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STANNOXANE OLIGOMERS AND POLYMERS

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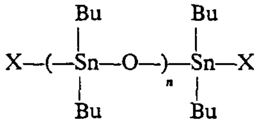
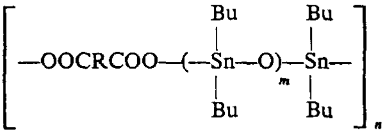
Abstract—Oligomeric and polymeric stannoxanes having the general formula



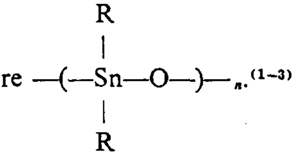
$$X-(-\underset{Bu}{\overset{Bu}{Sn}}-O-)_n-\underset{Bu}{\overset{Bu}{Sn}}-X$$

where X = RCOO, ArO, RSO_3, Cl and $0<n<100$, were prepared by heating a carboxylic acid, phenol, sulphonic acid or hydrochloric acid with polymeric dibutyltin oxide at molar ratios less than 1. The basic reaction is probably the cleavage of a stannoxane bond in the polydibutyltin oxide and formation of shorter polymers having the acid residue as end groups. Polyorganotin esters having a required number of dibutyltin recurring units having the general formula



$$\left[-OOCRCOO-(-\underset{Bu}{\overset{Bu}{Sn}}-O)_m-\underset{Bu}{\overset{Bu}{Sn}}-\right]_n$$

were prepared by heating dicarboxylic acids with polydibutyltin oxide at appropriate ratios, or by reacting oligomeric dichlorostannoxanes with the disodium salts of dicarboxylic acids under interfacial conditions. Some of the properties of the oligomers were investigated.

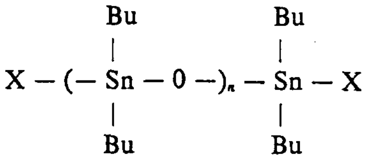
POLYDIORGANOTIN oxides are white infusible powders which have been described as "infinite" polymers having the structure  $-(-\underset{R}{\overset{R}{Sn}}-O-)-_n$.⁽¹⁻³⁾ This structure is analogous to that of the siloxanes and yet the compounds are very different in their properties. Unlike the polysiloxanes, the polytin oxides melt at high temperatures and are insoluble.

The reaction of phenols with diorganotin oxides to give distannoxanes has been reported.⁽⁴⁾ With monofunctional acids, diorganotin esters were formed;⁽¹⁾ with dicarboxylic acids, organotin polyesters, $-[-OOC-R-COOSn-]-_n$ were obtained.⁽⁵⁾ With metal halides, the diorganotin oxides reacted to form functionally substituted metallostannoxanes.⁽⁶⁾

Oligostannoxanes (I) having a controlled molecular weight were obtained by reaction of diazomethane with dibutyltin diacetate,⁽⁷, ⁸⁾ $CH_3COO-(R_2SnO)_nR_2Sn-$

OOCCH$_3$, n $\leqslant$ 14 (I). Oligomers were obtained by insertion of dialkyltin oxide units between tin halide bonds,(9, 10) $Bu_2SnCl_2 + (Bu_2SnO)_n \longrightarrow Cl(Bu_2SnO)_nSnBu_2Cl$.

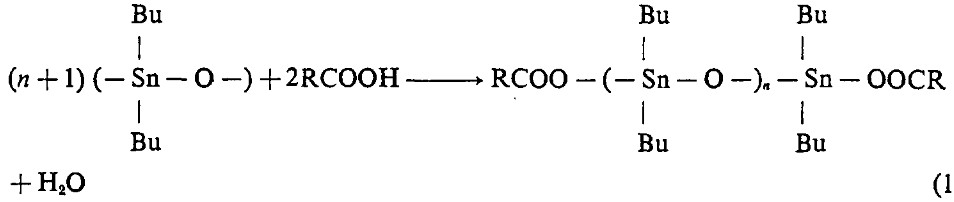
We have prepared new oligomeric and polymeric stannoxanes of the general formula:



