(IV) complexes of 2-tert-butyl-4-methyl phenol

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Abstract. The di- and trialkyltin(IV) complexes of composition $R_2SnCl_{2-x}(OAr)$, and $n-Bu_3Sn(OAr)$ ($R = n-Bu$ and Me ; $x = 1$ and 2 ; $OAr = OC_6H_3Bu^t-2-Me-4$) have been synthesized by the reactions of di-*n*-butyl and dimethyltin dichlorides and tri-*n*-butyltin(IV) chloride with 2-tert-butyl-4-methylphenol and triethylamine in tetrahydrofuran. The reaction of triphenyltin chloride with trimethylsilyl-2-*t*-butyl-4-methylphenoxide in the same solvent however, gives a complex of composition $Ph_3Sn(OAr)$. The complexes have been characterized by microanalyses, molar conductance measurements, molecular weight determinations and IR and 1H , ^{13}C and ^{119}Sn NMR and mass spectral studies. Thermal behaviour of the complexes has been studied by TGA and DTA techniques. From the non-isothermal TG data, the kinetic and thermodynamic parameters have been calculated employing Coats–Redfern equation and the mechanism of decomposition has been computed using non-isothermal kinetic method. Thermal investigations on the blends of poly(methylmethacrylate). PMMA, with organotin(IV)-2-tert-butyl-4-methylphenoxides have shown increased thermal stability compared to pure PMMA suggesting thereby their potential as additives towards PMMA.

Keywords. Organotin(IV) complexes; 2-tert-4-methylphenol; spectroscopic characterization; thermal investigations of PMMA.

1. Introduction

The interest in organotin chemistry is based on its vast industrial, medicinal and agricultural applications.^{1–11} Of numerous organotin compounds, complexes with phenols have found special attention owing to the fact that organotin(IV) phenoxides are known to be effective antibacterial and form an important constituent of catalytic systems.¹² It is surprising to note that only a few reports describing the synthesis of organotin(IV) complexes of phenols are found in literature.^{13–17} In continuation of our previous work^{18–21} on the synthesis of organotin(IV) phenoxides, the present paper reports the synthetic approach to organotin(IV) complexes of unexplored 2-*t*-butyl-4-methylphenol. Besides the structural and spectroscopic characterization of the newly synthesized complexes, an emphasis has also been placed to explore their thermal behaviour. Thermal behaviour of the blends of PMMA with organotin(IV)-2-tert-butyl-4-methylphenoxides has also been investigated.

2. Experimental

2.1 Materials and physical measurements

2-Tert-butyl-4-methylphenol (Merck) was recrystallized from THF and the purity was checked by sharp melting point. *N*-Dibutyltin dichloride, dimethyltin dichloride and *n*-tributyltin chloride (all grade Merck) and triphenyltin chloride (Fluka) were used as received.

Tin was determined as SnO_2 by decomposing the complexes with the mixture of conc. H_2SO_4 (2 vol.) and conc. HNO_3 (3 vol.). Chlorine was estimated by Volhard's method. Microanalyses for carbon and hydrogen were performed on Elementar Vario EL III Carlo Erba 1108 analyser. The conductivity measurements in nitrobenzene were made on Elico conductivity bridge CM-Type 82T. Molecular weights of the complexes were determined by Rast's camphor method. FTIR spectra were collected with Nicolet 5700 spectrophotometer and 1H NMR spectra were recorded on Jeol PMX 60 SI spectrometer using $CDCl_3$ as solvent. The ^{13}C NMR spectra of the complexes were recorded on Bruker-AC-300 MHz NMR spec-

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trometer in CDCl_3 ($\delta^{13}\text{C}$ CDCl_3) 77.0 ppm) and TMS as an internal reference. ^{119}Sn NMR spectra were obtained on JEOL AL 300 MHz FT NMR using Me_4Sn as an external reference. Mass spectra of complexes were recorded on NOMMASS (Ak4#156) mass spectrometer. Thermograms were recorded on simultaneous DT–TG Shimadzu thermal analyzer, DT-40 in air. The analytical constants were: heating rate $10^\circ\text{C min}^{-1}$, reference Al_2O_3 ; thermocouple Pt/Pt-Rh 10%.

