

Organotin Polyesters

MAX FRANKEL, D. GERTNER, D. WAGNER, and A. ZILKHA,
*Department of Organic Chemistry, The Hebrew University
of Jerusalem, Jerusalem, Israel*

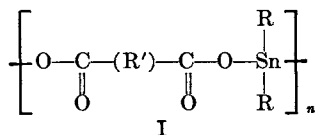
Synopsis

The interfacial polymerization technique was used in the preparation of organotin polyesters. Dialkyltin dihalides dissolved in an organic solvent immiscible with water were reacted with the dialkali metal or ammonium salt of a dicarboxylic acid. High yields of polyesters were obtained after short reaction times. The polyesters were generally insoluble and were high melting. Copolymers were also obtained.

INTRODUCTION

Most of the known organotin polymers have a polymer backbone, containing tin-carbon and carbon-carbon bonds only. Exceptions are the stannoxanes, which contain tin-oxygen bonds and some short oligomers containing tin-tin bonds.^{1,2}

While organotin esters of the general formula $\text{RCO}_2\text{SnR}'_3$ have received much attention,^{3,4} organotin polyesters having the structure I



received only little attention. Andrews et al.⁵ synthesized some short organotin polyesters by reaction of dibutyltin diacetate or oxide with dicarboxylic acids in boiling xylene. The oligomers thus obtained were cyclic or open-chained, had relatively low melting points, and were soluble in organic solvents. Only in the case of terephthalic acid a high melting polymer was obtained.

The present paper reports the application of the interfacial polymerization procedure,⁶ in which two reactive monomers are brought into reaction at the interface between two immiscible solvents, to the field of organotin polyesters. Use is made of the reactivity of the tin-halogen, tin-acetate, and tin-formate bonds which enable the reaction to proceed.

RESULTS AND DISCUSSION

The polyorganotin esters were prepared by the following procedure. A polycarboxylic acid in water, neutralized to phenolphthalein with an or-

ganic or inorganic base, was reacted under stirring with a solution of dialkyltin dihalide, diacetate, or diformate in a water-immiscible solvent. The polymer usually started to form immediately and, provided that it was insoluble in the reaction mixture, precipitated out. The preparation by this procedure was easy and gave generally good yields.

Some characteristics of this procedure have to be pointed out. The polymerization is conducted in a neutral medium as the acids are introduced to the reaction mixture in the form of their salts. The mixture here remains neutral during the polymerization reaction, in contrast to the procedure of Andrews et al.⁵ in which acetic acid is given off. As organotin esters are sensitive to acids and bases, it is clear that neutrality of the reaction mixture is essential for the formation of high polymers.

This polymerization procedure is not greatly influenced by variations in reaction conditions. With a given solvent for the organotin component similar results were obtained at temperatures between about -10 to $50^{\circ}\text{C}.$, and 1.0 – $0.1M$ concentrations of the reactants were found to be suitable. It was found that the melting points of the polymers obtained were influenced by the organic solvent in which the organotin dihalide was dissolved. Thus, on using petroleum ether as the organic phase in the reaction of disodium adipate with di-*n*-butyltin dichloride, the resulting polymer had a melting point of $220^{\circ}\text{C}.$, whereas the polymer obtained on using xylene as a solvent melted at 132 – $133^{\circ}\text{C}.$ The differences in the melting points suggest differences in the molecular weights of the polymers which, in turn, may originate from the varied solubility of the growing polymers in the organic solvents.

In contrast to the organotin esters which are soluble in organic solvents, the organotin polyesters are insoluble in solvents such as alcohols, dimethylformamide, dimethyl sulfoxide, ether, ketones, hydrocarbons, and chlorinated hydrocarbons, even on boiling. Some of the polyesters derived from aliphatic polycarboxylic acids dissolved with decomposition in solvents such as acetic acid, acetic anhydride, *m*-cresol (only on boiling). Poly(di-*n*-butyltin adipate) was found to be soluble in trifluoroethanol, and measurements of viscosity were carried out in this solvent.

