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Synthesis of Organometallic Polymers by the Interfacial Technique. XXVIII. Synthesis of Oligomeric Tin Polyamines and Polyhydrazides

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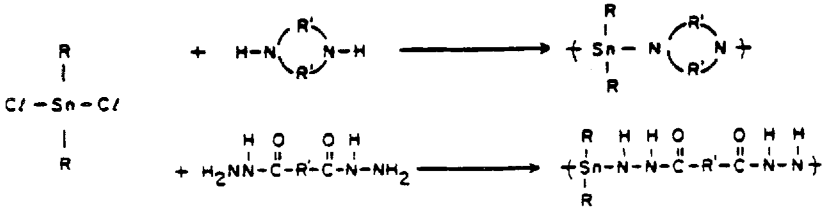
ABSTRACT

Synthesis of oligomeric tin polyamines and polyhydrazides of the below form is reported. Thermal properties were studied. Degradation in the region beyond about 300°C is via an oxidative mode in air. Transitions below this region are identical in air and N_2, and are accompanied by weight loss when R = phenyl but not when R = C_4H_9.



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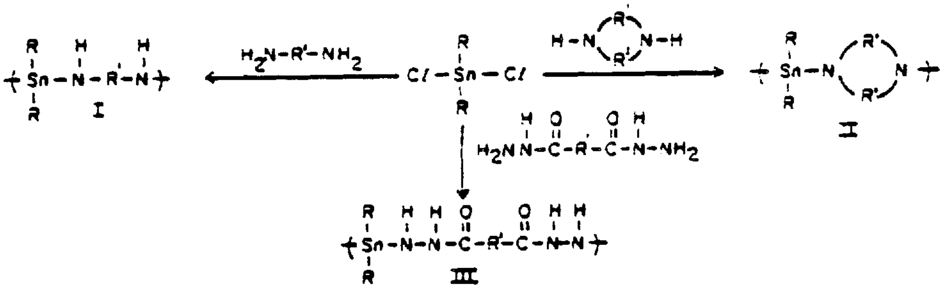
INTRODUCTION

We have been active in the synthesis of metal-containing polymers and oligomers [1-4]. Recently we reported the synthesis of tin polyamines of Form I [5]. We now report the synthesis of oligomeric tin polyamines of Form II and tin polyhydrazides of Form III. This represents the initial synthesis of such materials.



We have been particularly interested in the inclusion of tin into products because of the large number of organotin products which exhibit useful properties such as being antifungal and antibacterial. In fact, analogous tin polyesters are found to exhibit these properties [6-8].

EXPERIMENTAL

Polymerization and isolation procedures are similar to those described in detail elsewhere [5]. In general, stannanes in decane were added to stirred solutions of nitrobenzene containing amine or hydrazide.

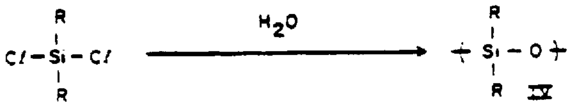
Viscometry was performed in chloroform at 30° C using a Cannon-Ubbelohde viscometer. IR spectra were obtained with Perkin-Elmer 237 and Beckman IR-10 instruments using KBr pellets. Elemental analyses and IR spectra are in agreement with repeating units depicted by Forms II and III. Examples of tin analyses are as follows: For the product from diphenyltin dichloride with 1,3-di-4-piperidylpropane, % calculated = 31, found = 33; dibutyltin dichloride with succinic acid dihydrazide, % calculated = 44, found 43; diphenyltin dichloride with 2,5 dimethylpiperazine, % calculated = 38, found 38.

Thermal gravimetric analysis (TGA) was carried out using a Du Pont 950 TGA. Differential scanning calorimetry (DSC) was conducted by employing a Du Pont 900 thermal unit with a Du Pont DSC cell.

A linear baseline compensator was used with the DSC cell to insure a constant energy baseline. A Mettler H2OT semimicro balance was used for the DSC sample weighings. DSC measurements were obtained on samples contained in an open aluminum cup to allow the free flow (away from the solid) of volitilized gases, thus more closely simulating the conditions under which TGA studies were conducted. A gas flow rate (air and nitrogen) of about 0.3 liter/min was maintained for both the DSC and the TGA studies.

