

SYNTHESIS OF ORGANOTIN POLYMERS BY POLY-ADDITION

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The results of a synthetic program directed towards the preparation of IVth main group organometallic polymers are presented.

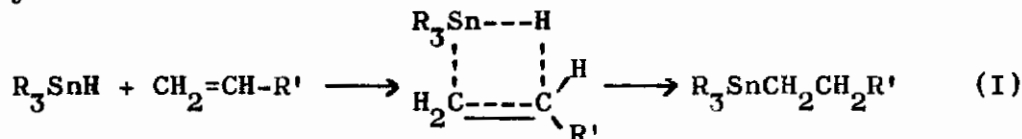
The main body of the report is concerned with the synthesis of linear polymers having a carbon chain regularly interrupted by tin (and in some cases other IVth group) atoms. Such polymers have been obtained by means of true poly-addition reactions (hydrogen transfer polymerization) involving an organotin dihydride and either a dienic or a diynic or a monocyclic compound.

The synthesis of IVth group organometal-substituted polystyrenes-carbon chain polymers containing the organometallic moiety as a substituent group-as well as of a series of poly-p-phenylenesilanes-polymers consisting of chains of p-phenylene groups connected by dialkyl(aryl) silane groups- are dealt with briefly.

I. ORGANOTIN POLY-ADDITION POLYMERS

In recent years at our Institute much attention had been paid to the formation of tin-carbon bonds by the reaction of organotin hydrides with carbon-carbon unsaturated compounds<sup>1-4</sup>. When our organometallic polymer program was initiated it was decided to apply this reaction principle to the synthesis of organotin polymers. Aspects of the chemistry of organotin hydrides related to the possibility of preparing polymers<sup>5</sup> have been discussed at the 1959 Polymer Branch Contractors' Conference<sup>6</sup>. Some points will be recalled briefly as this will lead to a better appreciation of the scope of the polymer-forming reaction.

Adducts are formed upon reaction of triorganotin monohydrides with a variety of monosubstituted terminal olefins<sup>2,3</sup>:

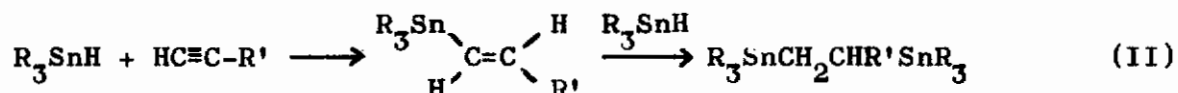


Reactions involving triphenyltin hydride proceed smoothly at moderate temperatures (70-100°). Both the reaction time (usually a few hours, sometimes as short as few minutes) and the yield (generally high, in some cases quantitative) depend on the substituent R'. Trialkyltin hydrides react slower and only if the olefinic bond is activated sufficiently by R' (e.g. when R' represents an aryl group).

Where investigated (e.g. n-octene, acrylonitrile, styrene) the organotin group was found to have added to the terminal olefinic carbon atom. Whereas polar effects influence the rate of the reaction, steric factors mainly determine its course. Terminal addition seems to be the rule.

With the exception of certain reactions of alkyltin hydrides for which very recently peroxide catalysis has been applied<sup>6</sup>, these reactions proceed in the absence of any added catalyst. Similar reactions of carbon or silicon hydrides require among others peroxide catalysts or U.V. light or high temperatures. These circumstances promote homopolymerization of reactive olefins. Owing to the much greater reactivity of organotin hydrides reaction conditions minimizing this unwanted reaction may be selected. It can be eliminated completely by using an inhibitor like hydroquinone. This is clearly of importance for the realization of the reaction on a polymeric level.

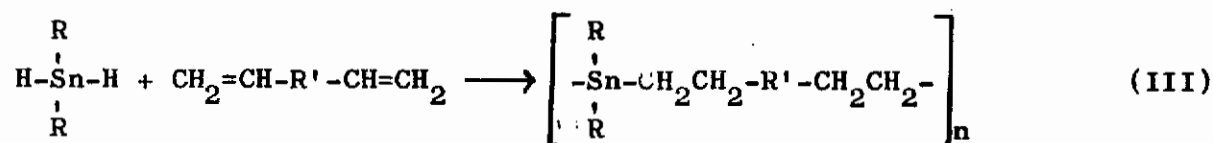
Similar reactions have<sup>3</sup> been realized using acetylenic derivatives as the unsaturated partner<sup>3</sup>:



