

ORGANOTIN POLYESTER DERIVATIVES OF BIFUNCTIONAL ACIDS CONTAINING SILICON

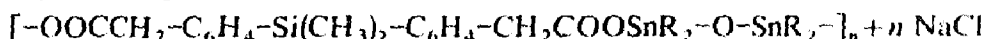
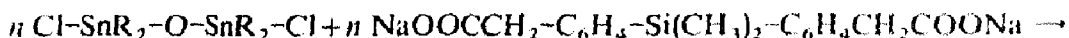
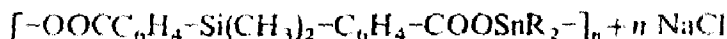
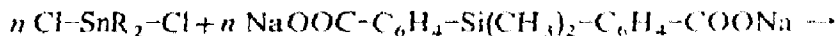
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In previous work we have shown that the interfacial technique of polymerization in which two reactive monomers are brought into reaction at the interface between two immiscible solvents, can be applied successfully to the formation of organotin esters of carboxylic acids¹ as well as of polyesters. Use is made of the reactivity of the tin-halogen bond which enables the reaction to proceed. Thus reaction of organotin dihalides such as dibutyltin dichloride dissolved in an organic solvent immiscible in water with the disodium salt of adipic acid in water led to the formation of poly-(dibutyltin adipate)².

We have extended these investigations to the preparation of organotin polyesters of bifunctional carboxylic acids containing silicon, namely bis(*o*-carboxyphenyl)-, bis(*p*-carboxyphenyl)-, bis[*o*-(carboxymethyl)phenyl]- and bis[*p*-(carboxymethyl)phenyl]dimethylsilane. The polyesters contain both tin and silicon atoms in the parent polymer backbone.



The bifunctional carboxylic acids were suspended in water and neutralized to phenolphthalein with sodium hydroxide. To the resulting aqueous solution which was cooled to 0°, dialkyltin dichloride or dichlorotetraalkyldistannoxane dissolved in petroleum ether, carbon tetrachloride or dichloromethane was added with strong stirring. In the former solvent, the polymer usually precipitated during formation, and the reaction was complete in a short time (about 15 min). In the latter solvents, the polymer was usually recovered on evaporation of the solvent and addition of acetone. Volhard titration of the aqueous layer at the end of the reaction showed that from 85–100% of the chlorine has passed into the aqueous layer, indicating that the reaction was almost quantitative (Table 1).

This interface technique was found to lead to the formation of polyesters having higher melting points than those obtained by refluxing the dicarboxylic acids with dibutyltin oxide in benzene³.

The structure of the polymers seems to be linear, since the production of a cyclic product even with bis(*o*-carboxyphenyl)dimethyl silane and dibutyltin dichloride requires the formation of a 10-membered ring.

TABLE I
SYNTHESIS OF ORGANOTIN POLYESTER DERIVATIVES OF BIFUNCTIONAL ACIDS CONTAINING SILICON

Reactants ^a	Organic		Yield (%)	Formula	Carbon (%)		Hydrogen (%)		η_{sp}/C (dl/g) ^f	Mol. wt. (Rast)
	Diacid ^b	solvent ^c			M.p. (°C)	Polylester	Calcd.	Found		
R_2SnCl_2										
Bu	P-A	CCl_4	54 ^d	$(C_{24}H_{36}O_2SiSn)_n$	55.84	55.08	6.44	6.47	0.023	
Bu	P-A	PAc	28 ^e	$(C_{26}H_{36}O_4SiSn)_n$	55.84	55.60	6.44	6.64	0.025	
Et	P-B	CH_2Cl_2	54 ^e	$(C_{20}H_{24}O_2SiSn)_n$	50.05 ^g	49.35	5.11 ^g	5.04		2200
Bu	o-B	PAc	87 ^d	$(C_{24}H_{32}O_4SiSn)_n$	53.66 ^g	53.49	6.09 ^g	6.14	0.023	1800 ^f
Et	o-B	CH_2Cl_2	100 ^f	$(C_{20}H_{24}O_4SiSn)_n$	50.56	52.01	5.06	5.32	0.022	
$R_4Sn_2Cl_2O$										
Bu	P-A	PAc	58 ^e	$(C_{34}H_{54}O_5SiSn_2)_n$	50.53	50.45	6.69	6.55		2400
Bu	o-B	PAc	81 ^d	$(C_{32}H_{50}O_5SiSn_2)_n$	49.27	50.41	6.41	6.69		
Et	o-B	PAc	26 ^{e,h}	$(C_{24}H_{34}O_5SiSn_2)_n$	43.16	43.25	5.09	5.01		

