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# POLY(ORGANOTIN PHOSPHONATES)

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## SUMMARY

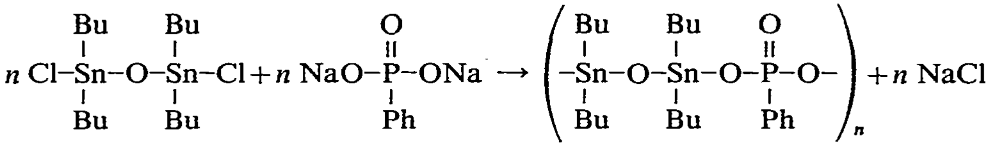
The interfacial polymerization technique has been used in the preparation of poly(organotin phosphonates). Dialkyltin dichloride, tetraalkyldichlorodistannoxane or hexaalkyldichlorotristannoxane dissolved in an organic solvent immiscible with water was brought into reaction with the disodium salt of phenylphosphonic acid to give the corresponding poly(organotin phosphonate). The solubility of the polymers in organic solvents decreased with increasing tin content.

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 acids[1] as well as of polyesters[2]. Use is made of the reactivity of the tin–halogen bond which enables the reaction to proceed.

We have now extended these investigations to the preparation of organotin phosphonates as well as poly(organotin phosphonates), having a desired proportion of Sn–O bonds in their backbone. There is interest in the preparation of such compounds having tin–oxygen–phosphorus bonds because of their many possible uses[3]. Simple organotin phosphonates and poly(organotin phosphonates) having one recurring Sn–O bond in their backbone have been reported[4]; they were prepared by the reaction of organotin hydrides, bis(trialkyltin) oxide, or dialkyltin oxide with phosphonic or phosphinic acids or by the reaction of the sodium salt of the phosphonic acid with trialkyltin halide in an organic solvent under reflux.

## RESULTS

The interfacial reaction for the preparation of the organotin phosphonates is fast and gives high yields. The reaction may be represented as follows:



$$n\,\mathrm{Cl{-}\overset{Bu}{\underset{Bu}{Sn}}{-}O{-}\overset{Bu}{\underset{Bu}{Sn}}{-}Cl} + n\,\mathrm{NaO{-}\overset{O}{\underset{Ph}{P}}{-}ONa} \longrightarrow \left(\mathrm{-\overset{Bu}{\underset{Bu}{Sn}}{-}O{-}\overset{Bu}{\underset{Bu}{Sn}}{-}O{-}\overset{O}{\underset{Ph}{P}}{-}O{-}}\right)_n + n\,\mathrm{NaCl}$$

The trialkyltin organophosphonates and the polymer obtained from n-dibutyltin dichloride were soluble in benzene in which the reaction was carried out, and were recovered on evaporation of the solvent. Polymers having a distannoxane linkage in their backbone and based on phenylphosphonic acid were partially soluble in benzene while those having a tristannoxane linkage were insoluble in benzene and immediately precipitated on formation. The polymer obtained from n-dibutyltin dichloride and (*m*-nitrophenyl)phosphonic acid had similar properties as that with the corresponding phenylphosphonic acid. The polymers having one or three recurring –SnO– units in their backbone did not melt below 300°, that having two such units melted at about 225–230°. To establish the thermal stability of these polymers they were subjected to thermogravimetric analysis in air. It was found that the polymers obtained from phenylphosphonic acid and dibutyltin dichloride or hexabutyldichlorotristannoxane started to decompose at about 200° (Fig. 1).

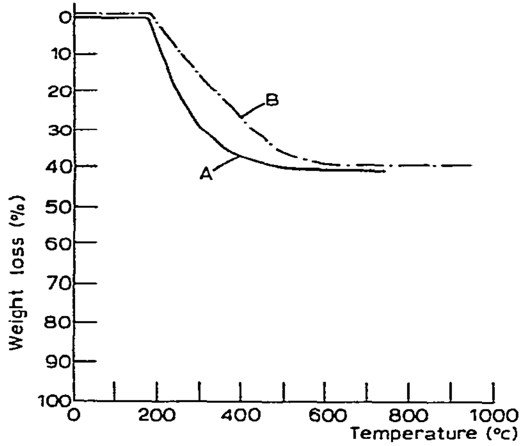
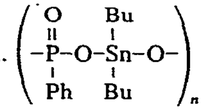
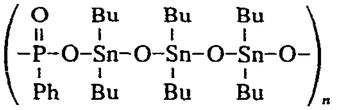


Fig. 1. Thermogravimetric analysis curves for Sn–O–P polymers.