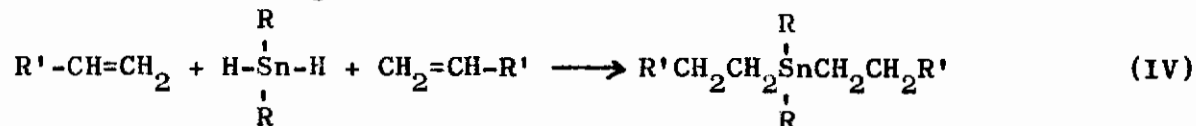
However, the reactivity of organotin hydrides towards carbon-carbon triple bonds is much higher than towards olefinic double bonds. Mostly, these reactions proceed exothermally in the absence of any added catalyst. Consequently, when applying one mole of a monohydride per mole of a monoacetylenic compound, only the olefinic adduct is being formed. Similarly, when applying two moles of a monohydride, two separate reaction steps can be distinguished, the second one requiring more severe conditions.

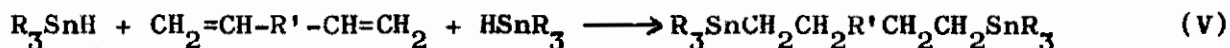
Considering the foregoing, the possibility of applying this reaction principle to the synthesis of polymers is evident.

A. Upon reaction of an organotin dihydride with an appropriate diolefine (preferably an  $\alpha, \omega$ -diene) linear polymers are being<sup>7</sup> formed under incorporation of organotin groups in the main chain:



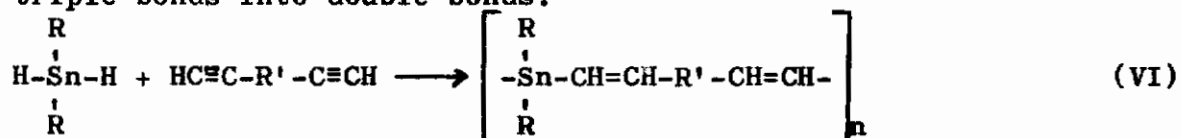
Optimal conditions for polymer-formation have been determined for each combination of R and R' by studying both the model reactions, viz. between dihydride and mono-olefine and between monohydride and diolefine (see e.g. ref.<sup>7</sup>):



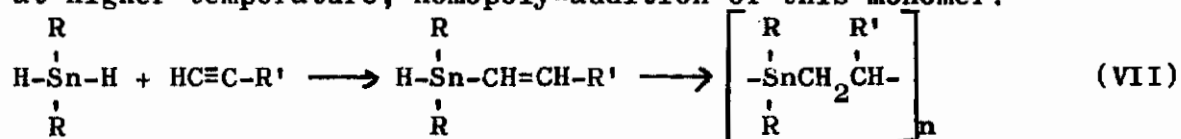


B. Starting from acetylenic compounds as the unsaturated reaction partner, and making use of the earlier mentioned marked difference in reactivity of the organotin hydride towards double and triple bonds, two different routes leading to polymers can be followed<sup>8</sup>:

1. Reaction of an  $\alpha,\omega$ -diyne with an organotin dihydride in a 1:1 ratio under very mild conditions will result in the formation of a linear polymer. In this case the reaction ends after conversion of the triple bonds into double bonds:



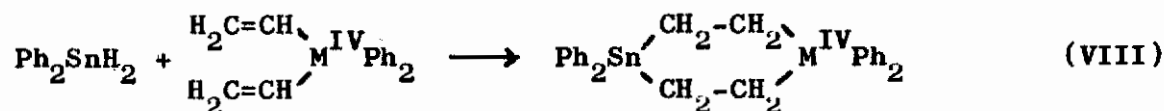
2. Reaction of a monoacetylenic compound with an organotin dihydride again in an exactly 1:1 ratio will proceed in two steps, viz. formation of an olefinic organotin monohydride and subsequently, at higher temperature, homopoly-addition of this monomer:



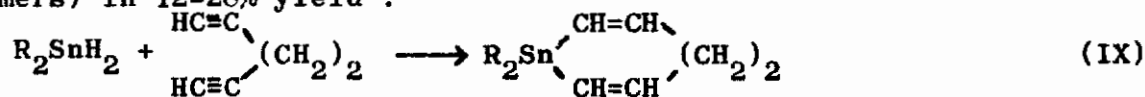
Two molecules of the 1:1 addition intermediate can form a six-membered cyclic dimer with the two tin atoms in 1,4-position. As appears from an absorption peak at  $988\text{ cm}^{-1}$ , originating from the C-H bending vibration of trans-disubstituted ethylene groups, the olefinic intermediate has the trans structure, its formation presumably being promoted by steric factors. The trans structure, in its turn, favours the formation of the distannacyclohexane system. This reaction course has been observed upon reaction of diphenyltin dihydride with phenylacetylene.