^a The diacid (1 g) was dissolved in water by addition of an equivalent of sodium hydroxide and an equivalent of dialkyltin dichloride or tetraalkyldichlorodistannoxane dissolved in carbon tetrachloride (CCl_4), petroleum ether (PAc) or dichloromethane (CH_2Cl_2) was added at 0°. ^b A = bis[(carboxymethyl)phenyl]dimethylsilane; B = bis(carboxyphenyl)dimethylsilane. ^c Measured in benzene at a concentration $c = 0.4$ g/100 ml. ^d The polyester was obtained by evaporation of the organic solvent. ^e The polyester precipitated from the reaction mixture. ^f Molecular weight by VPO, 1950. ^g Analysis calculated according to molecular weight. ^h Evaporation of the organic solvent left a solid (yield 72%), m.p. 194° (Found: C, 45.64; H, 5.45%).

From the range of polymers prepared it may be seen that the melting points of the polymers having diethyltin groupings melt at a higher temperature than those having dibutyltin. Polyesters having $-\text{Sn}-\text{O}-\text{Sn}-$ linkages melt at a higher temperature than those having $-\text{Sn}-$ linkages. Polyester derivatives of the *para* acids have higher melting points than the corresponding derivatives of the *ortho* acids.

The polymers are usually soluble in benzene, chloroform, dimethylformamide and *o*-dichlorobenzene, and are only slightly soluble in acetone. The polymers are thermoplastic and can be cast into films. The polymers had a low relative viscosity in benzene, and had a low molecular weight (2000–2400).

EXPERIMENTAL

Melting points were determined on a Fisher–Johns apparatus. Bis(*p*-carboxyphenyl)dimethylsilane⁴ and bis(*p*-carboxymethylphenyl)dimethylsilane⁵ were prepared as previously described. The *ortho* isomers which are new compounds were prepared as described below.

Dimethylbis(o-tolyl)silane

o-Chlorotoluene (363 g; 2.88 moles) (Fluka Puriss) in dry ether (250 ml) was dropped with efficient stirring during 2.5 h into lithium wire (40 g; 5.76 moles) in dry ether (500 ml) at -10° under argon atmosphere. The reaction mixture was then stirred at room temperature for 14 h, cooled to -10° and a solution of dimethyldichlorosilane (156 g; 1.21 moles) in dry ether (200 ml) was added dropwise during 2.5 h and the reaction mixture was stirred at room temperature for 20 h. Excess lithium was filtered off on glass wool under argon, and the solution treated with ice water. The ethereal layer was separated, washed with water, 5% hydrochloric acid followed by 5% sodium hydroxide and water, dried (calcium chloride) and evaporated. Dimethylbis(*o*-tolyl)silane was collected at $143^\circ/3$ mm, yield 221 g (76%); $n_D^{20} = 1.570$. (Found: C, 80.95; H, 8.46. $\text{C}_{16}\text{H}_{20}\text{Si}$ calcd.: C, 80.0; H, 8.34%.)

Bis(o-bromomethylphenyl)dimethylsilane

To a solution of dimethylbis(*o*-tolyl)silane (96 g; 0.4 mole) in dry carbon tetrachloride (400 ml), *N*-bromosuccinimide (142.4 g; 0.8 mole) was added followed by dibenzoyl peroxide (2 g) and the mixture was stirred and heated to reflux. A vigorous reaction set in. After the reaction subsided the heating and stirring was continued for 4 h, and the reaction mixture was cooled and filtered. The filtrate was washed with 2.5% sodium hydroxide solution, followed by water and dried over calcium chloride. The carbon tetrachloride was driven off and the residue fractionally distilled. The lachrimatory bis[*o*-(bromomethyl)phenyl]dimethylsilane (119 g; 75%) passed at $195\text{--}207/2$ mm and solidified on standing, m.p. $34\text{--}35^\circ$. It is soluble in petroleum ether, and partially soluble in alcohol. (Found: C, 48.62; H, 4.54; Br, 40.81. $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{Si}$ calcd.: C, 48.24; H, 4.52; Br, 40.20%.)

Bis(o-(cyanomethyl)phenyl)dimethylsilane

To a stirred solution of sodium cyanide (27 g; 0.55 mole) in water (15 ml), bis[*o*-(bromomethyl)phenyl]dimethylsilane (99.5 g; 0.25 mole) and ethanol (30 ml) was refluxed for 5 h. The alcohol was distilled off, the residue cooled, filtered, and the

salts washed with ether. The organic layer of the filtrate was separated and the aqueous layer extracted with ether. The combined organic layers were dried over sodium sulphate and fractionally distilled. The bis[*o*-(cyanomethyl)phenyl]dimethylsilane (37.3 g; 51%) passed at 210–234°/1 mm and solidified on cooling, m.p. 73° after standing under petroleum ether. (Found: C, 74.19; H, 6.32; N, 9.66. $C_{18}H_{18}N_2Si$ calcd.: C, 74.48; H, 6.21; N, 9.66%.)

