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Abstract

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ON THE SYNTHESIS OF POLYORGANOSTANNOXANES

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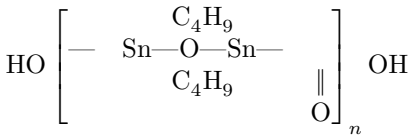
In recent years interest has grown in organotin compounds, which have found broad practical application for the stabilization of chlorine-containing polymers. Recently, low-molecular-weight tin-containing polymers have begun to be used for these purposes ([1] [2]). In view of the absence of literature data (apart from patents) on the synthesis of polyorganostannoxanes containing in the main chain the grouping Sn–O–Sn , we undertook an investigation of the possibility of obtaining such tin-containing polymers. For this purpose we used the polycondensation reaction, previously successfully employed by Andrianov ([3]) and Henglein ([4]) for the synthesis of various polyorganostannosiloxanes.

We studied the reaction of diacetates of *n*- and *iso*-butyltin with tetraethoxytin, in which formation of the –Sn–O–Sn bond occurred through interaction of acetate and ethoxyl groups according to the equation:

$$\mathrm{CH_3COO{-}}\begin{matrix}\mathrm{C_4H_9}\\ \mathrm{Sn}\\ \mathrm{C_4H_9}\end{matrix}\mathrm{{-}OCOCH_3} + \mathrm{C_2H_5{-}O{-}}\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{Sn}\\ \mathrm{OC_2H_5}\end{matrix}\mathrm{{-}O\cdot C_2H_5} \rightarrow$$

$$\rightarrow \mathrm{CH_3COO}\left[\mathrm{-}\begin{matrix}\mathrm{C_4H_9}\\ \mathrm{Sn{-}O{-}Sn}\\ \mathrm{C_4H_9}\end{matrix}\begin{matrix}\mathrm{OC_2H_5}\\ \\ \mathrm{OC_2H_5}\end{matrix}\right]_n \mathrm{OC_2H_5} + \mathrm{CH_3COOC_2H_5} \qquad \text{(I)}$$

Polymer (I) was isolated as a light-yellow powder with a softening temperature of 70–75° (in the case of (*iso*-$C_4H_9)_2Sn(OAc)_2$) or 60–70° (in the case of (*n*-$C_4H_9)_2Sn(OAc)_2$). The molecular weight of polymer (I) was 1890–1990 (for the tetramer, 1936). Thus, under the experimental conditions formation of a linear low-molecular-weight ($n = 4$) polyorganostannoxane was observed. The polymer is hydrolyzed on heating with water, with elimination of ethoxyl and acetate groups, forming an insoluble, infusible compound (II) of composition:



(II)

Experimental Part

Dibutyltin diacetates were obtained from the corresponding dichlorides ([4]). Diisobutyltin diacetate is a liquid with b.p. 140–141° (10 mm).

$C_{12}H_{24}O_4Sn$.	Found, %:	Sn 34.1
	Calculated, %:	Sn 33.9

Diacetate of di-(*n*-butyl)tin—a liquid with b.p. 146–147° (10 mm), n_D^{20} 1.4707.

Found, %:	C 46.30;	H 7.19;	Sn 34.21
$C_{12}H_{24}O_4Sn$. Calculated, %:	C 46.72;	H 6.81;	Sn 33.93

Tetrastoxytin was obtained by the method of Meerwein and Bersin ([5]).

Reaction of $(C_2H_5O)_4Sn$ with $(n\text{-}C_4H_9)_2Sn(OCOCH_3)_2$ in molar ratios of 1 : 1. Heating on a glycerol bath at 140° for 28 hr in a stream of inert gas, with distillation of the ethyl acetate formed, of which 74.6% (of theory) was collected. Treatment of the polycondensation product with benzene gave an insoluble, infusible up to 250° crystalline precipitate containing 57.9–58.1% Sn. From the benzene solution a light-yellow polymer with a softening temperature of 70–75° was isolated. The molecular weight, determined by the cryoscopic method, was found to be 1890 (1936 calculated for the tetramer).

Found, %:	C 30.02;	H 5.78;	Sn 50.41
$C_{52}H_{120}O_{15}Sn_8$. Calculated, %:	C 32.22;	H 6.19;	Sn 49.17

The polymer is hydrolyzed on boiling with water, with formation of a white insoluble and infusible product.

Found, %:	Sn 60.92
$C_{32}H_{74}O_{10}Sn_8$. Calculated, %:	Sn 60.63

Reaction of $(C_2H_5O)_4Sn$ and $(n\text{-}C_4H_9)_2Sn(OCOCH_3)_2$—the conditions were the same as in the case of $(n\text{-}C_4H_9)_2Sn(OCOCH_3)_2$. An insoluble and infusible precipitate was obtained, containing 56.71–57.2% Sn. From the benzene solution a light-yellow polymer with a softening temperature of 60–70° was isolated. Molecular weight of the polymer (cryoscopically) 1991.

Found, %:	Sn 50.1
$C_{52}H_{120}O_{15}Sn_8$. Calculated, %:	Sn 49.17

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Note: Figure translations are in progress. See original paper for figures.