2.2 Synthesis

2.2a Synthesis of $\text{Me}_3\text{Si}(\text{OAr})$: The trimethylsilyl derivative of 2-*t*-butyl-4-methylphenol was prepared by reacting hexamethyldisilazane (3.8 ml, 0.018 mol) with two equivalents of 2-*t*-butyl-4-methylphenol (5.8 g, 0.036 mol) in CCl_4 under reflux till evolution of NH_3 gas ceased. The solvent was distilled off. The concentrate was then distilled under reduced pressure (15 mmHg) to collect the liquid product (boiling point 182°C).

2.2b Synthesis of $n\text{-Bu}_2\text{SnCl}_{2-x}(\text{OAr})_x$ (where $x = 1$ and 2): To a solution of $n\text{-Bu}_2\text{SnCl}_2$ (1.85 g, 0.006 mol) in THF (25 ml) an equi- or bimolar amounts of 2-*t*-butyl-4-methyl phenol (1 g, 0.006 mol/2 g, 0.012 mol) and triethylamine (0.84 ml, 0.006 mol/1.68 ml, 0.012 mol) were added. The mixing of the components resulted in an immediate separation of Et_3NHCl . The reaction mixture was stirred for 8–10 h. It was then filtered to remove Et_3NHCl and the filtrate was concentrated under vacuum. It was then treated with petroleum ether. The light yellow and creamish solids formed were re-crystallized from carbon tetrachloride and were dried under vacuum.

2.2c Synthesis of $\text{Me}_2\text{SnCl}_{2-x}(\text{OAr})_x$ (where $x = 1$ and 2): In a similar synthetic method, a solution of Me_2SnCl_2 (2 g, 0.009 mol) in THF (30 ml) was treated with an equimolar or bimolar amounts of 2-*t*-butyl-4-methylphenol (1.49 g, 0.009 mol/2.98 g, 0.018 mol) and triethylamine (1.26 ml, 0.009 mol/2.52 ml, 0.018 mol) in separate experiments. The mixing of reactants resulted in an instantaneous formation of white solid Et_3NHCl . The contents were stirred for 8–10 h at room temperature. The Et_3NHCl formed was removed by filtration. The filtrate was concentrated under vacuum. It was then treated with petroleum ether, whereupon cream-coloured solids were obtained. These were re-

crystallized from tetrahydrofuran and were dried under vacuum.

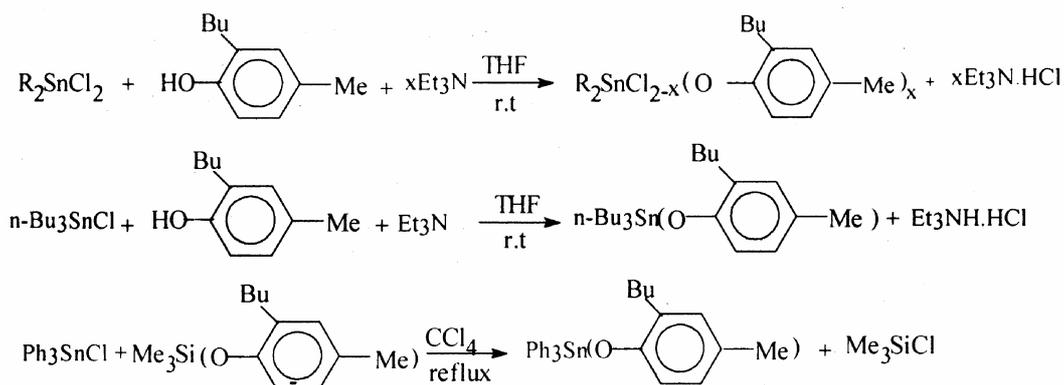
2.2d Synthesis for $\text{Ph}_3\text{Sn}(\text{OAr})$: To the solution of Ph_3SnCl (3.2 g, 0.008 mol) in CCl_4 , an equimolar amount of trimethylsilyl derivative of 2-*t*-butyl-4-methyl phenol (2.02 ml, 0.008 mol) was added. The reaction mixture was refluxed for 4–6 h to ensure the completion of the reaction. The solvent was removed by evaporating under vacuum. The concentrate was then treated with petroleum ether, whereupon a creamy white solid separated out. It was re-crystallized from CCl_4 and was dried under vacuum.