*Bis[*o*-(carboxymethyl)phenyl]dimethylsilane*

Bis[*o*-(cyanomethyl)phenyl]dimethylsilane (27.3 g; 0.094 mole), ethylene glycol (200 ml), potassium hydroxide (28 g), and water (40 ml) were heated under reflux for 18 h. The reaction mixture was cooled and acidified with 1 : 1 hydrochloric acid (about 200 ml). The bis[*o*-(carboxymethyl)phenyl]dimethylsilane was taken up in ether, and the acid was extracted from the ethereal solution with 2.5% sodium hydroxide solution, decolorized, and precipitated by addition of hydrochloric acid, filtered off and washed thoroughly with water; yield, 13.9 g (45%) m.p. 178° on recrystallization from methanol-water, followed by recrystallization from aqueous ethanol and washing with chloroform. (Found: C, 65.50; H, 6.07; neutralization equivalent, 167. $C_{18}H_{20}O_4Si$ calcd.: C, 65.85; H, 6.10%; neutralization equivalent, 164.)

*Bis(*o*-carboxyphenyl)dimethylsilane*

To a solution of dimethylbis(*o*-tolyl)silane (20 g; 0.083 mole) in pyridine (80 ml) and water (60 ml), potassium permanganate (60 g; excess) was added in portions of 4–7 g, with efficient stirring during 50 min. The reaction mixture was heated under reflux for 2 h, filtered, and excess permanganate in the filtrate was destroyed by addition of a 15% hydrogen peroxide solution (about 10 ml), and the precipitated manganese dioxide was filtered off, and the filtrate evaporated in vacuo. The residue was dissolved in sodium hydroxide solution, washed with ether, decolorized, and acidified with hydrochloric acid. The bis(*o*-carboxyphenyl)dimethylsilane was filtered off and washed thoroughly with water, yield 14.4 g (58%); m.p. 243° on recrystallization from aqueous methanol, and washing with chloroform. (Found: C, 64.31; H, 5.08. $C_{10}H_{16}O_4Si$ calcd.: C, 64.00; H, 5.33%.)

The interfacial polymerization technique is illustrated in the following typical example. The preparation of the other polymers is given in Table 1.

*Poly(*di-n*-butyltin) ester of bis(*p*-carboxyphenyl)dimethylsilane*

Bis(*p*-carboxyphenyl)dimethylsilane (1.00 g; 3.33 mmoles) suspended in water (2 ml) was neutralized to phenolphthalein with aqueous 1 *N* sodium hydroxide and thus brought into solution. *n*-Dibutyltin dichloride (1.01 g; 3.33 mmoles) in petroleum ether (40–60°) (25 ml) was added with vigorous stirring at 0°. The poly(*di-n*-butyltin) ester of bis(*p*-carboxyphenyl)dimethylsilane precipitated immediately. The polyester was filtered off, washed with water, acetone and petroleum ether, yield 0.98 g (55%), m.p. about 100°. The polymer is soluble in carbon tetrachloride, chloroform, benzene, dimethylformamide and *o*-dichlorobenzene. It is slightly soluble in acetone. [Found: C, 54.29; H, 5.60. $(C_{24}H_{32}O_4SiSn)_n$ calcd.: C, 54.27; H, 6.03%.] On evaporation of the organic layer a viscous oil remained (Found: C, 53.41; H, 7.11%.)

The same reaction conducted in carbon tetrachloride gave a polyester, m.p. about 80°. (Found: C, 54.26; H, 6.34%.) Rast and VPO molecular weight determinations gave molecular weights of 2200 and 2300, respectively. $[\eta_{sp}/c$ in benzene = 0.038 dl/g ($c=0.4$ g/ml)].

The same procedure was used with only slight modifications to obtain the polyesters summarized in Table I.

SUMMARY

The interfacial polymerization technique has been used in the preparation of organotin polyesters having both silicon and tin in the polymer backbone. Dialkyltin dichlorides or tetraalkyldichlorodistannoxanes dissolved in an organic solvent immiscible with water were brought into reaction with the sodium salts of bis[*o*-(carboxymethyl)phenyl]- and bis[*p*-(carboxymethyl)phenyl]dimethylsilane. The polyesters had a low molecular weight and were thermoplastic and soluble in benzene, chloroform, etc. Their melting points depended on their composition.

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