Dienic or diyne compounds having the two unsaturated groups in a sterically favourable position have also been found to yield cyclic oligomers in addition to linear polymers:

Reaction of diphenyltin dihydride with divinyl organometallic derivatives yields the bimetallic cyclohexane analogues (cyclic monomers) as the main product<sup>9</sup>:

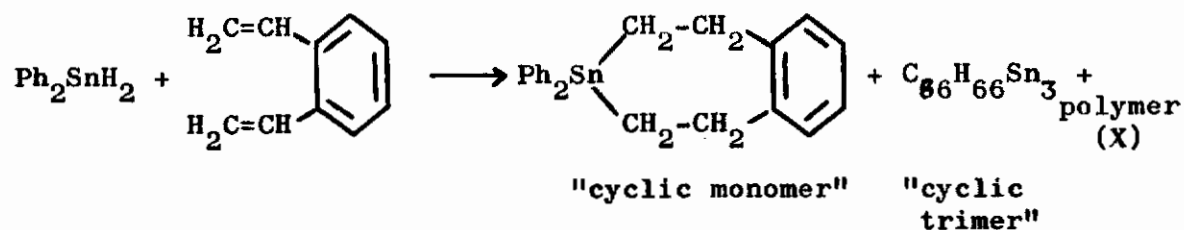


Reaction of organotin dihydrides with hexadiyne-1,5 in addition to the expected polymers yields 1-stannacycloheptadiene-2,5 derivatives (cyclic monomers) in 12-28% yield<sup>8</sup>:



(R = Ph, Me, Et, Pr, Bu)

Reaction of diphenyltin dihydride with *o*-divinyl benzene in addition to polymer (70%) affords the cyclic monomer (M.p. 98-100°C; 16% yield) and the 21-membered cyclic trimer (M.p. 277-280°C; 14% yield), both having been characterized by analysis, infrared spectrum and molecular weight:



The basic reaction underlying the polymer-forming interactions just discussed is an example of a true poly-addition reaction (hydrogen transfer polymerization). The close resemblance to the formation of polyurethane from diols and diisocyanates is evident. In our case an active hydrogen atom bound to tin reacts with a carbon-carbon double or triple bond; in the other process an active hydrogen of a hydroxyl group reacts with a carbon-nitrogen double bond of an isocyanate.

The polymer-forming reactions were carried out under nitrogen in order to eliminate oxidative degradation of the organotin hydrides. Low reaction temperatures (60-110°C) were employed in order to prevent disproportionation of the dihydrides leading to mono- and trifunctional hydrides which would act as chain-stopping and cross-linking agents respectively. In reactions involving acetylenic reactants a solvent was applied in the first stage in order to warrant its smooth course. Ultimately, the resulting polymeric products were heated *in vacuo*.

The progress of the reaction can be determined very easily by I.R. absorption measurements. The disappearance of the characteristic Sn-H stretching vibration in the 1800-1840 cm<sup>-1</sup> region (5.5 μ)<sup>10</sup>, together, of course, with the disappearance of vibrations connected with the presence of olefinic or acetylenic unsaturation, is the most clear-cut indication that the reaction has gone to completion. Absence of these vibrations in the I.R. spectra of low molecular weight products reveals their cyclic nature. The phenyl-substituted compounds and polymers, containing both germanium and tin, or both lead and tin, display in their infrared spectra distinctive perturbed phenyl vibrational absorptions<sup>11</sup>, the relative intensities of which are indicative of the ratio in which these elements are present<sup>7</sup>.

The polymers obtained have been characterized by analysis, infrared spectroscopy, solubility, polymer melt temperature and in some cases by weight-average molecular weight (ultracentrifuge measurements<sup>12</sup>) or thermogravimetric analysis.

A survey of the combinations of reaction partners investigated is presented below.

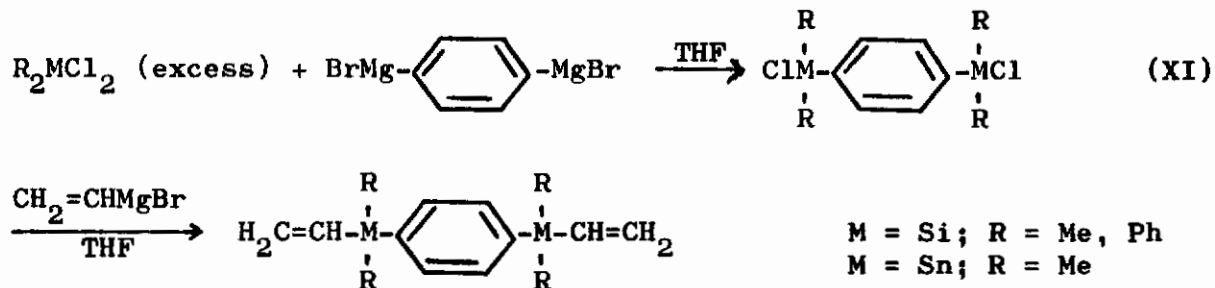
#### A. Polymers from reactions of organotin dihydrides and dienic compounds