2.2e Synthesis of $n\text{-Bu}_3\text{Sn}(\text{OAr})$: To the solution of $n\text{-Bu}_3\text{SnCl}$ (3.32 ml, 0.012 mol) in dry CCl_4 an equimolar amount of 2-*t*-butyl-4-methyl phenol (2 g, 0.012 mol) and triethylamine (1.72 ml, 0.012 mol) were added at room temperature. The formation of Et_3NHCl was observed upon mixing the components. The reaction mixture was stirred for 8–10 h at room temperature. It was then filtered to remove Et_3NHCl . The filtrate was then concentrated by distilling off the solvent. The concentrate was treated with many organic solvents to obtain compound as a solid but by no means, the concentrate could be transformed into solid. It was then distilled under reduced pressure whereupon a light yellow liquid compound was collected at $52^\circ\text{C}/15$ mmHg.

2.2f Preparation of blends of PMMA with organotin(IV)-2-*t*-butyl-4-methylphenoxides: The PMMA: tin blends of 1 : 1 and 1 : 2 combinations by weight were prepared by mixing acetone solutions of the PMMA and organotin(IV)-2-*t*-butyl-4-methylphenoxides in separate experiments. The mixture solution was stirred for about 24 h. It was then treated with methanol to extract the polymeric material and was dried in an oven at 40°C .

3. Results and discussion

The interaction between di- and triorganotin(IV) chlorides with 2-*t*-butyl-4-methyl phenol in the presence of triethylamine or with trimethylsilyl 2-*t*-butyl-4-methylphenoxide in predetermined molar ratios afforded the formation of new complexes in good yields as shown in scheme 1. The analytical data of isolated complexes agreed well with the stoichiometric formulations given in table 1. Except for the tributyltin phenoxide, which is light-yellow



Scheme 1.

Table 1. Analytical data of di- and triorganotin(IV)-2-tert-butyl-4-methylphenoxides.

Complex	Colour	M.Pt./B.Pt* (°C)	Elemental analyses % found (calcd.)				Molar cond. in PhNO ₂ (Ω ⁻¹ cm ² mol ⁻¹)	Mol. Wt. Found (calcd.)
			Sn	Cl	C	H		
<i>n</i> -Bu ₂ SnCl(OAr)	Light-yellow	96	28.0 (27.5)	8.5 (8.2)	52.3 (52.8)	8.1 (7.6)	2.1	428 (431.5)
<i>n</i> -Bu ₂ Sn(OAr) ₂	Cream	75	20.9 (21.2)	—	64.7 (64.4)	8.0 (8.5)	1.3	562 (559)
Me ₂ SnCl(OAr)	Cream	106	33.7 (34.2)	9.1 (9.0)	44.3 (44.8)	5.8 (6.0)	5.5	341 (347.5)
Me ₂ Sn(OAr) ₂	Cream	94	24.9 (25.0)	—	60.8 (60.6)	8.0 (7.5)	4.0	478 (475)
<i>n</i> -Bu ₃ Sn(OAr)	Light-yellow	63*/540 nm	26.5 (26.2)	—	60.4 (60.9)	8.8 (9.2)	3.5	—
Ph ₃ Sn(OAr)	Cream	100	22.6 (23.1)	—	68.1 (67.8)	6.3 (5.8)	1.0	509 (513)

liquid, the rest of the complexes are cream-to-light-yellow solids. The complexes are quite stable under dry conditions. All solid complexes are sharp melting while liquid tributyltin-2-tert-butyl-4-methylphenoxide is low boiling. The complexes are soluble in most of the common organic solvents. The low values of molar conductance of the millimolar solutions of complexes in nitrobenzene have indicated their non-electrolytic nature. The molecular weight determinations of the complexes by Rast's camphor method suggested them to exist as monomers.

