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WADC TECHNICAL REPORT 58-44
PART II
ASTIA DOCUMENT NO. AD 215425

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ORGANOMETALLIC POLYMERS

OFFICIAL FILE COPY

PAUL E. KOENIG
RONALD D. CRAIN
ETHYL CORPORATION

JUNE 1959

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WADC TECHNICAL REPORT 58-44
PART II
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ORGANOMETALLIC POLYMERS

*PAUL E. KOENIG
RONALD D. CRAIN
ETHYL CORPORATION*

JUNE 1959

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-3848
PROJECT NO. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Ethyl Corporation under USAF Contract No. AF 33(616)-3848. This contract was initiated under Project No. 7340, "Rubber-Plastic, and Composite Materials"; Task No. 73404, "Synthesis of Tin-Containing Polymers". The work was monitored under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with 1/Lt. Myron W. Black and 1/Lt. William E. Gibbs acting as project engineers.

This report covers work conducted from January 1958 to December 1958.

Ethyl personnel who have contributed to this effort have been Dr. F. Conrad, Dr. R. P. Curry, Dr. A. J. Haefner, Dr. P. E. Koenig, Dr. R. D. Crain and Mr. W. J. Easley.

ABSTRACT

Continued investigation of stannosiloxane polymers has led to the conclusion that relatively large organic substituents must replace the methyl and phenyl groups thus far studied, if high thermal stability is to be obtained. The polyorganostannosiloxanes have been found to undergo extensive decomposition and disproportionation on prolonged heating above 300°C.

Reactions of organotin disodium derivatives with organic dihalides to prepare linear polymers containing tin-carbon chains are described.

A very convenient method is reported for the preparation of tin-sulfur polymers (stanthianes) by reaction of sulfur with divalent organotin compounds.

Explorations have been initiated to prepare aluminum oxide polymers. The thermal stability of the aluminum-oxygen bond should lead to polymers of improved heat and oxidative stability. The extreme reactivity of the aluminum-alkyl bond has been utilized in an effort to obtain high molecular weights.

Four methods of approach have been explored:

1. Trialkylaluminum compounds were reacted with dihydroxy monomers to produce products which are insoluble, infusible powders with good thermal stabilities.

2. Dialkylaluminum alkoxides were reacted with dihydroxy compounds to form similar products. In this instance, however, it was ascertained through molecular weight studies that the alkoxides were stable trimers, hence multifunctional, and the polymers obtained were therefore highly cross-linked.

3. Various "difunctional" aluminum chelates were prepared. The polymers obtained were infusible and insoluble powders except in one case where diphenylsilanediol was used.

4. Polymers obtained from aluminum salts such as sodium aluminum hydride gave brittle solids.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

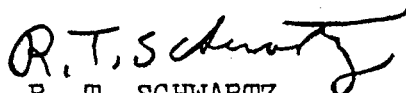

R. T. SCHWARTZ
Chief, Organic Materials Branch
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SECTION I

INTRODUCTION

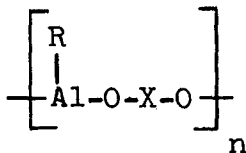
The organometallic oxide polymers, of which the siloxanes were the prototype, have long been considered likely possibilities for thermally stable polymers. Stannosiloxanes, in which some of the silicon of a siloxane has been replaced by tin, have been studied fairly extensively in this laboratory and by other investigators^{1,2,3,4}. The stability of these compounds has been good but not outstanding. Very few of the metallosiloxanes⁵ have been prepared in high molecular weight form. This general class of materials will have only limited utility as plastics or elastomers until molecular weights can be improved.

Our work on tin-containing polymers has recently been oriented toward structural considerations, particularly with regard to the stannosiloxanes. Limited work has been conducted on the synthesis of sterically hindered monomers. Some effort has also been applied to the tin-alkylene polymers, but the results are inconclusive.

Although continued fundamental studies involving sterically hindered monomers is worthwhile, it was felt that the specific objective of this program could be better met by placing more emphasis on other metal oxide polymers. An outstanding candidate for investigation is the aluminum oxide structure.

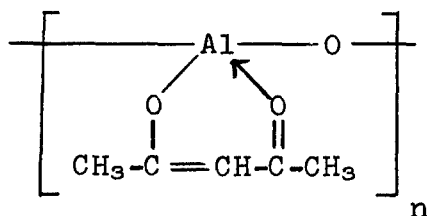
The utilization of aluminum should impart the thermal stability of the aluminum-oxygen bond to a polymer. This is demonstrated by improvements in siloxanes upon the addition of small amounts of aluminum compounds^{6,7,8} and the formation of resins with organic moieties⁹. A greater amount of thermal stability is possible in an aluminum oxide structure and several resins of this type have been reported^{10,11}. Unfortunately, the hydrolytic stabilities of these polymers have been poor.

The hydrolytic stability of the aluminum-containing polymers should be achieved through steric hinderance or through chelation. An example of the former is



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where R is alkyl, aryl, alkoxy, etc., and X is an organic group or metal atom (e.g., a disubstituted silicon atom). The latter type of polymer can be exemplified by:



This type of polymer structure should help solve the hydrolytic problems of the aluminum and at the same time retain the thermal stability.