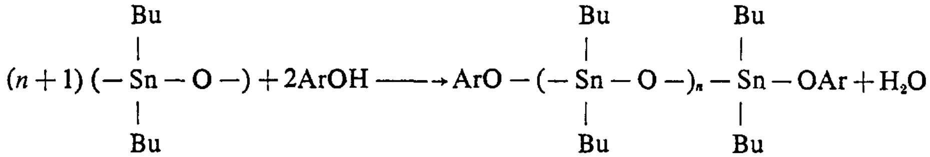
$$X-(-\underset{Bu}{\overset{Bu}{Sn}}-O-)_n-\underset{Bu}{\overset{Bu}{Sn}}-X$$

X = RCOO, ArO, RSO$_3$, Cl, $0 < n < 100$.

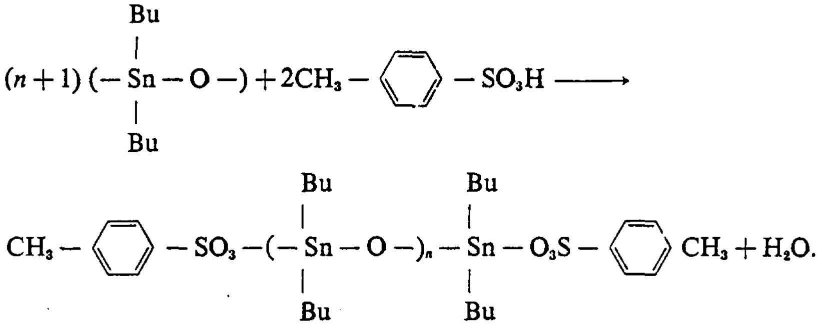
These polymers were obtained by reaction of phenols or acids with polymeric dibutyltin oxide, at molar ratios less than 1, as shown in the following equations:



$$(n+1)(-\underset{Bu}{\overset{Bu}{Sn}}-O-)+2RCOOH \longrightarrow RCOO-(-\underset{Bu}{\overset{Bu}{Sn}}-O-)_n-\underset{Bu}{\overset{Bu}{Sn}}-OOCR + H_2O \qquad (1)$$



$$(n+1)(-\underset{Bu}{\overset{Bu}{Sn}}-O-)+2ArOH \longrightarrow ArO-(-\underset{Bu}{\overset{Bu}{Sn}}-O-)_n-\underset{Bu}{\overset{Bu}{Sn}}-OAr+H_2O \qquad (2)$$

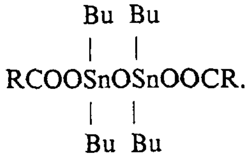


(3)

The reactions were conducted in boiling toluene or benzene and the water formed was removed by azeotropic distillation. The insoluble polydibutyltin oxide reacted and dissolved completely in the hot solvent. The polymers either precipitated out on cooling or were recovered on evaporation of the solvent. By suitable variation of the molar ratio of acid or phenol to the dibutyltin oxide, it was possible to obtain polymers having a required number of dibutyltin recurring units.

The course of the reaction is probably the cleavage of a stannoxane bond in the polymer and formation of shorter polymers having the acid residues as end groups.

The reaction conducted at a ratio of acid to dibutyltin oxide of 1 : 1 gave the known distannoxanes:



$$\mathrm{RCOO}\overset{\overset{\mathrm{Bu}}{|}}{\underset{\underset{\mathrm{Bu}}{|}}{\mathrm{Sn}}}\mathrm{O}\overset{\overset{\mathrm{Bu}}{|}}{\underset{\underset{\mathrm{Bu}}{|}}{\mathrm{Sn}}}\mathrm{OOCR}.$$

Most probably the higher polymers, obtained at suitable acid to dibutyltin oxide molar ratios, contained the acid residue as end groups from both sides of the polymer. Sn—OH end groups, even if initially formed, are too reactive to remain as such under the reaction conditions, and will pass to stannoxanes.

With monofunctional acids, it was possible to determine the molecular weights of the polymeric stannoxanes by titration of the carboxylate end groups with $0\cdot1$N alkali. Molecular weight determinations by V.P.O. (in benzene) on some soluble oligomers confirmed these results. The $\overline{DP}$ of the stannoxane polymers was consistent with the acid to dibutyltin oxide molar ratio used in their preparation.