3.1 IR spectra

In the IR spectra of the complexes, the complete absence of bands in 3400–3300 cm⁻¹ region due to

hydrogen bonded phenolic (OH) group suggested deprotonation of phenol. The absorption bands observed in 1245–1165 cm⁻¹ region assigned to ν(C–O) mode in complexes relative to those known to occur in free phenols in 1260–1180 and 1300–1200 cm⁻¹ regions^{22,23} indicated bonding through the phenolic oxygen to tin. The occurrence of bands in 520–460 cm⁻¹ region which may be ascribed to ν(Sn–O)^{24–26} mode further supported the formation of complexes. The bands observed at 360 cm⁻¹ and 345 cm⁻¹ in case of *n*-Bu₂SnCl(OAr) and Me₂SnCl(OAr) have been ascribed to ν(Sn–Cl) mode.²⁷ The absorption bands observed at 595 and 522 cm⁻¹; 560 and 522 cm⁻¹; 592 and 522 cm⁻¹; 275 and 260 cm⁻¹ may be attributed to ν(Sn–C)^{28–30} mode in case of di-*n*-butyl, dimethyl, tri-*n*-butyl and triphenyltin(IV)-2-tert-butyl-4-methylphenoxide respectively.

3.2 NMR spectra

3.2a ^1H NMR: The formation of organotin(IV) phenoxides has further been ascertained from their room temperature ^1H NMR spectra recorded in CDCl_3 . A comparison of ^1H NMR spectra of the complexes with that of 2-tert-butyl-4-methylphenol provided supporting evidences for their formation. The ^1H NMR spectrum of 2-tert-butyl-4-methylphenol exhibited signals at δ 4.71, δ 1.26, δ 2.51 and δ 6.52–7.25 ppm attributed to phenolic –OH group, the –Bu^t and Me substituents and aromatic protons respectively. The ^1H NMR spectra of organotin(IV)-2-tert-butyl-4-methylphenoxides did not display any signal due to –OH proton which confirmed the deprotonation of the phenolic proton. The signals due to Bu^t and Me substituents on aromatic ring remained almost unaltered upon complex formation. The resonances due to organic groups attached to tin metal in complexes under study have also remained unchanged compared to organotin(IV) chlorides. The resonances due to aromatic protons of the phenolic ring suffered a downfield shift on complex formation and appeared in δ 6.75–7.83 ppm region. The observed downfield shift in the aromatic ring proton resonances may be ascribed to the deshielding of these protons due to drainage of electron density from the ring to tin metal³¹ (table 2).

3.2b ^{13}C NMR: The ^{13}C NMR spectra of 2-tert-butyl-4-methylphenol in CDCl_3 displayed signals at δ 34.48, δ 29.74 and δ 20.82 ppm and in δ 116.61–151.96 ppm range attributed to methane, methyl carbons of tert-butyl and methyl substituents and carbon resonances of the phenolic ring respectively. A close examination of ^{13}C NMR spectra of organotin(IV) 2-tert-butyl-4-methylphenoxides showed that the resonances due to the carbons of the 2-tert-butyl and methyl substituents on the phenolic ring suffered insignificant changes on complex formation. The appreciable downfield shifts observed for carbon resonances of the phenolic ring supported the formation of complexes. The carbon resonances due to organic groups attached to tin remained almost unaltered in complexes relative to the di- and triorganotin(IV) chloride precursors (table 2).

3.2c ^{119}Sn NMR: The ^{119}Sn nucleus is one of the most attractive nuclei for NMR analysis due to the relatively simple spectra often produced and wide chemical shift range. ^{119}Sn chemical shifts are quoted with downfield shifts having a positive sign or vice-versa relative to tetramethyltin. In case of alkyltin compounds as the electron releasing power of the alkyl group increases, the tin atom becomes progressively more shielded and the δ ^{119}Sn values move to higher field. An increase in the coordination

Table 2. ^1H , ^{13}C and ^{119}Sn NMR spectral data of organotin(IV)-2-tert-butyl-4-methyl phenoxides.