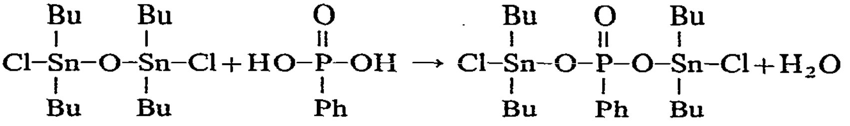
A.

$$\left(\begin{array}{ccccc} O & & Bu & & \\ \| & & | & & \\ -P & -O- & Sn & -O- & \\ | & & | & & \\ Ph & & Bu & & \end{array}\right)_n$$

B.

$$\left(\begin{array}{ccccccc} O & & Bu & & Bu & & Bu \\ \| & & | & & | & & | \\ -P & -O- & Sn & -O- & Sn & -O- & Sn-O- \\ | & & | & & | & & | \\ Ph & & Bu & & Bu & & Bu \end{array}\right)_n$$

The molecular weight of the polymers soluble in benzene was measured by vapor phase osmometry. Molecular weights of about 7000–10000 were obtained which did not vary significantly with the temperature of the reaction, but varied with the organic solvent in which the polymerization was carried out. The molecular weight of the polymer obtained by heating $Bu_2SnO$ with $PhP(O)(OH)_2$ under azeotropic conditions (benzene) was of the same order as that obtained by the interfacial method using benzene as solvent.

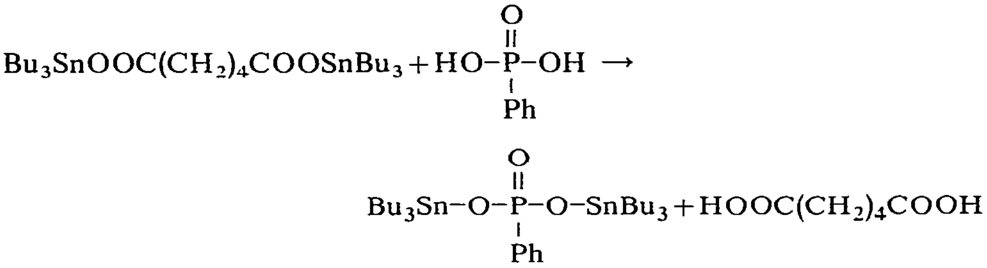
The tin–organophosphonate linkage can be titrated quantitatively by sodium methoxide in methanol/benzene using thymol blue as indicator.

The possibility of obtaining organotin polyesters having alternating carboxylic and phosphonic acid residues was investigated. A suitable organotin intermediate for the preparation of such polyester by the interfacial method seemed to be (I), which was obtained by heating phenylphosphonic acid with tetrabutyldichlorodistannoxane


$$\begin{array}{ccccccccccccc} & Bu & & Bu & & & O & & & Bu & & O & & Bu & \\ & | & & | & & & \| & & & | & & \| & & | & \\ Cl- & Sn & -O- & Sn & -Cl+HO- & & P & -OH \longrightarrow Cl- & & Sn & -O- & P & -O- & Sn & -Cl+H_2O \\ & | & & | & & & | & & & | & & | & & | & \\ & Bu & & Bu & & & Ph & & & Bu & & Ph & & Bu & \end{array}$$

However, subsequent reaction under interfacial conditions with two moles of sodium *p*-nitrobenzoate led to cleavage of the SnO–P bonds and formation of dibutyltin bis(*p*-nitrobenzoate), which was identified by m.p., mixed m.p. and IR spectrum. This behaviour is similar to that previously found in attempts to prepare mixed organotin esters of carboxylic acids.

Phenylphosphonic acid was found to undergo an interchange reaction with organotin esters of carboxylic acids. Thus, phenylphosphonic acid reacted in benzene solution with bis(tri-n-butyltin) adipate to give bis(tri-n-butyltin) phenylphosphonate and adipic acid



$$Bu_3SnOOC(CH_2)_4COOSnBu_3 + HO-\underset{\displaystyle Ph}{\overset{\displaystyle O}{\overset{\|}{P}}}-OH \rightarrow Bu_3Sn-O-\underset{\displaystyle Ph}{\overset{\displaystyle O}{\overset{\|}{P}}}-O-SnBu_3 + HOOC(CH_2)_4COOH$$

*Biocidal activity*

The biocidal activity of poly(di-n-butyltin phenylphosphonate) was investigated. It was found that the material did not inhibit the growth of the bacteria: (1) *Proteus mirabilis* TH 3333; (2) *Salmonella typhimurium*; (3) *Pseudomonas pyocyaneam*. It also did not inhibit the growth of the yeasts *Candida albicans* or *Cryptococcus neoformans* "A". A very small inhibition was observed with the bacteria: (1) *Staphylococcus aureus* "Tour"; (2) *Bacillus cereus* I; (3) *Escherichia coli* $0_{111}13_4H_{12}$.

## EXPERIMENTAL

Molecular weights were determined by vapour phase osmometry with a Hitachi–Perkin–Elmer instrument. Thermogravimetric analysis was carried out on a Stanton instrument; a heating rate of 5°/min in air was used.