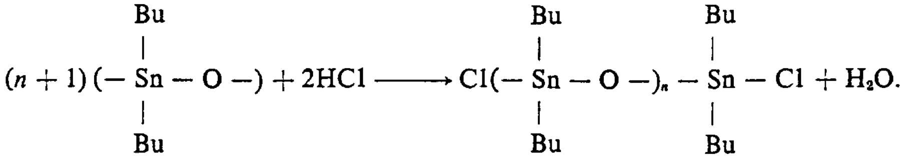
Although short oligomers having a small number of recurring dibutyltin oxide units are uniquely obtained by choosing appropriate acid to dibutyltin oxide ratios, it is very probable that mixtures of polymers are obtained at still lower ratios of acid to dibutyltin oxide which lead to higher $\overline{DP}$s. Reversible interchange reactions are possible, and probably the molecular weights of the polymers obtained are those given by an equilibrium molecular weight distribution.(11)

It was possible to obtain polymers having a relatively large number of recurring dibutyltin units. With *p*-nitrobenzoic acid the reaction was investigated to find out the minimum equivalent of acid required to react completely with the polymeric dibutyltin oxide and bring it into solution in toluene. This molar ratio was found to be acid/dibutyltin oxide = 1/56. This means that a polystannoxane having 112 dibutyltin oxide units and 2 *p*-nitrobenzoate end groups was formed. This may indicate that the $\overline{DP}$ of the polymeric dibutyltin oxide is not less than 112.

The polymers obtained from the carboxylic acids were amorphous powders with varied melting points. Their i.r. spectra showed the characteristic absorptions for the stannoxane carboxylate bonds. The solubility of the polymers depended on the molecular weights. Polymers having five or more tin recurring units were insoluble in cold toluene.

In a homologous series of polystannoxanes having the same end group, the melting point was found to depend on the molecular weight; it depended also on the type of the end group. Thus in the case of polymers having *p*-nitrobenzoate end groups, the melting points decreased sharply from 187° for the distannoxane to 85° for the tristannoxane and 71° for the hexastannoxane, and then increased to a flat maximum (~ 110°) with increasing the molecular weight (n = 10–110). The melting point of the polymeric dibutyltin oxide is high (340°) being due to a fairly ordered molecular arrangement.(2) Introduction of the nitrobenzoate end groups apparently affects this regularity and leads to lowering in melting point. Furthermore the inhomogeneity of the molecular weights of the polymers will also lower the melting point.

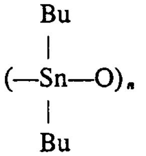
The reaction of dibutyltin oxide was also investigated with inorganic acids. With hydrochloric acid, it was possible to obtain oligomeric dichlorostannoxanes



$$(n+1)(-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O}-)+2\mathrm{HCl}\longrightarrow \mathrm{Cl}(-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O}-)_n-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{Cl}+\mathrm{H_2O}. \quad (4)$$

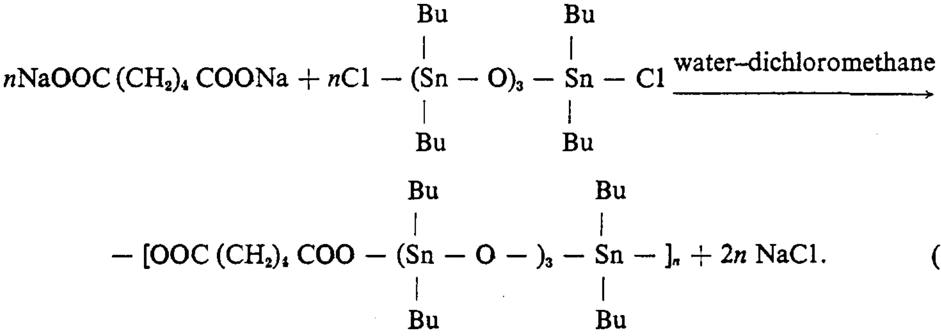
These were compared with products obtained recently by other methods.(9, 10)

The oligomeric dichlorostannoxanes have reactive Sn—Cl bonds. We have shown previously that under interfacial conditions these bonds react with alkali metal carboxylates at room temperature leading to the formation of organotin esters.(12) With salts of dicarboxylic acids organotin polyesters were formed.(13) We have now utilised this interfacial method for the preparation of organotin esters and organotin polyesters having in their backbone the group



$$(-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O})_n$$

as a recurring unit by starting with suitable oligomeric dichloro stannoxanes.