Compound	^1H NMR δ (ppm)				^{13}C NMR δ (ppm)						^{119}Sn NMR
	Phenolic group	Phenolic ring protons	Tert-butyl substituent protons	Methyl protons	R–Sn	Tert-butyl substituent –CH ₃	–C	Phenolic ring carbon		R–Sn	
								<i>o, m</i> and <i>p</i>	C _{ipso}		
HOAr	4.71	6.52–7.25	1.26	2.51	–	29.74	34.48	116.61–136.02	151.98	–	–
<i>n</i> -Bu ₂ SnCl(OAr)	–	6.75–7.28	1.21	2.52	0.94–2.01	29.66	32.94	117.60–137.77	153.47	13.64–27.28	–135.31
<i>n</i> -Bu ₂ Sn(OAr) ₂	–	6.77–7.27	1.20	2.48	0.94–2.23	29.47	34.32	117.71–137.84	153.99	13.49–27.02	–139.09
Me ₂ SnCl(OAr)	–	6.85–7.26	1.21	2.52	1.16–1.28	29.53	33.88	116.26–136.72	152.43	12.08	–64.97
Me ₂ Sn(OAr) ₂	–	6.82–7.23	1.24	2.51	1.16–1.27	29.71	33.96	116.47–136.82	153.50	12.11	–117.85
Bu ₃ Sn(OAr)	–	6.72–7.30	1.21	2.50	0.94–2.15	29.45	33.75	117.98–136.96	152.42	13.66–27.48	130.50
Ph ₃ Sn(OAr)	–	7.42–7.83	1.28	2.51	8.24	29.62	33.51	117.55–137.25	153.69	129.01–136.11	–46.31

Table 3. Mass spectral data of organotin(IV)-2-tert-butyl-4-methylphenoxides.

Complexes	<i>m/e</i> (relative intensity %) (identify)
<i>n</i> -Bu ₂ SnCl(OAr)	431 (0.9) [M] ⁺ ; 396 (6.9) [M-Bu] ⁺ ; 339 (5.0) [M-2Bu] ⁺ ; 282 (9.4) [Sn(OAr)] ⁺ ; 269 (14.3) [Bu ₂ SnCl] ⁺ ; 233 (5.0) [Bu ₂ Sn] ⁺ ; 212 (12.5) [BuSnCl] ⁺ ; 176 (19.0) [BuSn] ⁺ ; 163 (2.8) [OAr] ⁺ ; 155 (40.7) [SnCl] ⁺ ; 119 (8.5) [Sn] ⁺ ; 77 (100) [C ₆ H ₅] ⁺
<i>n</i> -Bu ₂ Sn(OAr) ₂	559 (1.4) [M] ⁺ ; 445 (1.9) [Sn(OAr) ₂] ⁺ ; 397 (2.2) [Bu ₂ SnOAr] ⁺ ; 282 (13) [Sn(OAr)] ⁺ ; 233 (5.4) [Bu ₂ Sn] ⁺ ; 176 (10) [BuSn] ⁺ ; 163 (0.6) [OAr] ⁺ ; 119 (8.5) [Sn] ⁺ ; 77 (100) [C ₆ H ₅] ⁺
Me ₂ SnCl(OAr)	347 (1.2) [M] ⁺ ; 312 (7.0) [Me ₂ Sn(OAr)] ⁺ ; 297 (5.2) [MeSn(OAr)] ⁺ ; 282 (10) [Sn(OAr)] ⁺ ; 185 (3.6) [Me ₂ SnCl] ⁺ ; 170 (16.9) [MeSnCl] ⁺ ; 163 (1.5) [OAr] ⁺ ; 155 (31) [SnCl] ⁺ ; 149 (0.9) [Me ₂ Sn] ⁺ ; 134 (66.4) [MeSn] ⁺ ; 119 (8.4) [Sn] ⁺ ; 77 (100) [C ₆ H ₅] ⁺
Me ₂ Sn(OAr) ₂	475 (0.7) [M] ⁺ ; 445 (0.9) [Sn(OAr) ₂] ⁺ ; 313 (2.8) [Me ₂ Sn(OAr)] ⁺ ; 282 (9.3) [Sn(OAr)] ⁺ ; 149 (3.7) [Me ₂ Sn] ⁺ ; 134 (7.5) [MeSn] ⁺ ; 119 (8.6) [Sn] ⁺ ; 163 (1.6) [OAr] ⁺ ; 77 (100) [C ₆ H ₅] ⁺
<i>n</i> -Bu ₃ Sn(OAr)	453 (5.7) [M] ⁺ ; 396 (5.8) [M- <i>n</i> -Bu] ⁺ ; 339 (1.7) [M-2Bu] ⁺ ; 290 (100) [Bu ₃ Sn] ⁺ ; 282 (4.2) [Sn(OAr)] ⁺ ; 233 (8.6) [Bu ₂ Sn] ⁺ ; 176 (19) [BuSn] ⁺ ; 114 (2.6) [Bu ₂] ⁺ ; 119 (8.5) [Sn] ⁺ ; 163 (0.9) [OAr] ⁺ ; 77 (17.2) [C ₆ H ₅] ⁺
Ph ₃ Sn(OAr)	513 (1.1) [M] ⁺ ; 436 (7.6) [M-Ph] ⁺ ; 345 (1.9) [M-2Ph] ⁺ ; 350 (16.7) [Ph ₃ Sn] ⁺ ; 273 (1.9) [Ph ₂ Sn] ⁺ ; 231 (1.1) [Ph ₃] ⁺ ; 196 (14.8) [PhSn] ⁺ ; 154 (100) [Ph ₂] ⁺ ; 119 (8.5) [Sn]; 163 (0.5) [OAr] ⁺ ; 77 (16.1) [C ₆ H ₅] ⁺