A number of reactive aliphatic dienic compounds (glycol diacrylate, glycol dimethacrylate, methacrylic anhydride and allyl methacrylate)

yielded polymeric products ranging from hard, brittle or tough solids to viscous oils. These products which are likely to contain cyclic oligomers have not been characterized in any detail. Some were slightly cross-linked as a result of the occurrence of vinyl-type polymerization.

Reactions with cyclopentadiene afforded the 1:1 adducts only, the reactivity of its double bond apparently being insufficient for poly-addition to occur.

Reactions with divinyl organometallics resulted mainly in cyclization reactions<sup>9</sup>. With this in mind, we synthesized some divinyl derivatives of a novel type:



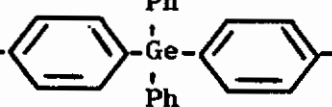
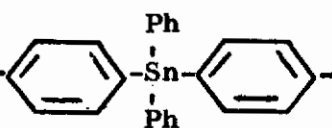
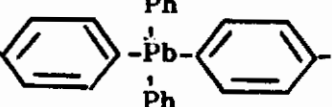


These, owing to the presence of the 1,4-phenylene group, were expected to yield linear polymers upon reaction with organotin dihydrides. However, reaction of these compounds with triphenyltin hydride, although affording the expected products, was attended by some decomposition. Reaction with diphenyltin dihydride did not produce products with any appreciable molecular weight, considerable evolution of gas and formation of metallic tin being observed. Apparently the p-phenylene divinyl derivatives are susceptible to the reducing action of the organotin hydrides.

In Table I poly-addition polymers are summarized which have been obtained from 1,4-divinylbenzene, 3,9-divinylspirobi (meta-dioxane) as well as from di-p-styrenyl-substituted derivatives of germanium, tin and lead<sup>7</sup>. The position of the vinyl groups in these dienes sterically disfavors ring-formation.

TABLE I

Polymers from  $R_2SnH_2$  and  $CH_2=CHR'CH=CH_2$  (Equation III)

R	R'	Appearance of polymer	T <sub>melt</sub> (°C)	Solubility	$\bar{M}_w$
Ph		glasslike	75	$C_6H_6, CHCl_3$	33,000 <sup>a</sup>
Pr	id.	rubbery, tacky		id.	
Ph		glasslike	90	id.	19,000
Ph		hard, brittle	110	id.	27,000
Pr	id.	tough solid	240	$C_6H_6$ (slightly)	
Ph, Pr <sup>b</sup>	id.	hard $\xrightarrow{120^\circ}$ rubbery		id.	
Ph		hard, brittle	100	$C_6H_6, CHCl_3$	48,000
Pr	id.	tough $\xrightarrow{130^\circ}$ rubbery		swells in $C_6H_6$	
Bu	id.	hard, tough		id.	
Ph, Pr <sup>b</sup>	id.	glasslike	130	$C_6H_6$	
Ph		glasslike	70	$C_6H_6, CHCl_3$	14,000
Pr	id.	tough $\xrightarrow{90^\circ}$ rubbery		$C_6H_6$ (slightly)	

<sup>a</sup> Osmometric measurement ( $\bar{M}_n$ )

<sup>b</sup> Equimolar mixture of  $Ph_2SnH_2$  and  $Pr_2SnH_2$

These polymers after reprecipitation from benzene showed the correct analysis indicating that these were indeed true 1:1 poly-addition products and that vinyl-type polymerization was negligible under the reaction conditions employed.

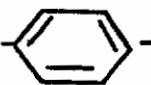
In general polymer melt temperatures are quite low. Interchain forces will be rather weak, because of lack of hydrogen bonding. Moreover, the relatively large metal atoms and their bulky substituents will hamper Van der Waals interaction and crystallization.

**B. Polymers from organotin dihydrides and acetylenic compounds**

**1.** Organotin dihydrides have been reacted with hexadiyne-1,5, nonadiyne-1,8 and 1,4-diethynylbenzene. The resulting polymers, ranging from rubberlike, elastic solids to viscous oils, are summarized in Table II.