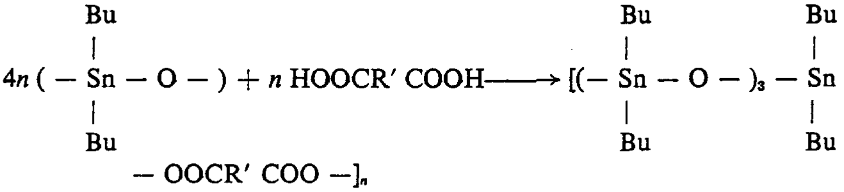


$$n\mathrm{NaOOC(CH_2)_4COONa}+n\mathrm{Cl}-(\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O})_3-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{Cl}\xrightarrow{\text{water–dichloromethane}}$$

$$-[\mathrm{OOC(CH_2)_4COO}-(\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O}-)_3-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-]_n+2n\,\mathrm{NaCl}. \quad (5)$$

The simple organotin esters obtained by the interfacial method with the oligomeric dichlorostannoxanes were identical with those obtained by direct reaction of the carboxylic acid with polymeric dibutyltin oxide, at the appropriate molar ratios.

It is possible by this method to prepare polyorganotin esters having a required amount of organotin as a recurring unit. Such polymers have not been prepared previously. These polymers were also obtained by reacting dicarboxylic acids, such as adipic acid, with dibutyltin oxide in refluxing toluene.



$$4n(-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O}-)+n\,\mathrm{HOOCR'COOH}\longrightarrow[(-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{O}-)_3-\underset{\mathrm{Bu}}{\overset{\mathrm{Bu}}{\mathrm{Sn}}}-\mathrm{OOCR'COO}-]_n \quad (6)$$

From phenolic acids such as *p*-hydroxybenzoic acid, polymers having several stannoxane recurring units between phenolate and carboxylate bonds were also obtained. The polymers containing four dibutyl tin recurring units obtained from terephthalic acid and *p*-hydroxy benzoic acid did not melt below 300° and were insoluble. Those obtained from aliphatic dicarboxylic acids, such as adipic acid and succinic acid, were partially soluble in hot chlorinated solvents, and melted at about 160–165° and 210–220° respectively. These melting points are lower than those obtained for polydibutyl tin adipate or succinate.(13)

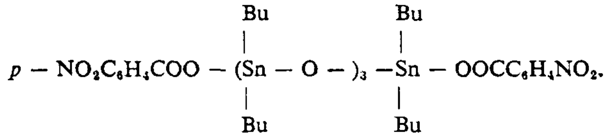
These organotin polymers may have special biological activity. It may be mentioned that dibutyltin dilaurate, dibutyltin maleate and many other organotin esters are very effective agents for the control of helminthic and protozoal infections in poultry.(14)

EXPERIMENTAL

Molecular weights of the polystannoxanes obtained from monofunctional acids were determined by end group analysis. Polymer (10–20 mg) suspended in alcohol (1 ml) was titrated by 0·1N aqueous sodium hydroxide, using an "Agla" micrometer syringe, with thymol blue as indicator. The titration was carried out until the blue colour of the indicator persisted for more than 5 min.

A typical procedure for the preparation of the oligomers or polymers is given below. Others are summarized in Table 1.