The organotin polyesters were obtained from the reaction mixture as white powders which could be hot-pressed to transparent films. Films could also be obtained from mixtures of these polymers with polymers such as polystyrene or polymethylmethacrylate.

The organotin polyesters may have interesting fungicidal properties, since organotin esters are known to possess such properties.^{3,7}

In contrast to the organotin esters, which are readily hydrolyzed by dilute alkali or acids at room temperature, the organotin polyesters are relatively stable towards these reagents; no consumption of dilute aqueous hydrochloric acid or sodium hydroxide was observed even after prolonged treatment, which may be partly due to their water-repelling properties. Glass surfaces coated with any of these polymers were not wetted by water.

The interfacial polyesterification can be used also for the preparation of copolymers by reacting either two acids and an organotin dihalide or a mixture of two organotin dihalides and a dicarboxylic acid.

Preliminary experiments to find out the scope of the interfacial polymerization as applied to the formation of organotin polymers were carried out. Compounds having two acidic groups such as *p*-sulfamoylbenzoic acid, *p*-xylylenedithiol, pyromellitimide, bisphenol-A, 1,5-dihydroxynaphthalene, and *p*-hydroxybenzoic acid were converted to their dipotassium salts with the calculated amount of potassium hydroxide and brought to reaction with a dialkyltin dihalide. In the case of *p*-sulfamoylbenzoic acid and pyromellitimide, solid polymers as yet not fully defined were obtained. *p*-Xylylenedithiol gave a transparent semisolid, soluble in hydrocarbons and chlorinated hydrocarbons but not in alcohol and acetone. Bisphenol A, *p*-hydroxybenzoic acid, and 1,5-dihydroxynaphthalene gave no polymeric products. It is known from the work of Considine⁸ that compounds of the type $R_2Sn(OAr)_2$ are sensitive to moisture and decompose to distannoxanes. This sensitivity may explain why no organotin polyethers were obtained by the above method.

The reaction between dibutyltin dichloride and naphthalene 2,6-disodium sulfonate did not lead to the formation of polymer. The reaction between R_2SnX_2 and the salt of the diacidic compounds constitutes an interchange between the anions X and those of the diacids. Thus, for example, if X is chlorine and the acidic anion is a carboxylate group, the chloride, which is an anion derived from a stronger acid (hydrochloric acid) than the carboxylic acid will exchange the carboxylate group. This means that the X group of the R_2SnX_2 must be an anion derived from a stronger acid than that of the anion which it is going to replace. These considerations suggest that the use of $R_2Sn(ClO_4)_2$ might yield a polymer with the disulfonic acid salt, since perchloric acid is stronger than sulfuric acid.

EXPERIMENTAL

Melting points were determined on a Fisher-John's apparatus. Di-*n*-butyltin dichloride was obtained from Fluka and recrystallized from petroleum ether.

Poly(di-*n*-butyltin Adipate)

Adipic acid (1.46 g., 0.01 mole) suspended in water (5 ml.) was neutralized to phenolphthalein with aqueous 5*N* sodium hydroxide and thus brought into solution. *n*-Dibutyltin dichloride (3.03 g., 0.01 mole) in petroleum ether (b.p. 40–60°C.) (50 ml.) was added with vigorous stirring at 0°C. After 20 min., acetone (100 ml.) was added to coagulate the polymer, and the reaction mixture was filtered. The solid polymer was washed several times with water, ethanol followed by acetone. Poly(di-

butyltin adipate) (3.2 g., 85%), was obtained, m.p. 220°C. It has an intrinsic viscosity of 0.05 dl./g. in trifluoroethanol.

ANAL. Calcd. for $(C_{14}H_{26}O_6Sn)_n$: C, 44.6%; H, 6.9%; Sn, 31.5%. Found: C, 44.5%; H, 6.5%; Sn, 32.4%.

Similar yields were obtained when the adipic acid was neutralized with an equivalent amount of triethylamine, or on using tetralin, decalin, chloroform, carbon tetrachloride and methylene chloride as solvents for the dibutyltin dichloride. In the last three solvents, the polymer separated out as a viscous paste, which coagulated readily on addition of acetone.