*Bis(tributyltin) phenylphosphonate*

Phenylphosphonic acid (Aldrich) (1.58 g, 0.01 mole) was suspended in water and neutralized to phenolphthalein with sodium hydroxide (1 *N*). The solution was made up to 100 ml, and tributyltin chloride (6.5 g, 0.02 mole) dissolved in 100 ml benzene was added with strong stirring. The mixture was stirred for 20 min, the benzene layer was separated, washed with water, dried over magnesium sulfate, evaporated *in vacuo* and the residue dried at 50° *in vacuo* to give the oily ester (6 g, 82%). (Found: C, 49.20; H, 8.15; P, 3.70; Sn, 31.9. $C_{30}H_{59}O_3PSn_2$ calcd.: C, 48.97; H, 8.03; P, 4.21; Sn, 32.3%.)

*Bis(triphenyltin) phenylphosphonate*

This was prepared as before. M.p. 143°. The material solidified on further heating. Yield 87%. (Found: C, 58.74; H, 4.27; P, 3.38; Sn, 27.3. $C_{42}H_{35}O_3PSn_2$ calcd.: C, 58.92; H, 4.09; P, 3.62; Sn, 27.7%.)

*Tributyltin dibutyl phosphate*

This was prepared as before from dibutyl phosphate and tributyltin chloride. The product was an oily ester, yield 88 %. (Found: C, 48.00; H, 9.46; Sn, 23.6. $C_{20}H_{45}O_4PSn$ calcd.: C, 48.12; H, 9.02; Sn, 23.8 %.)

*Poly(dibutyltin phenylphosphonate)*

Phenylphosphonic acid (5 g, 0.032 mole) was neutralized with sodium hydroxide and the solution was diluted to 100 ml. Recrystallized dibutyltin dichloride (9.7 g, 0.032 mole) in 100 ml benzene was added with strong stirring at room temperature. The mixture was stirred for 15 min, the benzene layer was separated, washed with water, dried over magnesium sulfate and evaporated to dryness in vacuum. The residue was dissolved in carbon tetrachloride and the polymer was precipitated by methanol; yield 10.3 g (83 %); it did not melt below 300°. [Found: C, 43.38; H, 6.29; P, 7.55; Sn, 30.0. $(C_{14}H_{23}O_3PSn)_n$ calcd.: C, 43.22; H, 5.92; P, 7.97; Sn, 30.5 %.]

The same polymerization was carried out in different solvents and at different temperatures. The molecular weights at 0° are: in benzene 10040, in carbon tetrachloride 7880, in methylene chloride 6900. In the same solvents at 25° the molecular weights were: 10200, 8140, and 7500 respectively.

*Poly[dibutyltin (m-nitrophenyl)phosphonate]*

This was prepared as before. M.p. >300. (Found: C, 38.02; H, 5.24; N, 3.43; Sn, 26.9. $C_{14}H_{22}NO_5PSn$ calcd.: C, 38.74; H, 5.08; N, 3.23; Sn, 27.4 %.) Molecular weight in benzene 10000.

*Poly(tetrabutyldistannoxane phenylphosphonate)*

This was prepared similarly starting with tetrabutyldichlorodistannoxane dissolved in benzene which was reacted with disodium phenylphosphonate. The polymer was dissolved in carbon tetrachloride and precipitated by methanol. M.p. 225–230. Yield 93%. (Found: C, 41.57; H, 6.32; P, 4.64; Sn, 36.8. $C_{22}H_{41}O_4PSn_2$ calcd.: C, 41.42; H, 6.43; P, 4.86; Sn, 37.2 %.)

*Poly(hexabutyltristannoxane phenylphosphonate)*

This polymer was similarly prepared starting from hexabutyldichlorotristannoxane in 84% yield. It did not melt below 300°. (Found: C, 40.58; H, 6.99; P, 2.72; Sn, 40.8. $C_{30}H_{59}O_5PSn_3$ calcd.: C, 40.62; H, 6.66; P, 3.50; Sn, 40.2 %.)

*Bis(chlorodibutyltin) phenylphosphonate (I)*

A mixture of phenylphosphonic acid (3.16 g, 0.02 mole) and tetrabutyldichlorostannoxane (11.1 g, 0.02 mole) were heated azeotropically in dry benzene (150 ml) for 4 h. The benzene was evaporated in vacuum and yielded bis(chlorodibutyltin)phenylphosphonate, 13.3 g (96 %), m.p. 42–43°. (Found: C, 38.30; H, 6.10; Cl, 10.21; P, 3.90; Sn, 34.2. $C_{22}H_{41}Cl_2O_3PSn_2$ calcd.: C, 38.13; H, 5.92; Cl, 10.25; P, 4.48; Sn, 34.3 %.)

*Reaction of phenylphosphonic acid with bis(tri-n-butyltin) adipate*

Bis(tri-n-butyltin) adipate (3.6 g, 0.005 mole) was dissolved in benzene (10 ml) and phenylphosphonic acid (0.8 g, 0.005 mole) was added with strong stirring at room temperature. After 15 min the precipitated acid was filtered off and the benzene was evaporated *in vacuo*. The residue was identified as bis(tri-n-butyltin) phenylphosphonate contaminated by a trace of bis(tri-n-butyltin) adipate; yield 3.1 g (84%).

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