Octa-butyl di(*p*-nitrobenzoyloxy)tetrastannoxane



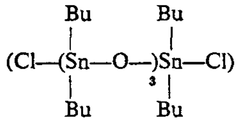
$$p-NO_2C_6H_4COO-(\underset{Bu}{\overset{Bu}{Sn}}-O-)_3-\underset{Bu}{\overset{Bu}{Sn}}-OOCC_6H_4NO_2.$$

Method A

To a suspension of polydibutyltin oxide (1 g, 4 mmole) in toluene (50 ml), *p*-nitrobenzoic acid (0·33 g, 2·01 mmole) was added. The mixture was heated under reflux (2·5 hr), the water which formed was removed by azeotropic distillation. A clear solution was formed within 15 min, indicating that all the polydibutyltin oxide reacted. The solution was diluted with petroleum ether (50 ml) and left overnight. The oligomer precipitated as pale yellow crystals, yield 0·93 g (71 per cent), m.p. 83°. (Calcd. for $C_{16}H_{80}N_2O_{11}Sn_4$: N, 2·1. Mol. wt, 1312. Found: N, 2·4. Mol. wt, 1270).

Method B

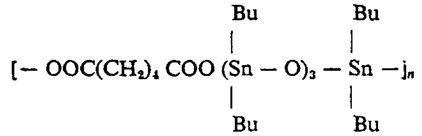
p-Nitrobenzoic acid (0·4 g, 2·4 mmole) was suspended in water and neutralized to phenolphthalein with 1N sodium hydroxide. To the clear solution octabutyl dichloro tetrastannoxane



$$(Cl-(\underset{Bu}{\overset{Bu}{Sn}}-O-)_3\underset{Bu}{\overset{Bu}{Sn}}-Cl)$$

(1 g, 0·95 mmole) in dichloromethane (50 ml) was added. The mixture was stirred at room temperature for 5 hr. The organic layer was washed, dried (sodium sulphate) and the solvent evaporated in vacuum. The residue was recrystallized from benzene-heptane, yield 0·79 g, (63 per cent), m.p. 83°. (Found: N, 2·4. Mol. wt, 1300). The aqueous layer contained 92 per cent of the chloride ions.

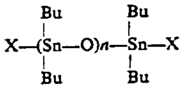
Poly (octabutyl adipoyloxy) tetrastannoxane



$$[-OOC(CH_2)_4COO(\underset{Bu}{\overset{Bu}{Sn}}-O)_3-\underset{Bu}{\overset{Bu}{Sn}}-]_n$$

Adipic acid (0·131 g, 0·95 mmole) was suspended in water (5 ml) and neutralized with 1N sodium hydroxide. Octabutyl dichloro tetrastannoxane (1 g, 0·95 mmole) in dichloromethane (80 ml) was added and the reaction mixture was stirred at room temperature overnight. The polymer precipitated out (0·9 g, 90 per cent), was filtered and washed with water, alcohol and dichloromethane; m.p. 158–168°. (Calcd. for $(C_{38}H_{80}O_7Sn_4)_n$: C, 40·6; H, 7·1; mol. wt of recurring unit 1124. Found: C, 40·2; H, 7·2; mol. wt of recurring unit, 1140).

TABLE 1. OLIGOMERS AND POLYMERS OF DIBUTYLTIN OXIDE*



$$X{-}(\overset{Bu}{\underset{Bu}{|}}\!\!Sn{-}O)_n{-}\overset{Bu}{\underset{Bu}{|}}\!\!Sn{-}X$$