DISCUSSION AND RESULTS

Interfacial systems usually include an aqueous phase. We have found for dihalosilicon dichlorides that condensation with diols and diamines in the presence of water does not lead to the desired inclusion product, i.e., polyether or polyamine, but rather resulted in the synthesis of oligomeric silicon oxides of Form IV. While the order of hydrolysis for organic Group IVA dichlorides is Si > Ge > Sn [9], hydrolysis is important enough in systems containing tin to yield significant amounts of —Sn—OH and +Sn—O+ units rather that the desired inclusion product. Thus nonaqueous interfacial systems were devised [9]. Such a system was utilized in this study. Nitrobenzene was utilized in place of water as the solvent for the piperazine or hydrazide. While a number of "aqueous substitutes" such as acetonitrile and 2,5-hexanedione have been utilized in such nonaqueous interfacial systems, only nitrobenzene serves as a solvent for the dihydrazides utilized in this study. Even so, many dihydrazides were either insoluble or only partially (about 1 to 0.1 wt%) soluble in nitrobenzene. Additionally, most dihydrazides are largely insoluble in water and 1 $\underline{M}$ NaOH aqueous solution. This lack of solubility is a major deterrent to their use in interfacial condensations. It also may account for the sparsity for their use as a polycondensating reactant.



$$Cl-\overset{R}{\underset{R}{Si}}-Cl \xrightarrow{H_2O} \left(\overset{R}{\underset{R}{Si}}-O \right) \quad IV$$

From the results in Table 1, one trend is evident. Tin reactants containing phenyl substituents give higher yields than corresponding tin reactants except those containing n-butyl substituents (for amines). This trend is opposite to that observed in the analogous synthesis of tin polyamines of Form I where there was a noticable trend for tin substituents such that yield was aliphatic > aromatic. That trend was

TABLE 1. Results from the Condensation of Organotin Dichlorides with Dihydrazides and Piperazines[a]

Stannene	Piperazine or hydrazide	Yield (%)	[η] (ml/g)
Dibutyltin dichloride	2,5-Dimethylpiperazine	30	
Dibutyltin dichloride	Piperazine	22	
Dibutyltin dichloride	4-DI-PIP[b]	23	
Dibutyltin dichloride	Glutaric acid dihydrazide	9[c]	
Dibutyltin dichloride	Succinic acid dihydrazide	56[c]	3
Dibutyltin dichloride	Azelaic acid dihydrazide	32[c]	2
Dibutyltin dichloride	2,5-Dimethylpiperazine	85	
Diphenyltin dichloride	Piperazine	88	
Diphenyltin dichloride	4-DI-PIP[b]	89	
Diphenyltin dichloride	2,5-Dimethylpiperazine	96	

[a] Reaction conditions: stannane(0.0025 m) in 50 ml decane added to stirred solutions of piperazine or hydrazide(0.0025 mole) with triethylamine (0.0050 mole) in 50 ml nitrobenzene at 25° C, 23,500 rpm stirring rate for 1 min.

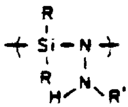
[b] 1,3-Di-4-piperidylpropane received as a gift from Reilly Tar and Chemical Corp., Indianapolis, Indiana.

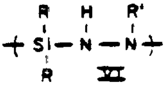
[c] Same as in Footnote a except stannane = 0.0015 mole, hydrazide = 0.0015 mole, and triethylamine = 0.0030 mole.

found to hold over a wide range of substituents whereas the current trend is based only on two sets of substituents. It may be due to a difference in reaction site, reactant solubility and transport values, reaction mechanism, etc. in comparison with the tin polyamine syntheses; however, as noted above, lack of sufficient results must preclude such speculation.

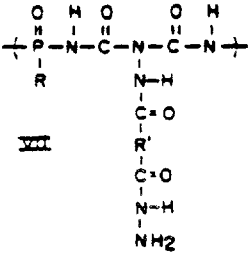
Solubility of analogous Group IV polymers has followed the order Si > Ge > Sn where several tin products have been insoluble in all the solvents tried [9]. Such is unfortunately largely true for the reported products. A wide range of solvents were tested with emphasis given to dipolar aprotic solvents and other polar solvents. If apparent solubilization occurred, further tests were performed to determine whether degradation had occurred. Only two products appeared to dissolve without detectable degradation. Both are oligomeric. Viscometry results appear in Table 1. Past experience in attempting to determine number-average molecular weights of analogous products via freezing point lowering in formic acid have been unreliable; thus an attempt was not made to determine their molecular weights. Tin polyamines of Form I presented degrees of polymerization in the range of 4 to 100 [5].

The structure of the repeating unit for the tin polyamine is straightforward, but this is not so for the tin polyhydrazides. Previous work with silicon hydrazides showed that products of Form V could be formed as well as the expected 1,2 product (Form VI) [10].