TABLE II

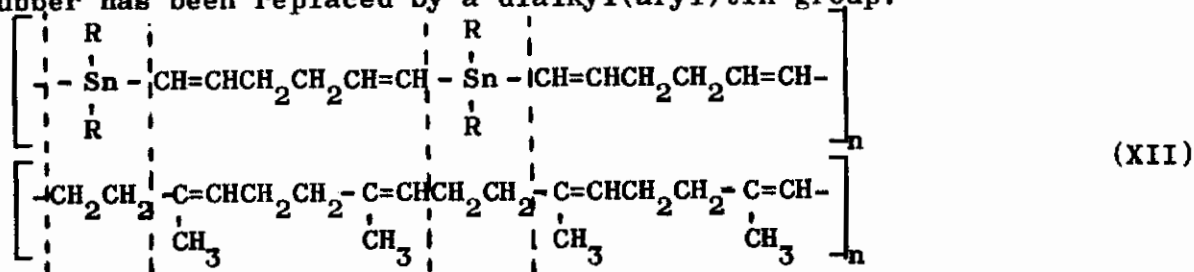
Polymers from  $R_2SnH_2$  and  $HC=CR'C\equiv CH$  (Equation VI)

R	R'	Appearance of polymer <sup>a</sup>	Soluble in <sup>a</sup>	$\bar{M}_w$	Cyclic monomer formed
Ph	$-(CH_2)_2-$	rubberlike, completely resilient	$C_6H_6$ (partly)	75,000	yes
Me	id.	rubbery solid	crosslinked swells in $C_6H_6$	-	id.
Et	id.	id.	id.	-	id.
Pr	id.	soft, slightly elastic, viscous flow	$C_6H_6$	50,000	id.
Bu	id.	id.	id.	50,000	id.
Ph	$-(CH_2)_5-$	soft, tacky viscous flow	$C_6H_6, CHCl_3$	100,000	no
Bu	id.	viscous oil	id.	45,000	id.
Ph		solid $\xrightarrow{160^\circ}$ rubbery	$C_6H_6$	65,000	id.

<sup>a</sup>After heating in vacuo

No well-defined polymers could be isolated from the reaction of organotin dihydrides and certain pentadiyne-1,4 derivatives (R' = -CHOH- and -CPhOH-).

Polymers obtained from hexadiyne-1,5 were freed from the cyclic monomer by heating in high vacuum (150-250° at 10<sup>-3</sup> mm.Hg). These polymers show some structural resemblance to natural rubber. Apart from the presence of methyl groups, every second -CH<sub>2</sub>CH<sub>2</sub>- group in natural rubber has been replaced by a dialkyl(aryl)tin group:



Replacement of the ethylene group in this type of organotin polymer by the pentamethylene group results in the loss of the rubberlike properties. The polymer derived from 1,4-diethynylbenzene, having much greater chain rigidity, is solid.

As might be expected, the molecular weights of the poly-addition polymers obtained from diynes are appreciably higher than those of the polymers obtained from dienes.

2. Organotin dihydrides (R = Pr, Bu, Ph) have been reacted with phenylacetylene (R' = Ph) (Equation VII)<sup>8</sup>. Benzene-soluble polymeric products with the expected composition were formed, these products ranging from very viscous oils (R = Pr, Bu) to a hard, brittle solid with m.p. ca. 80° (R = Ph). In the latter case isolation of the cyclic dimer in crystalline form was successfully carried out<sup>9</sup>. No attempts have been made to separate cyclic oligomers from the two liquid polymers which were found to have a rather low average molecular weight (R = Pr,  $\bar{M}_w = 3,400$ , n = 11).

The results of thermogravimetric tests on some poly-addition polymers (Chevenard thermobalance, N<sub>2</sub> atmosphere, heating rate 2.5° per min.) are presented in Table III. Temperature at which 5 and 50% weight-loss has occurred (T<sub>5%</sub> and T<sub>50%</sub>), residual weight at 900° (RW) and the percentage of inorganic elements in the original polymer are given.