SECTION II

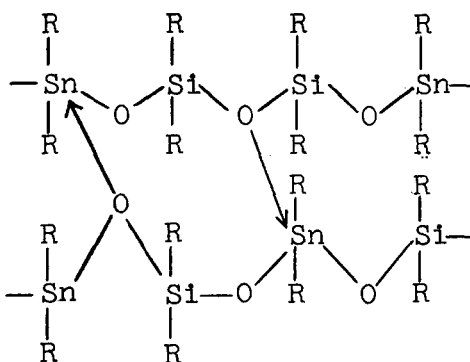
DISCUSSION

A. TIN OXIDE POLYMERS

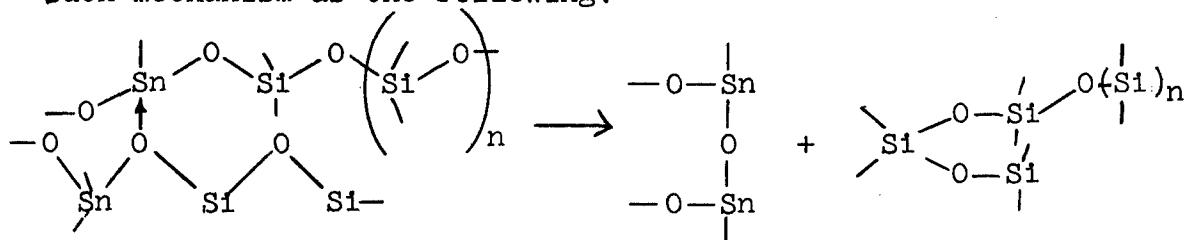
A great amount of effort has been expended in preparing various stannosiloxane polymers. Various substituents on the tin and silicon atoms have been examined and numerous techniques employed to improve the molecular weights. So far, only low molecular weight resins have been made and we have not been able to demonstrate significant superiority to the known polysiloxanes. These results have led us to speculations on the structural considerations required for the observed properties of the stannosiloxane polymers.

Siloxane polymers owe their rather remarkable properties (i.e., their small temperature coefficient of viscosity and their good thermal stability) to two related factors, namely: their highly ionic Si-O bond with its "soft" bond angles¹², and their low degree of intermolecular attraction¹³. These same factors lead to failure of the siloxanes in certain applications; their extremely low viscosity changes (very low second-order transition temperatures) make it unlikely that a useful thermoplastic will be found which possesses a simple polysiloxane structure¹⁴. Likewise, the highly ionic bond structure probably contributes to the ease of intra- and intermolecular rearrangement which results in the thermal degradation of long chain siloxanes to volatile small-ring compounds.

The introduction of other metals into siloxane chains alters these properties in several ways. Short-chain stannosiloxane polymers have been observed to have much higher brittle temperatures and temperature coefficients of viscosity than the analogous siloxane polymers. This effect is no doubt the result of increased inter-chain attraction, which may be accounted for on the assumption that substitution of some of the silicon atoms by more electropositive metals (e.g., tin, in stannosiloxanes) produces some even more highly ionic bonds. The charge separation produces more extensive interchain interaction - particularly when metals such as tin are present which, even more readily than silicon, tend to form penta- and hexacovalent structures:



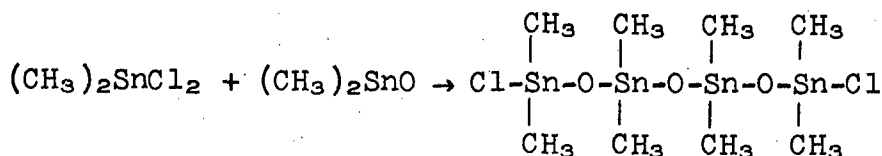
The result is a much higher second-order transition temperature, or "brittle temperature", than that observed in the siloxanes. A further and less fortunate result, however, is the thermal disproportionation of metallosiloxane chains, possibly according to some such mechanism as the following:



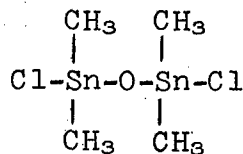
This picture is consistent with the mechanism proposed for rearrangement of siloxanes by alkali hydroxides¹⁵. Rearrangement has also been produced by addition of metal silanolates, probably by substantially the same mechanism¹⁶.

Considerations such as these lead to the conclusion that organic substituents of increased bulk offer the most promising path for improving the present deficiencies of both the siloxanes and stannosiloxanes. A moderate effort has been expended on the synthesis of sterically hindered monomers, as subsequently described.