number of tin from four to five, six and seven is usually known to produce a large upfield shift of δ ¹¹⁹Sn. The δ ¹¹⁹Sn values also depend on the nature of the inorganic radical X and generally move to low field as the electronegativity of the latter increases in a given series of R₃SnX, R₂SnX₂ or RSnX₃ compounds.

The ¹¹⁹Sn NMR data for investigated compounds is given in table 2. The ¹¹⁹Sn NMR signals observed in complexes may be compared with those of di- and trialkyltin(IV) and triphenyltin(IV) chlorides and closely related phenoxide and alkoxide analogues. The ¹¹⁹Sn NMR signals are known to occur at δ +122, +141, -141 and -44.7 ppm in *n*-Bu₂SnCl₂, Me₂SnCl₂, *n*-Bu₃SnCl and Ph₃SnCl³²⁻³⁴ respectively. It is quite noteworthy that the spectra of metal alkoxides show a great complexity. The literature data suggest that the alkyltin alkoxides owing to their tendency to undergo auto-association via intermolecular O→Sn coordinate bonds display interesting set of NMR parameters. The oligomeric species exist in rapid dynamic equilibrium with lower oligomers and the monomer so that the measured NMR parameters are the weighted time averages of those for the various species present. Although the enhanced coordination number at tin is reflected in changes in ¹¹⁹Sn NMR shifts, yet the steric bulk on the OR (R = Pr^t, Bu^t, Bu^s) ligand inhibits dimer formation. A moderate upfield/downfield shift has been observed in di- and triorganotin(IV)-2-tert-butyl-4-methylphenoxides. The observed trend in shifts may be attributed to an in-

creased electron density at tin and to the $p\pi \rightarrow d\pi$ bonding upon complexation. The observed shifts are suggestive of four-coordinate tetrahedral geometry around tin metal in complexes in line with previous report.³⁵ In the present work the steric bulk of the 2-tert-butyl-4-methylphenoxide ion perhaps seems to inhibit auto-association.

3.3 Mass spectra

The major FABMS peaks observed for the complexes are given in table 3. The molecular ion peak has been observed in all the complexes. The most intense peaks are at *m/e* 77 for di-*n*-butyl and dimethyltin(IV) derivatives corresponding to (C₆H₅)⁺ ion, while at *m/e* 290 and 154 corresponding to [*n*-Bu₃Sn]⁺ and [Ph₂]⁺ ions appeared in case of tri-*n*-butyl and triphenyltin(IV) analogues respectively. The common ions observed in complexes are [Sn(OAr)]⁺, [Sn]⁺, [OAr]⁺. The structurally important fragment ions are also clearly discernible (table 3).

Thus based on the limited analytical and IR and ¹H, ¹³C and ¹¹⁹Sn NMR and mass spectral data, a distorted tetrahedral structure for organotin(IV) 2-tert-butyl-4-methylphenoxides may tentatively be proposed as presented in figure 1.