TABLE III

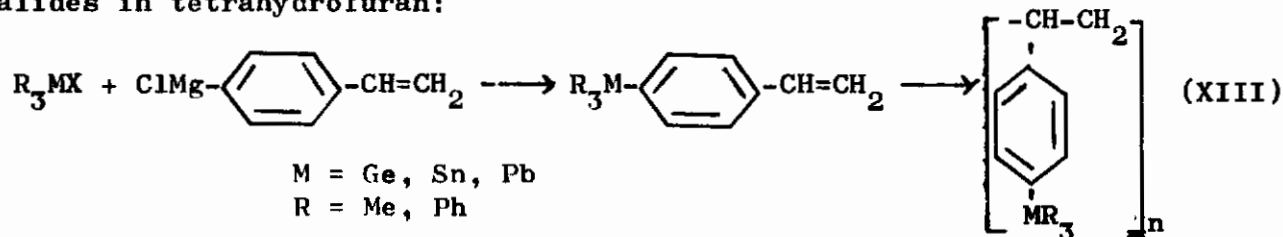
Thermogravimetric analysis of some IVth group metal polymers

Polymer	T <sub>5%</sub>	T <sub>50%</sub>	RW %	% inorg. elements
$\left[ \begin{array}{c} \text{Ph} \\   \\ -\text{SnCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2- \\   \\ \text{Ph} \end{array} \right]_n$	300	385	28	29.3
$\left[ \begin{array}{c} \text{Ph} \\   \\ -\text{SnCH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{Ge}(\text{Ph})_2-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2- \\   \\ \text{Ph} \end{array} \right]_n$	325	460	30	27.1
$\left[ \begin{array}{c} \text{Ph} \\   \\ -\text{SnCH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}- \\   \\ \text{Ph} \end{array} \right]_n$	280	355	27	33.6

II. IVth GROUP ORGANOMETALLIC DERIVATIVES OF STYRENE AND  $\alpha$ -METHYLSTYRENE

Current interest in organometallic monomers suitable for vinyl-type polymerization led us to synthesize a number of IVth group organometallic derivatives of styrene and  $\alpha$ -methylstyrene and to study their polymerization<sup>13,14</sup>.

The triphenylmono-, diphenyldi- and the trimethylmono-p-styrenyl derivatives of germanium, tin, and lead were obtained by interaction of p-vinylphenylmagnesium chloride<sup>15</sup> with the appropriate organometallic halides in tetrahydrofuran:



Whereas triphenyl-p-styrenylsilane, due to steric factors cannot be obtained in this way, the trimethylsilyl derivative was readily formed.

Similar reactions involving p-isopropenylmagnesiumchloride afforded organometal-substituted  $\alpha$ -methyl-styrenes<sup>14</sup>.

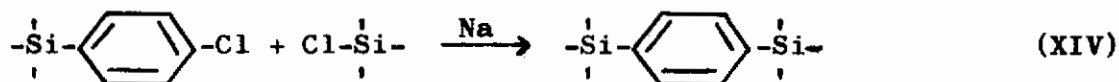
The styrene monomers are readily polymerized, thermally or using peroxide catalysis, to afford solid, transparent products with an appreciable metal content (e.g. poly-trimethyl-p-styrenyllead contains 58.2% by weight of lead).

A rather interesting dependency was found to exist between the nature of the metal atom and the polymerization velocity. A quantitative study (including the carbon analogue p.tert.butylstyrene) revealed the sequence Pb > Si > C > Ge > Sn<sup>14</sup>. Homolytic cleavage of lead-carbon bonds during polymerization, providing a source of extra chain-initiating radicals and resulting in a crosslinked product, is probably responsible for the greater rate of polymerization of the styrenyllead monomer. The sequence Si > C > Ge > Sn is best related to a decreasing electron-attracting effect of the organometallic substituents. It might be that for silicon electron-attraction as a result of  $d_{\pi}-p_{\pi}$  interaction with the styrenyl group surpasses the effect of electronegativity which decreases in the order C, Si, Ge, Sn. Korshak et al.<sup>16</sup> have found a similar sequence Si > C > Ge > Sn for the polymerization of vinyl-substituted organometallics. The thermal stability of these carbon chain polymers is determined by the temperature at which the depolymerization reaction starts, e.g. for poly-p-trimethylgermylstyrene (when heated at a rate of 2.5° per min.) at 325°, zero residual weight being attained at 440°.

### III. POLY-p-PHENYLENESILANES

Silicon-aryl bonds are quite stable towards heat and oxidation. Polymers consisting of chains of p-phenylene groups, connected by organosilyl groups might be expected to have good thermal stability. Moreover, these polymers because of their inherent chain rigidity may be expected to have better crystalline properties than the poly-addition polymers mentioned in Section I. The latter have an amorphous structure as appeared from X-ray data and this was reflected in their low melting temperatures.

The feasibility of obtaining poly-p-phenylene silanes by Wurtz-type condensation reactions involving appropriate combinations of p-chlorophenyl- and chlorosilanes has been studied:



Model reactions involving combinations of monofunctional with mono- or difunctional reactants were carried out in order to find suitable reaction conditions. Using refluxing toluene as the solvent and sodium sand as the condensing agent, products with the expected composition were isolated in satisfactory yields. Some oligomeric compounds obtained analytically pure are summarized in Table IV.