X	X—H/Oxide	Yield† %	M.P. °C	C	H	N, Cl, or S	Mol. wt. Found (calcd.)	$\bar{n}$ Found (calcd.)
				Found, % (calcd.)				
p—$NO_2C_6H_4COO$	2	83	218‡	46·8 (46·7)	4·8 (4·6)	5·3 N (5·0)	570 (565)	0 (0)
p—$NO_2C_6H_4COO$	1	35	187‖			3·5 N (3·4)	830 (814)	1 (1)
p—$NO_2C_6H_4COO$	0·66	79	85¶	43·1 (42·9)	5·6 (5·8)	2·7 N (2·6)	955 (1063)	2 (2)
p—$NO_2C_6H_4COO$	0·33	54	71	40·1 (41·1)	6·5 (6·4)	1·9 N (1·6)	1790** (1810)	5 (5)
p—ClC_6H_4COO	0·66	53	144††	43·2 (43·8)	6·0 (6·0)	7·3 Cl (6·8)	1180 (1042)	2 (2)
o—ClC_6H_4COO	1	56	81‡‡	45·4 (45·4)	5·3 (5·5)	8·7 Cl (8·9)	795 (793)	1 (1)
o—ClC_6H_4COO	0·66	80	119	42·5 (43·8)	6·1 (6·0)	6·6 Cl (6·8)	1130 (1042)	2 (2)
$CHCl_2COO$	0·5	86	131			11·3 Cl (11·5)	1240 (1236)	3 (3)
CH_3COO	0·5	65	104	38·9 (39·3)	6·9 (7·1)		1230 (1098)	3 (3)
$C_{10}H_{19}COO$	0·25	65	97–104				2300 (2342)	7 (7)
C_6H_5O	0·66	100	91	46·6 (47·1)	6·6 (6·9)		970 (917)	2 (2)
p—$NH_2C_6H_4O$	0·5	86	108–115	44·1 (44·1)	6·7 (7·0)	2·4 N (2·4)	(1196)†††	(3)†††
p—$NH_2C_6H_4O$	0·33	73	105–115	41·5 (42·5)	6·9 (7·1)	1·7 N (1·7)	(1694)†††	(5)†††
p—$NO_2C_6H_4O$	0·66	86	171***	42·8 (42·8)	6·1 (6·3)	2·8 N (2·8)	1000 (1009)	2 (2)
p—$CH_3C_6H_4SO_3$	0·5	89	190	41·6 (41·7)	6·4 (6·5)	4·4 S (4·8)	1350 (1322)	3 (3)
$OOC(CH_2)_2COO$	0·5	76	210–225	39·3 (39·3)	7·2 (6·9)		1160 (1096)§§	3 (3)
$OOC(CH_2)_4COO$	0·5	82	153–160				1120 (1124)§§	3 (3)
Cl	1	48	110‖‖	34·9 (34·7)	6·6 (6·5)	12·8 Cl (12·8)		1 (1)
Cl	0·5	55	102¶¶	36·2 (36·5)	6·9 (6·6)	6·6 Cl (6·7)	1050 (1051)	3 (3)

* Polydibutyltin oxide (1–2 g) suspended in toluene (50–80 ml) and an appropriate amount of an acid or phenol were refluxed for several hours (2–3 hr). The polymer was usually recrystallized from toluene-heptane or toluene alone. Molecular weights were determined from end group analysis. When X was difunctional, polymers $(—OOCRCOO(SnBu_2—O)_3—SnBu_2—)_n$, were formed. The molecular weight of the recurring unit was determined by titration.

† After recrystallisation.

‡ Ref.(12) 218°.

§ Determined by V.P.O. in benzene at 37°.

‖ Ref.(12) 187°.

¶ Ref.(10) 85°.

** Molecular weight by V.P.O. (benzene) 1710.

†† Ref.(10) 144°.

‡‡ Ref.(10) 81°.

§§ Molecular weight of recurring unit.

‖‖ Ref.(15) 110°.

¶¶ Ref.(9) 94–95°. Ref.(10) 102°.

*** Ref.(10) 171°.

††† Calculated from the X—H/Oxide ratio used.

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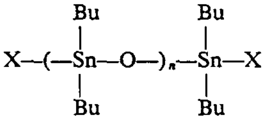
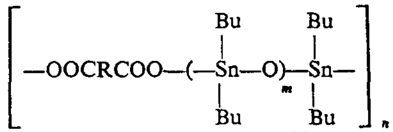
Résumé—On a préparé des stannoxanes oligomériques et polymériques de structure générale



$$X{-}({-}\underset{Bu}{\overset{Bu}{Sn}}{-}O{-})_n{-}\underset{Bu}{\overset{Bu}{Sn}}{-}X$$

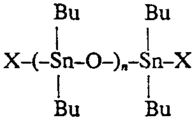
où X = RCOO, ArO, RSO_3 ou Cl et *n* est compris entre 0 et 100. La méthode utilisée consiste à chauffer un acide carboxylique, un phénol, un acide sulfonique ou l'acide chlorhydrique en présence d'oxyde de dibutylétain dans un rapport molaire inférieur à 1. La réaction débute probablement par une rupture de la liaison stannoxane dans l'oxyde de dibutylétain et conduit à polymères plus courts ayant le résidu acide en bout de chaîne. On a préparé des esters polyorganostanniques possédant le nombre requis d'unités dibutylétain:



$$\left[{-}OOCRCOO{-}({-}\underset{Bu}{\overset{Bu}{Sn}}{-}O)_m{-}\underset{Bu}{\overset{Bu}{Sn}}{-}\right]_n$$

