

Preparation and Infrared Characterisation of Some New Organotin Carboxylate Polymers

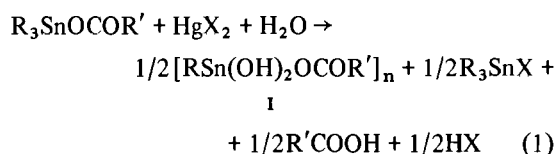
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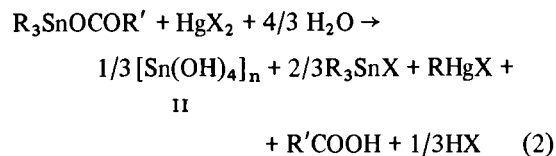
There has been considerable interest in recent years in the synthesis and structure of monoorganotin polymers [1–3] containing carboxylate groups. Cleavage of the tin–carbon bond by carboxylic acids under rigorous conditions has so far been applied for the synthesis of these polymers. In this paper we wish to report the preparation of a few new polymers using a relatively convenient route involving cleavage reactions of tin–carbon bonds in triorganotin carboxylates ($R_3SnOCOR'$ where R = phenyl, Ph; Propyl, Pr; Butyl, Bu; Cyclohexyl and $R' = H, CH_2, CH_2CH_3$) with mercury(II) salts such as mercuric halides and acetate.

In a typical reaction run, to a solution of triorganotin carboxylate in ether or benzene, a solution of mercuric salt (1:1) in ether was added dropwise with stirring. Although a white precipitate was formed immediately, the mixture was stirred for a further 4 hours at room temperature to ensure complete reaction. The volatiles were removed and the residual solid was extracted with hot benzene which left a white insoluble polymeric material (infusible up to 360 °C, except for the formate; –COOH group containing polymers which decomposed at about 270 °C). The benzene extract on fractional crystallisation afforded triorganotin halide and organomercuric halide. By contrast, reaction of mercuric acetate with triphenyltin acetate afforded diphenyl mercury and a tin polymer. The products obtained from these reactions were characterised by analytical and spectral data. Considering the stoichiometry, the following equations may be proposed to account for the reaction products:

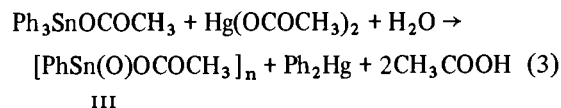


(a, R = Ph, $R' = H, CH_3, CH_2CH_3$; X = Br, I; b, R = Ph, $R' = H, X = Cl$ and c, R = Pr, Bu; $R' = CH_3, X = Cl$).

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(R = Ph, $R' = CH_3, CH_2CH_3$; X = Cl)



It was observed that in the reactions of mercuric chloride with tripropyl and butyltin acetates only about fifty percent of the $HgCl_2$ could be converted to the corresponding organomercuric halide whereas tricyclohexyltin acetate did not react at all in our reaction conditions. The ease with which mercuric chloride reacts with triorganotin acetates could thus be represented by the following sequence, namely, Ph > Pr \approx Bu $\gg \gg$ cyclohexyl. This suggests an electrophilic substitution at carbon atom bonded to tin [4–6]; however, nucleophilic assistance either by halogen or carboxylate groups cannot be ruled out.

On the basis of elemental analysis (Table), preparation of oxine (8-hydroxyquinoline) derivatives and i.r. spectral data (Table) we have formulated these polymers as I, II and III. Reactions of excess oxine in boiling benzene with i) I, produced only $PhSnOx_3$ quantitatively which showed the presence of one phenyl group per tin atom in the polymer, ii) II, afforded (in about 1:5 ratio) $PhSn(Cl)Ox_2$ and a new polymeric oxinate (infusible up to 300 °C) which we formulated as $(OH)_6Ox_2Sn_2$ assuming structural analogy with $[Sn(OH)_4]_n$ polymers. Since the ratio of $PhSn(Cl)Ox_2$ to $(OH)_6Ox_2Sn_2$ obtained was very low, it was reasonable to believe that in polymer II, the $Ph(Cl)Sn=$ grouping might be present only as end-blocking groups, iii) III, gave $PhSn(OCOCH_3)Ox_2$ (a new oxinate, m.p. 243 °C) quantitatively showing the presence of one phenyl and one acetate group per tin atom and $Ph(CH_3OCO)Sn=$ grouping in the polymers.

$[Sn(OH)_4]_n$, II, Type Polymers

From the analytical data it appears that these polymers could either be formulated as $SnO_2 \cdot xH_2O$ with traces of organic impurities or $[Sn(OH)_4]_n$ with end-blocking organic and halogen groups. Since these polymers i) did not change fundamentally even after heating at 100 °C for 12 hours at 10^{-3} mm pressure, ii) had solubilities in solvents like pyridine and dimethylformamide, iii) had a broad and medium

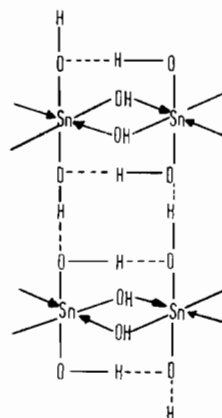
TABLE. Analytical Data^a and Relevant Infrared Frequencies (cm⁻¹)^b of the Polymers.