TABLE IV  
Synthesis of some oligomeric p-phenylenesilanes

Reaction	Product	M. p.
$\text{Me}_3\text{SiCl} + \text{Me}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Me}_3\text{SiC}_6\text{H}_4\text{SiMe}_3$	94-96
$\text{Me}_2\text{SiCl}_2 + 2 \text{Me}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Me}_3\text{Si}(\text{C}_6\text{H}_4\text{SiMe}_2)_2\text{Me}$	78-81
$\text{ClMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{Cl} + 2 \text{Me}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Me}_3\text{Si}(\text{C}_6\text{H}_4\text{SiMe}_2)_3\text{Me}$	131-133
$\text{Me}_2\text{SiCl}_2 + 2 \text{Me}_3\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Cl}^a$	$\text{Me}_3\text{Si}(\text{C}_6\text{H}_4\text{SiMe}_2)_4\text{Me}$	170-173
$\text{ClMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{Cl} + 2 \text{Me}_3\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Cl}^a$	$\text{Me}_3\text{Si}(\text{C}_6\text{H}_4\text{SiMe}_2)_5\text{Me}$	187-191
$\text{Ph}_3\text{SiCl} + \text{Ph}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Ph}_3\text{SiC}_6\text{H}_4\text{SiPh}_3$	337-341
$\text{Ph}_2\text{SiCl}_2 + 2 \text{Ph}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Ph}_3\text{Si}(\text{C}_6\text{H}_4\text{SiPh}_2)_2\text{Ph}$	365-368
$\text{ClMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{Cl} + 2 \text{Ph}_3\text{SiC}_6\text{H}_4\text{Cl}$	$\text{Ph}_3\text{Si}(\text{C}_6\text{H}_4\text{SiMe}_2)_2\text{C}_6\text{H}_4\text{SiPh}_3$	220-222

<sup>a</sup> Obtained via:  $\text{Me}_3\text{SiC}_6\text{H}_4\text{MgCl} + \text{ClSiMe}_2\text{C}_6\text{H}_4\text{Cl}$

Similar reactions involving difunctional reactants afforded polymeric products identified by analysis and infrared spectrum (comparison with model compounds) as poly-p-phenylenesilanes. Solubility of these polymers in aromatic solvents allowed removal of the lowest molecular weight products by fractional precipitation. In Table V melting point (temperature at which softening starts and at which a clear melt is obtained), number average molecular weight (ebullioscopic in benzene) and the results of thermogravimetric analyses for some of the poly-p-phenylene silanes isolated are presented.

TABLE V  
Synthesis of some poly-p.phenylene silanes

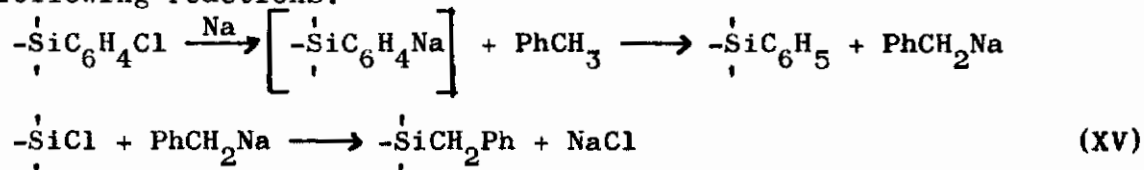
Polymer	M.p. (°C)	$\bar{M}_n$	Weight loss (%) at (°C)				
			400	450	500	600	900
$\text{Me} \left[ \begin{array}{c} \text{Me} \\   \\ -\text{SiC}_6\text{H}_4- \\   \\ \text{Me} \end{array} \right]_5 \text{SiMe}_3$	187-191	759 <sup>a</sup>	15	55	80	85	86
$\left[ \begin{array}{c} \text{Me} \\   \\ -\text{SiC}_6\text{H}_4- \\   \\ \text{Me} \end{array} \right]_n$	200-225	3800	-	2	22	56	58
$\left[ \begin{array}{cc} \text{Me} & \text{Ph} \\   &   \\ -\text{SiC}_6\text{H}_4- & -\text{SiC}_6\text{H}_4- \\   &   \\ \text{Me} & \text{Ph} \end{array} \right]_n$	155-170	2400	2	9	16	49	53
$\left[ \begin{array}{ccc} \text{Me} & \text{Me} & \text{Ph} \\   &   &   \\ -\text{SiC}_6\text{H}_4- & -\text{SiC}_6\text{H}_4- & -\text{SiC}_6\text{H}_4- \\   &   &   \\ \text{Me} & \text{Me} & \text{Ph} \end{array} \right]_n$	190-210	2900	1	7	30	47	47
$\left[ \begin{array}{ccc} \text{Me} & \text{Ph} & \text{Ph} \\   &   &   \\ -\text{SiC}_6\text{H}_4- & -\text{SiC}_6\text{H}_4- & -\text{SiC}_6\text{H}_4- \\   &   &   \\ \text{Me} & \text{Ph} & \text{Ph} \end{array} \right]_n$	215-245	2600	-	-	1	44	46
$\left[ \begin{array}{c} \text{Ph} \\   \\ -\text{SiC}_6\text{H}_4- \\   \\ \text{Ph} \end{array} \right]_n^b$	>360	-	2	5	20	30	35
id. <sup>c</sup>	235-260	2100	5	7	30	58	59