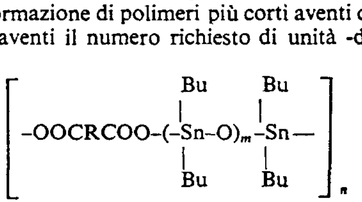
en chauffant des acides dicarboxyliques avec l'oxyde de dibutylétain dans les rapports molaires convenables. On a également fait réagir des dichlorostannoxanes avec des sels disodés d'acides dicarboxyliques dans des conditions interfaciales. On a examiné quelques propriétés des oligomères.

Sommario—Oligomeri e polimeri con formula generale



$$X{-}({-}\underset{Bu}{\overset{Bu}{Sn}}{-}O{-})_n{-}\underset{Bu}{\overset{Bu}{Sn}}{-}X$$

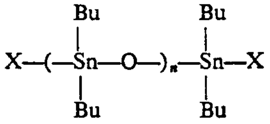
con X=RCOO, ArO, RSO_3, Cl e con 0 n 100 sono stati preparati per riscaldamento di un acido carbossilico, fenolo, acido solfonico o acido cloridrico con ossido dibutilstannico polimerico in rapporto molare inferiore a 1. La reazione basica è probabilmente la rottura del legame Sn–O nello ossido polidibutilstannico con formazione di polimeri più corti aventi come gruppo terminale residui acidi. Esteri poliorganostannici aventi il numero richiesto di unità -dibutilstanniche e con formula generale



$$\left[{-}OOCRCOO{-}({-}\underset{Bu}{\overset{Bu}{Sn}}{-}O)_m{-}\underset{Bu}{\overset{Bu}{Sn}}{-}\right]_n$$

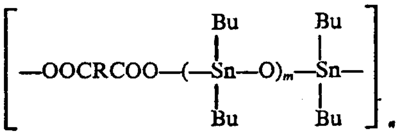
sono stati preparati riscaldando acidi dicarbossilici e ossido polidibutilstannico in rapporto opportnuo o per reazione di diclorostannossani oligomeri con i sali bisodici degli acidi bicarbossilici in condizioni interfacciali.

Zusammenfassung—Oligomere und polymere Stannoxane der algemeinen Formel



$$X\text{—}(\text{—}\overset{Bu}{\underset{Bu}{Sn}}\text{—}O\text{—})_n\text{—}\overset{Bu}{\underset{Bu}{Sn}}\text{—}X$$

wobei $X = RCOO$, ArO, RSO_3 Cl und $0 < n < 100$, wurden hergestellt durch Erhitzen einer Carboxylsäure, Phenol, Sulfonsäure oder Chlorwasserstoffsäure mit polymerem Dibutylzinnoxid bei molaren Verhältnissen kleiner als 1. Die Grundreaktion besteht vermutlich in der Spaltung einer Stannoxanbindung in dem Polydibutylzinnoxid und der Bildung kürzerer Polymerer, die den Säurerest als Endgruppen tragen. Polyorganozinnester, die die erforderliche Zahl sich wiederholender Dibutylzinn-Einheiten der allgemeinen Formel



$$\left[\text{—OOCRCOO—}(\text{—}\overset{Bu}{\underset{Bu}{Sn}}\text{—}O)_m\text{—}\overset{Bu}{\underset{Bu}{Sn}}\text{—}\right]_n$$

haben, wurden durch Erhitzen von Dicarboxylsäuren mit Polydibutylzinnoxid in entsprechenden Mengenverhältnissen hergestellt, oder durch Reaktion oligomerer Dichlorstannoxane mit den Dinatriumsalzen der Carboxylsäuren durch Grenzflächenkondensation. Einige Eigenschaften der Oligomeren wurden untersucht.