3.4 Thermal studies

Thermal behaviour of organotin(IV) complexes has been studied by TG/DTA techniques in air. A perusal

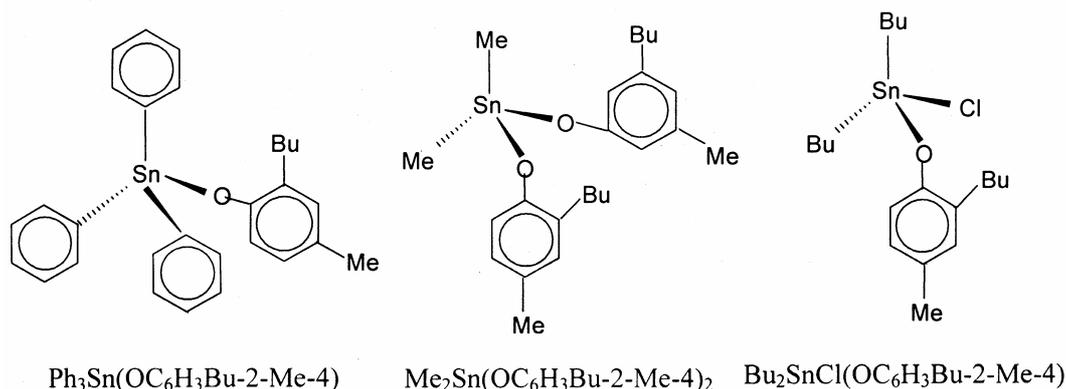


Figure 1.

Table 4. Thermal decomposition data of di- and triorganotin(IV)-2-tert-butyl-4-methylphenoxides.

Complexes	Initial decomp. temp. (IDT) (°C)	TG data		Decomp. product	DTA	
		Decom. range (°C)	% wt. loss		Peak temp. (°C)	Peak nature
<i>n</i> -Bu ₂ SnCl(OAr)	105.6	105.6–496.1	68	SnO	98.4 237.2 407.9	Endo Exo Exo
<i>n</i> -Bu ₂ Sn(OAr) ₂	61.6	61.6–425.8	94	¼SnO	75.0 245.5 108	Endo Exo Endo
Me ₂ SnCl(OAr)	112.6	112.6–450	89	¼SnO ₂	289 329	Endo Endo
Me ₂ Sn(OAr) ₂	96.0	96–460	84	½SnO ₂	946 256.0	Endo Exo
<i>n</i> -Bu ₃ Sn(OAr)	35.0	35.0–388	100	No residue	209.0 335.4	Exo Exo
Ph ₃ Sn(OAr)	155.8	155.8–315.8	100	No residue	100.1 298.1	Endo Exo

of thermal data presented in table 4 has revealed that based on IDT's of these complexes, triphenyltin(IV) derivative has been found to be thermally more stable. The tributyl complex has shown least stability than dibutyl and dimethyltin analogues. Interestingly, the chloride phenoxides have shown higher thermal stability than diphenoxo analogues. All the complexes have shown single stage decomposition pattern. Strikingly, the % weight loss in TG in case of dibutyl and dimethyltin(IV) complexes corresponded to the formation of SNO/¼SNO and ¼SnO₂/½SnO₂ as the ultimate decompositional product respectively. On the other hand, triphenyltin and tributyltin phenoxides depicted 100% weight loss thereby leaving behind no residue. The decompositions in TG are supplemented by both endothermic and exothermic peaks in DTA curves wherein, endothermic

peaks corresponded quite well to the melting points of the complexes (table 4).

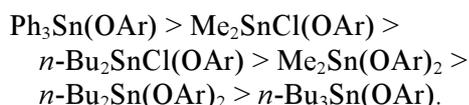
3.5 Kinetic parameters

The kinetic studies on thermal process are expected to provide sufficient information regarding Arrhenius parameters viz. activation energy (E^*), frequency factor (A), enthalpy of activation (H^*), entropy of activation (S^*), free energy of activation (G^*), etc. as well as the reaction model. From TG data employing Coats–Redfern equation³⁶ various kinetic parameters have been calculated and the data is summarized in table 5. Generally, the value of 'A' increases with decrease in ' E^* ' and higher value of activation energy suggests the higher thermal stability, yet, a deviation in this trend may occur due to

Table 5. Kinetic and thermodynamic parameters of organotin(IV)-2-tert-butyl-4-methyl phenoxides from TG data using Coats and Redfern equation.