<sup>a</sup> Theoretical value; <sup>b</sup> benzene-insoluble fraction;

<sup>c</sup> benzene-soluble fraction

Molecular weight determination by means of end-group analysis (determination of residual chlorine by Parr bomb fusion followed by electrometric titration) gave values five to ten times those found by the ebullioscopic method, the chlorine contents being unexpectedly low. The poly-p-phenylene silanes prepared so far contain on the average only 10-30 p-phenylene groups per molecule. The attainment of high molecular weights is hampered by the limited solubility of this type of polymer in the common organic solvents causing its precipitation from the reaction medium. The choice of toluene - one of the best solvents for this type of

polymer- as the reaction solvent has the disadvantage that it cannot be considered inert with respect to the polymer-forming reactions. It is known that toluene undergoes metallation by reactive organosodium compounds with the formation of benzylna. When it is assumed that the polycondensation involves the intermediate formation of organosodium derivatives, reaction with the solvent, i.e. toluene, instead of with a chlorosilyl group will result in chain termination by each of the two following reactions:



Thus, instead of p-chlorophenyl and chlorosilyl end-groups the polymer would contain phenyl- and benzyl-silicon end-groups. This mechanism of termination which would seem to prevent the attainment of appreciable molecular weights finds support in the actually observed low residual chlorine content of the fractions isolated.

The high thermal stability of fully alkylated or arylated silanes is reflected in that of the polymeric silanes. All polymer samples investigated remain perfectly stable during the initial heating period, then undergo rapid degradation over a narrow temperature range to give a stabilized residue of high thermal stability still containing an appreciable percentage of residual carbon.

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REFERENCES

- 1 G.J.M.van der Kerk, J.G.A.Luijten and J.G.Noltes, Chemistry and Industry 1956 352
- 2 G.J.M.van der Kerk, J.G.A.Luijten and J.G.Noltes, J.Appl.Chem. 7 356 (1957)
- 3 G.J.M.van der Kerk and J.G.Noltes, J.Appl.Chem. 9 106 (1959)
- 4 J.G.Noltes and G.J.M.van der Kerk, "Functionally substituted organotin compounds", Tin Research Institute, Greenford, England, 1958
- 5 J.G.Noltes, paper presented at WADC Materials Laboratory Conference on High Temperature Polymer and Fluid Research, Dayton, Ohio, May 26-28, 1959
- 6 W.P.Neumann, Angew.Chem. 73 768 (1961)
- 7 J.G.Noltes and G.J.M.van der Kerk, Rec.trav.chim. 80 623 (1961);
- 8 See also: N.A.Androva et al., Vysokomol.Soed. 3 1041 (1961)
- 9 J.G.Noltes and G.J.M.van der Kerk, Rec.trav.chim., in the press

# Contrails

- 9 M.C.Henry and J.G.Noltes, J.Am.Chem.Soc. 82 561 (1960)
- 10 R.Mathis-Noël et al., Compt.rend. 243 251 (1956). See also: M.C.Henry and J.G.Noltes, J.Am.Chem.Soc. 82 555 (1960)
- 11 J.G.Noltes, M.C.Henry and M.J.Janssen, Chemistry and Industry 1959, 298
- 12 W.J.Archibald, J.Phys.Chem. 51 1204 (1947)
- 13 J.G.Noltes, H.A.Budding and G.J.M.van der Kerk, Rec.trav.chim. 79 409 (1960)
- 14 J.G.Noltes, H.A.Budding and G.J.M.van der Kerk, Rec.trav.chim. 79 1076 (1960)
- 15 J.R.Leebrick and H.E.Ramsden, J.Org.Chem. 23 935 (1958)
- 16 V.V.Korshak et al., Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.nauk 178 (1959)