V


VI

Additional work on the synthesis of poly(phosphonylhydrazides) eliminated, at least in that instance, products with a structure analogous to Form V, illustrated as Form VII, and 1,2 reactions as illustrated in Form VIII [11]. Thus the presence or absence of units with structures similar to those presented by Forms V, VII, and VIII is unclear. Even so, from electronic and steric reasoning it is probable that the major unit is of Form III. Differentation and/or identification of such similar units is difficult because their close similarity and lack of solubility excludes specific chemical and physical identification procedures and instrumentation such as NMR.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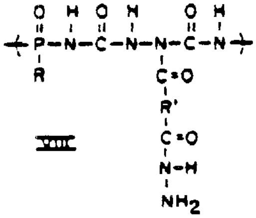
VIII

In an attempt to further characterize the products, thermal stabilities were studied in air and N_2. Representative results appear in Figs. 1 to 3. Several general characteristics were evident. First, DSC thermograms in air and N_2 were identical in all samples up to around 230 to 300°C. Transitions below this range were all endothermic. Transitions for products from R_2SnCl_2 (where R = phenyl) exhibit weight losses within this region, obviously corresponding to chemical

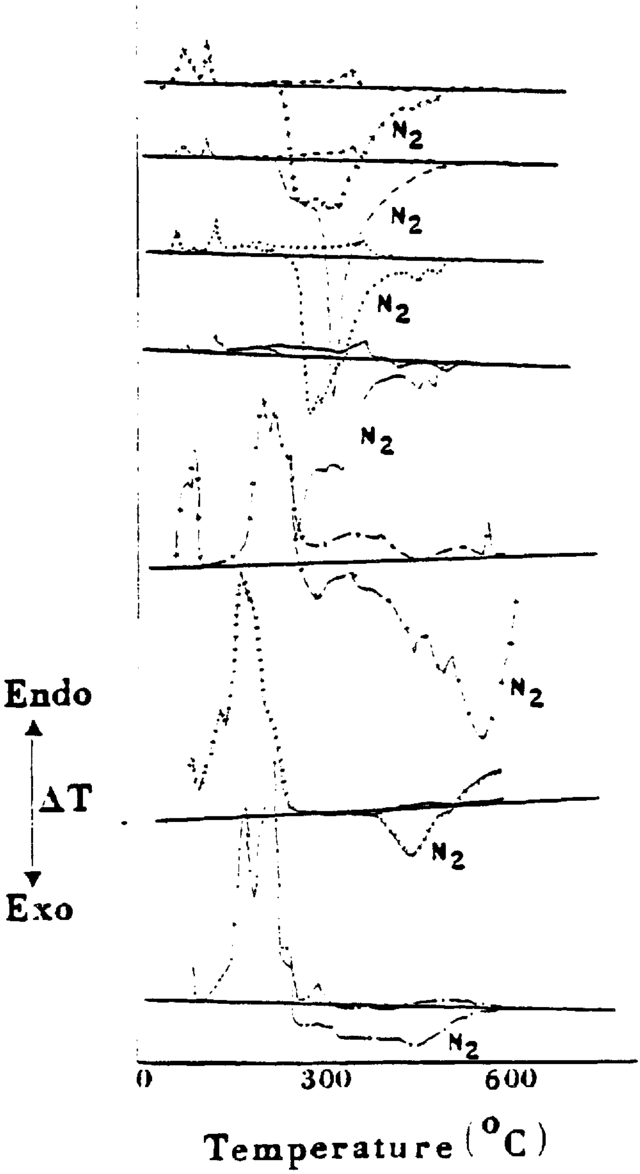

FIG. 1. DSC thermograms of the condensation products of dibutyltin dichloride with azelaic acid dihydrazide (+ +), with succinic acid dihydrazide (- -), with 2,5-dimethyl piperazine (· ·), with piperazine (—), and the condensation products of diphenyltin dichloride with 4-di-pip (- +), with 2,5-dimethyl piperazine (+-+), with piperazine

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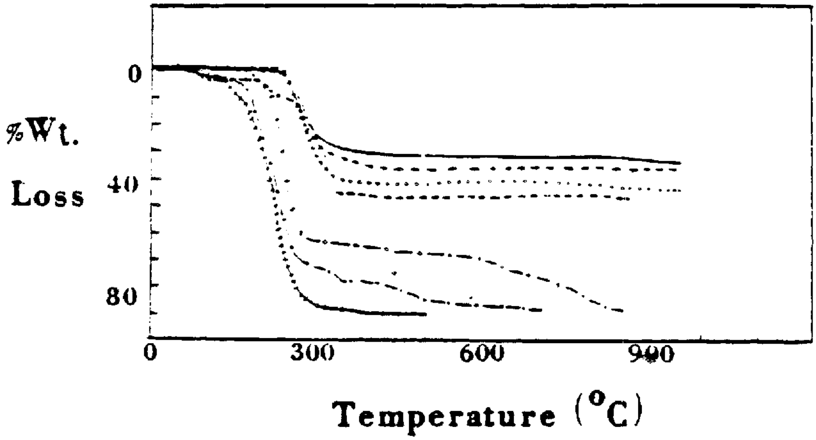