Poly(di-*n*-butyltin Fumarate)

Fumaric acid (1.16 g., 0.01 mole) was suspended in water and neutralized with sodium hydroxide as above. *n*-Dibutyltin dichloride (3.03 g., 0.01 mole) in petroleum ether (50 ml.) was added with vigorous stirring at 0°C. After 20 min. the polymer was filtered off, yield 3.15 g. (91%). It did not melt below 300°C.

ANAL. Calcd. for $(C_{12}H_{20}O_6Sn)_n$: C, 41.5%; H, 5.8%; Sn, 34.2%. Found: C, 41.3%; H, 5.8%; Sn, 33.2%.

Poly(di-*n*-butyltin *N*-Carbobenzoxy-L-glutamate)

N-carbobenzoxy-L-glutamic acid (1.2 g.) was dissolved in water (5 ml.) and neutralized with 5*N* sodium hydroxide. *n*-Dibutyltin dichloride (1.7 g.), dissolved in petroleum ether (50 ml.) was added with stirring at 0°C. After 1 hr. acetone was added and the reaction mixture filtered off. Poly(di-*n*-butyltin *N*-carbobenzoxy-L-glutamate (1.8 g., 82% yield), m.p. 163–165°C., was thus obtained.

ANAL. Calcd. for $(C_{21}H_{31}NO_6Sn)_n$: Sn, 23.2%. Found: Sn, 24.3%.

Poly(di-*n*-butyltin Terephthalate)

The polymer was obtained as above in 70% yield from terephthalic acid (1.66 g., 0.01 mole) and di-*n*-butyltin dichloride (3.03 g., 0.01 mole). The polymer did not melt up to 300°C.

ANAL. Calcd. for $(C_{16}H_{22}O_4Sn)_n$: C, 48.4%; H, 5.5%; Sn, 29.8%. Found: C, 48.1%; H, 5.7%; Sn, 30.4%.

Copolymer of Di-*n*-butyltin Adipate and Terephthalate

Adipic acid (0.73 g., 0.005 mole) and terephthalic acid (0.84 g., 0.005 mole) suspended in 10 ml. of water were neutralized with base and reacted with di-*n*-butyltin dichloride as described above. A yield of 52% of the copolymer di-*n*-butyltin adipate-terephthalate was obtained. It did not melt up to 300°C. Its structure was confirmed by infrared spectroscopy.

Poly(di-*n*-butyltin Acetylenedicarboxylate)

Acetylenedicarboxylic acid monopotassium salt (1.52 g., 0.01 mole) in 7 ml. water was neutralized with 20% potassium hydroxide. Di-*n*-butyltin dichloride (3.03 g., 0.01 mole) in petroleum ether (40–60°C.) (50 ml.) was added with stirring at 0°C. After 1 hr. the reaction mixture was filtered and washed with water, alcohol, and acetone. The yield of the polymer which did not melt up to 300°C. was 81%.

ANAL. Calcd. for $(C_{12}H_{18}O_4Sn)_n$: C, 41.7%; H, 5.2%; Sn, 34.4%. Found: C, 40.4%; H, 5.3%; Sn, 33.9%.

Poly(di-*n*-butyltin Succinate)

Succinic acid (1.18 g., 0.01 mole) was suspended in water (50 ml.) and neutralized with 5*N* sodium hydroxide. Di-*n*-butyltin dichloride (3.03 g., 0.01 mole) in petroleum ether (50 ml.) was added with vigorous stirring at room temperature. After 20 min. the reaction mixture was filtered, and the solid polymer was washed with alcohol, water, and acetone. Poly-(di-*n*-butyltin succinate) (2.7 g., 77%) was obtained, m.p. 235°C.

ANAL. Calcd. for $(C_{12}H_{22}O_4Sn)_n$: C, 41.3%; H, 6.3%. Found: C, 40.4%; H, 6.2%.

Preparation of Polyesters starting from Organotin Dicarboxylates

Use was made of the interfacial technique for the preparation of organotin dicarboxylates which were subsequently reacted with the salts of the dicarboxylic acids. The diesters were obtained in the organic phase. They may be used as such for subsequent polymerization or may be isolated.