Complex	Decomp. stage	Correlation coefficient 'r'	Activation energy E^* (kJ mol ⁻¹)	Frequency factor A^* (s ⁻¹) 10 ⁻⁶	Entropy of activation S^* (kJ mol ⁻¹)	Free energy of activation G^* (kJ mol ⁻¹)	Enthalpy of activation H^* (kJ mol ⁻¹)	Order of reaction 'n'	Model
Bu ₂ SnCl(OAr)	Single	0.9334	390.31	0.2	-363.53	187.87	390.31	1	R3
Bu ₂ Sn(OAr) ₂	Single	0.9502	234.45	1.4	-360.16	180.83	234.45	1	R3
Me ₂ SnCl(OAr)	Single	0.9604	502.58	0.1	-411.68	230.16	502.58	1	R3
Me ₂ Sn(OAr) ₂	Single	0.9668	238.06	2.3	-400.04	229.03	238.06	1	R3
Bu ₂ Sn(OAr)	Single	0.9744	542.13	7.5	-346.17	168.22	542.13	1	R3
Ph ₃ Sn(OAr)	Single	0.9407	169.47	0.1	-378.31	204.35	169.47	1	R3

some more inherent physical and chemical factors. The higher values of 'E*' and lower values of 'A' favour the reaction to proceed slower than normal.^{37,38} This relationship between 'A' and 'E*' has been observed to agree upon well for the complexes studied in the present work. Furthermore, from the initial decomposition temperatures (IDTs) and activation energy values (E*) of complexes, which are in accordance with each other, the following order of thermal stability has been inferred:



The negative values of 'S*' indicate that the activated complex has a higher ordered or more rigid structure³⁹ than that of either the reactants or intermediate. The magnitudes of 'E*' and 'H*' are equivalent.

For the mechanistic analysis of TG data, seven theoretical mechanisms proposed by Sestak and Berggren⁴⁰ and Lozano *et al.*⁴¹ have been tested for organotin(IV) 2-tert-butyl-4-methylphenoxides under study in order to ascertain as to which one best conforms to the non-isothermal i.e. linear programmed temperature TG data. The mechanisms studied include: D1, D2, D3 and D4 corresponding to one-dimensional diffusion, two-dimensional diffusion (cylindrical symmetry), three-dimensional diffusion (Ginstling-Brounshtein spherical symmetry); F1 (random symmetry); R2 and R3 (phase boundary reaction; cylindrical and spherical symmetry respectively). The analysis suggested that all the complexes follow R3 (phase boundary reaction-spherical symmetry) mechanism.

The effects of newly synthesized organotin(IV) 2-tert-butyl-4-methylphenoxides on the thermal degradation pathways of PMMA has been investigated

by TGA-DTA techniques. A comparison of TG-DTA curves of pure PMMA and PMMA:tin blends has shown that the blends display single step decomposition relative to two step decomposition of PMMA. The PMMA:tin blends have been observed to undergo incomplete decomposition compared to 100% decomposition of PMMA. The initial and final decomposition temperatures of the blends have been found to be higher than that of pure PMMA. The TG curve of pure PMMA has shown 246.6°C and 413.6°C as initial and final decomposition temperatures respectively. On the other hand, the 1:1 PMMA:tin blends have displayed IDT and FDT in 249–280°C and 388–478°C temperature range respectively. For 1:2 PMMA:tin blends the temperature range 260–289°C and 410–470°C respectively, has been exhibited. The hard acidic nature of the tin metal and organic groups linked to tin can be ascribed to provide thermal stability to the blends thereby showing their utility as probable stabilizers for PMMA⁴². The observance of DTA peaks in 404–429°C temperature range compared to that of pure PMMA at 380°C substantiated the interesting features depicted by TG analysis of the blends.

4. Conclusion

The di-*n*-butyl and methyl and tri-*n*-butyl and phenyltin(IV) complexes with 2-tert-butyl-4-methylphenol having potential utility as probable stabilizers for poly(methylmethacrylate) PMMA have been synthesized employing efficient synthetic procedures affording quantitative yields of the complexes. The characterization of the complexes by physico-chemical and various spectral techniques have suggested them to be mononuclear. Thermal investigations of the complexes have shown these to undergo decomposition in single stage completely thereby leav-

ing no residue or yielding SnO/SnO₂ as the ultimate decomposition products. The kinetic parameters evaluated from TG data of complexes using Coats–Redfern equation has substantiated their thermal stability order. The mechanistic analysis suggested all the complexes to follow R3 mechanism.

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