FIG. 2. TGA thermograms in air of products from the condensation of organotin dichlorides with piperazines and dihydrazides at a heating rate of 30°C/min and a gas flow rate of 0.3 liter/min. Designations are the same as in Fig. 1.

degradations involving weight losses. There are no accompanying weight losses for these transitions where R = C_4H_9. IR spectra of products where no weight loss occurs are largely identical with those taken of the product before heating but some do show a diminishing of bands characteristic of aliphatic C—H groups and the presence of a new band or bands around 800 cm^{-1}. Additionally, the product from dibutyltin dichloride and 1,3-di-4'-piperidylpropane was cycled several times through the temperature range of 30 to 200°C. The initial DSC was unlike that obtained after the product was cooled and reheated. DSC thermograms from subsequent heatings of the product were identical

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(Figure 1 continued)

(-·) on samples weighing 0.00100 g at a heating rate of 30°C/min. The Y-axis sensitivity for the products from dibutyltin dichloride was 0.5°C/in. (0.02 mV/in.) and for the products from diphenyltin dichloride 0.1°C/in. (0.004 mV/in.) with a gas flow rate of 0.3 liter/min. Each Y-axis unit represents 1 in. The straight line with each pair represents ΔT = 0. Lines appearing below this line indicate exothermicity whereas lines above represent endothermicity. Thermograms below the 230 to 300°C region are identical in air and N_2, thus only one line appears below this region. Above this region the thermograms differ greatly, with the exothermic portion occurring in N_2 marked accordingly.

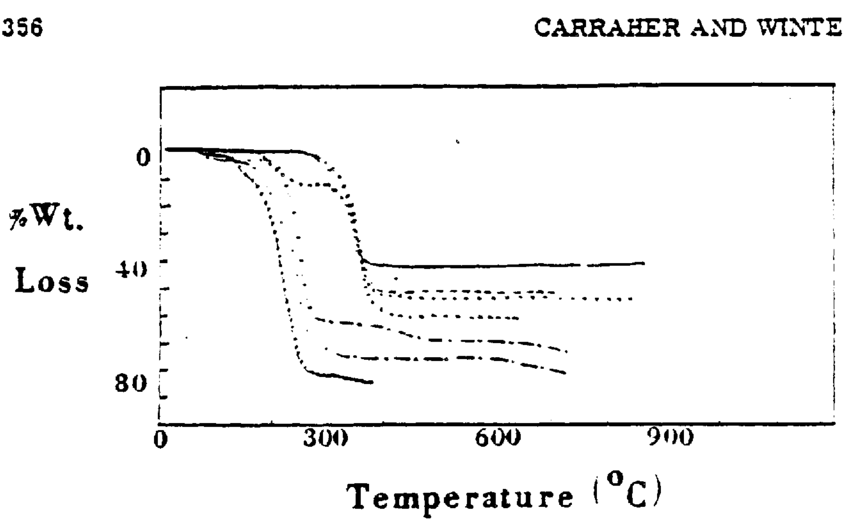

FIG. 3. TGA thermograms in N_2 of products from the condensation of organotin dichlorides with piperazines and dihydrazides. Designations are the same as in Fig. 1. The heating rate was 30°C/min with a gas flow rate of 0.3 liter/min.

with that obtained after the second heating. Thus a chemical reaction is occurring but without the accompanying weight loss.

Second, DSC thermograms in air and N_2 differ greatly at temperatures above 300°C. Transitions in N_2 were endothermic while transitions in air were exothermic and more energenic. Further, weight losses accompany the transitions occurring in both N_2 and air. Results in air are indicative of degradations occurring via oxidative modes.

Third, stability plateaus generally occur in the TGA thermograms. This is usual for organometallic polymers containing metals in their backbones and is probably due to a difference in the bond energies present in the oligomer.

Fourth, several of the products exhibit medium weight retention. The product from dibutyltin dichloride and azelaic acid dihydrazide shows a 65% weight retention at 1000°C. (The better weight retention in air than in N_2 for several products is not normal. The normal behavior has been N_2 > air for weight retention for organometallics presumably because of the availability on the metals of "low-lying" orbitals which are susceptible to oxidation.) The product from dibutyltin dichloride and piperazine also exhibited about a 65% weight retention in air, and a 60% weight retention in N_2, both to 950°C.

Lastly, products where R = C_4H_9 exhibit better overall weight retention when compared to products where R = phenyl.

Through visual observations the products appeared to remain solid throughout the tested range. Resulting materials, after being cooled, were generally colored white to light tan, and were powdery.

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