To prepare the di-*n*-butyltin dibenzoate, benzoic acid (12 g., 0.1 mole) was neutralized to phenolphthalein with potassium hydroxide, and the clear solution was added with stirring to di-*n*-butyltin dichloride (3.03 g., 0.01 mole) in petroleum ether, b.p. 60–80°C. (50 ml.). The reaction mixture was stirred for about 20 min., and the small precipitate was dissolved by addition of ethyl acetate. The dried organic layer was evaporated yielding di-*n*-butyltin dibenzoate (4.5 g., 95%) m.p. 65–67°C. (lit.:⁹ 65–67°C.). Determination of the chloride content of the aqueous layer showed also that the interchange was almost quantitative.

Similarly, di-*n*-butyltin diacetate was prepared from sodium acetate and di-*n*-butyltin dichloride in 88% yield, b.p. 145°C./10 mm. (lit.:³ 145°C./10 mm.). On subsequent reaction of the diacetate with the dipotassium salt of adipic acid, poly(di-*n*-butyltin adipate), m.p. 230°C., was obtained in 65% yield.

Di-*n*-butyltin diformate was similarly prepared in petroleum ether in nearly quantitative yield (as seen from determination of the chloride content of the aqueous layer) and used without isolation to prepare poly(di-*n*-butyltin adipate) in 80% yield, m.p. 230°C.

Di-*n*-butyltin dichloroacetate prepared in 70% yield from sodium di-

chloroacetate and di-*n*-butyltin dichloride, gave on reaction with dipotassium adipate poly(di-*n*-butyltin adipate) in 89% yield, m.p. 215°C.

ANAL. Calcd. for $(C_{14}H_{26}O_4Sn)_n$: C, 44.6%; H, 6.9%. Found: C, 44.5%; H, 6.6%.

Taken in part from the Ph.D. thesis to be submitted by D. W. to the Hebrew University of Jerusalem.

References

1. Creemers, H. M. J. C., J. G. Noltes, and G. J. M. van der Kerk, *Rec. Trav. Chim.*, **83**, 1284 (1964).
2. Neumann, W. P., and K. Konig, *Ann.*, **677**, 1 (1964).
3. Ingham, R. K., S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
4. Cummins, R. A., and P. Dunn, *Austral. J. Chem.*, **17**, 185 (1964).
5. Andrews, T. M., F. A. Bower, B. R. Laliberte, and J. C. Montermoso, *J. Am. Chem. Soc.*, **80**, 4102 (1958).
6. Morgan, P. W. in *Polymerization and Polycondensation Processes*, Adv. Chem. Ser. No. 34, American Chemical Society, Washington, D. C., 1962, pp. 191-199.
7. Graham, D. C., *European Potato J.*, **7** (1), 33 (1964).
8. Considine, W. J., J. J. Ventura, A. J. Gibbons, Jr., and A. Ross, *Can. J. Chem.*, **41**, 1239 (1963).
9. Alleston, D. L., and A. G. Davies, *J. Chem. Soc.*, **1962**, 2050.

Résumé

On a utilisé la technique de polymérisation à l'interface pour préparer des polyesters organostanniques. On a fait réagir des dihalogénures de dialcoylétain, dissous dans un solvant organique non miscible à l'eau, avec des métaux bibasiques ou des sels d'ammonium d'un acide dicarboxylique; on a obtenu des hauts rendements en polyesters après des courts temps de réaction. Les polyesters sont généralement insolubles et ont un point de fusion élevé. On a aussi obtenu des copolymères.

Zusammenfassung

Das Grenzflächenpolymerisationsverfahren wurde zur Darstellung von Organozinnpolyestern verwendet. Dialkylzinnndihalogenide wurden in einem mit Wasser nicht mischbaren organischen Lösungsmittel gelöst und mit dem Dialkalimetall- oder Ammoniumsalz einer Dicarbonsäure zur Reaktion gebracht. Hohe Polyesterausbeuten wurden nach kurzer Reaktionsdauer erhalten. Die Polyester waren im allgemeinen unlöslich und hochschmelzend. Auch Copolymere wurden dargestellt.

Received June 10, 1965