Compound	% of C	H	Sn	Cl
[C ₆ H ₅ Sn(OH) ₂ OCOCH ₃] _n , I, C ₈ H ₁₀ O ₄ Sn	33.59 (33.25)	3.56 (3.46)	40.78 (41.11)	
i.r. 3540; 3370(wb), ν _{OH} , 1560; 1540(vs) ν _{as} OCO, 560–520(sb) ν _{OSnOSn}				
[Sn(OH) ₄] _n , II, ^c	7.68	2.19	58.59	3.40
i.r. 3570–3200(wb) ν _{OH} , 1620; 1540(vw) ν _{as} OCO, 600–500(sb) ν _{OSnOSn}				
[C ₆ H ₅ Sn(O)OCOCH ₃] _n , III, C ₈ H ₈ O ₃ Sn	34.98 (35.46)	2.73 (2.96)	43.25 (43.85)	
i.r. 1570; 1540(vs) ν _{as} OCO, 610(s) ν _{SnOSn}				

^aFor I and II type polymers, analytical data for representative compounds from each class are only presented, figures in parentheses indicate calculated percentages. ^bs = strong, m = medium, w = weak, b = broad, v = very. I.r. spectra of the compounds as nujol mulls on suitable optics were measured using a Beckman IR-20 model spectrophotometer. ^cII contains C₆H₅, OCOCH₃ and Cl groups probably as end-blocking groups, exact numbers are uncertain.

absorption at about 3570–3200 cm⁻¹ (ν_{OH}) but a strong intensity band around 1630–1600 cm⁻¹ (H–O–H bending mode [7]) was absent, we feel that the presence of coordinated or lattice water as such in the polymer is most unlikely. Hence we suggest that the H₂O present in the molecule formed a part of the structure [Sn(OH)₄]_n. Very weak absorptions present at 1620 and 1540 cm⁻¹ could be tentatively assigned to the stretching frequencies for terminal –OCOR' groups. Most of the organotin hydroxides could be converted to the stannoxanes by mild heating, the great stability of these polymers toward heat probably suggests that the –OH groups are strongly coordinated or hydrogen bonded to other tin or oxygen atoms as a part of the polymer chain (note broad absorptions in –OH stretching region). These compounds, in addition, have a very strong and broad band near 600–500 cm⁻¹ which could be assigned to four membered ring vibrations in OSnOSn system [9, 10]. The –OH deformation modes in primary alcohols are present [8] at about 1050 cm⁻¹ but if the Sn–OH link possesses some ionic character then the frequency of the corresponding vibration in [Sn(OH)₄]_n would be reduced. In this case probably the Sn–OH bonds are so ionic that the deformation vibration has been reduced and merged into the strong 600–500 cm⁻¹ absorptions.

On the basis of these informations and considering the stability in particular, we suggest the following cyclic structure for the polymers, in which tin atoms are hexacoordinated and the –OH groups are stabilised either by coordinations with other tin atoms or forming strong intermolecular hydrogen bonds [8] under favourable conditions, thus reducing the chance of dehydration.

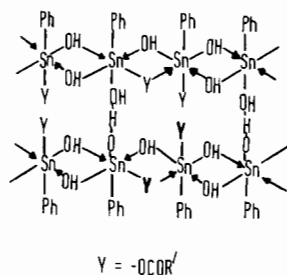


[RSn(OH)₂OCOR']_n, I, Type Polymers

Chemical analyses suggest that these polymers may contain halogen atoms (e.g. in polymers obtained from reactions of HgI₂ with Ph₃SnCOH or Ph₃Sn-OCOCH₃).

Two weak but broad absorptions at 3540 and 3370 cm⁻¹ together with strong and broad bands at 580–520 cm⁻¹ indicate the presence of coordinated –OH groups in four membered OSnOSn ring system and possible intermolecular hydrogen bonding. It is interesting to note the appearance of two very strong absorptions at about 1575 and 1550 cm⁻¹ for –OCO– stretching modes which we believe are due to the presence of two types of carboxylate groups in these polymers, one is chelated or ionic and the other is bridging groups between two tin atoms [1, 11]. Assuming tin atoms to be hexacoordinated in these polymers we suggest the following basic linear struc-

ture for these compounds in which some of $-\text{OCOR}'$ groups act as a bridge and some remain as non-bridged, the exact nature, however, cannot be determined with certainty.



$[\text{PhSn}(\text{O})\text{OCOCH}_3]_n$, III, Type Polymers

In the absence of $-\text{OH}$ stretching frequency the strong 610 cm^{-1} band could be assigned to ν_{as} (SnOSn) stretch which is in good agreement with reported data [12–14]. The strong 1570 and 1540 cm^{-1} bands could be assigned to ν_{as} (OCO) stretching modes for ionic/chelated and bridged acetate groups respectively as suggested before. Because of the presence of SnOSn stretch, we, like others [1–3], feel this polymer to be linear or cyclic. However, the possibility of the presence of intermolecular bridging acetate groups as well (to interpret the 1540 cm^{-1} band) could be tentatively suggested.

Acknowledgements

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