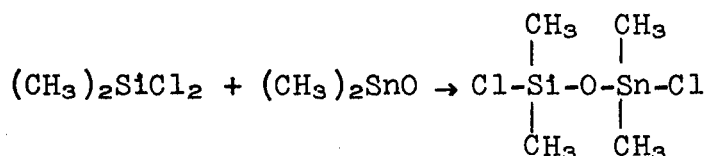
Because of their close relation to stannosiloxane polymers, we have also studied the "double salt" compounds initially described by Harada¹⁷. These compounds result when disubstituted organotin halides are partially hydrolyzed, or are heated with the corresponding organotin oxide. They presumably have a stannoxane structure, the chains being terminated by halogen or other anionic groups:



From equimolar amounts of dimethyltin dichloride and dimethyltin oxide we prepared a compound with a composition in fair agreement with that calculated for the "double salt" shown:



It was thought that analogous reactions might be observed between dichlorosilanes and organotin oxides, to produce stannosiloxane compounds which could be hydrolyzed to polymers:



Compounds of the desired composition were obtained, but they are apparently quite unstable. During attempted recrystallization these compounds evidently disproportionated to regenerate the starting materials. This surprisingly facile rearrangement provides no encouragement for the stability of the stannosiloxane polymers.

In the course of the stannosiloxane studies certain infrared absorption frequencies have been tentatively assigned as follows:

$\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{Si}-\text{O} \end{array}$	7.95 μ
$\emptyset-\text{Si}$	8.8-8.9 μ
$\emptyset-\text{Sn}$	9.3-9.4 μ
CH_3-Sn	8.3-8.4 μ
$\text{Si}-\text{O}-\text{Si}$	9-10 μ
$\text{Si}-\text{O}-\text{C}$	9-10 μ
$\text{Sn}-\text{O}-\text{Sn}$	12.75-13.0 μ

These data have been helpful in finding structural information regarding linearity, end groups, etc.

B. TIN SULFIDE POLYMERS

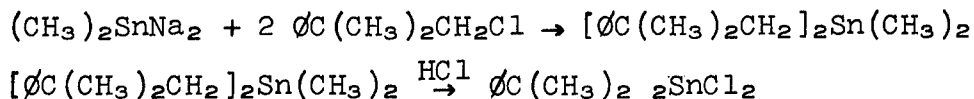
The rather unusual stabilities of the organic tin sulfides have led to earlier speculation by us that organostanthiane polymers might be of interest¹⁸; indeed some of these compounds were prepared by interaction of mixed organotin halides with sodium hydrogen sulfide. A more elegant method of synthesis has now been devised,

comprising reaction of mixtures of dimethyltin and diphenyltin, for example, with elemental sulfur in liquid ammonia solution. The reaction proceeds smoothly and rapidly to produce the copolymers.

The products obtained by this method have been (probably) of rather low molecular weight, as they are very mobile fluids at room temperature. They frequently possess a disagreeable sulfurous odor - possibly due to the presence of impurities such as trialkyltin sulfides. The compounds are thermally stable only up to about 250°C, but seem to retain their fluidity down to -20°C or so, and are not brittle even at solid CO₂ temperatures. Variation in properties may result from higher chain lengths or different organic substituents.

C. STERICALLY HINDERED MONOMERS

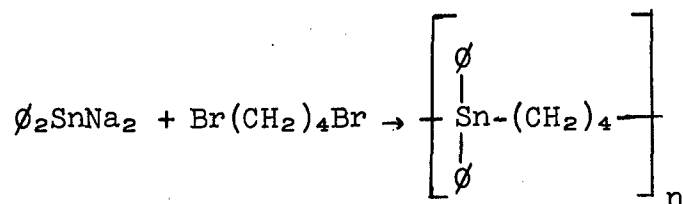
To bring about steric inhibition of chain interaction, it is necessary to prepare highly hindered monomers bearing bulky substituents such as *t*-butyl, neophyl, naphthyl, etc. These compounds have been surprisingly difficult to prepare, and a considerable amount of effort has been devoted to their synthesis without marked success. It was thought that a likely method of synthesis of hindered difunctional organotin compounds would make use of the di-sodium substituted intermediate described by Kraus¹⁹.



The results obtained from the studies of the synthesis of sterically hindered monomers are inconclusive. Whereas it is our continued belief that efforts expended with this objective are indeed worthwhile, such a program would be lengthy and laborious. Instead, efforts are now being concentrated on the equally promising aluminum oxide area.

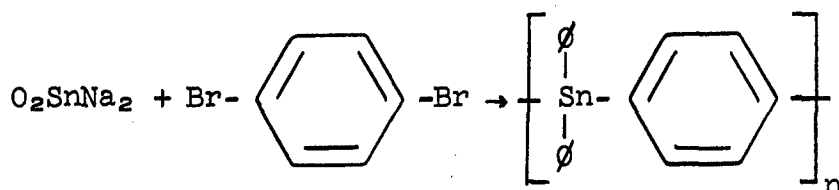
D. TIN ALKYLENE POLYMERS

Another type of polymer which is of interest is the true organometallic polymer with a chain that contains metal-carbon bonds rather than inorganic metal-oxygen bonds. These polymers have not been extensively investigated because of the difficulties inherent in the preparation of suitable monomers. We have conducted brief studies of reactions of organotin disodium derivatives with organic dihalides²⁰.



Elastomeric polymers of presumably fairly high molecular weight were obtained by this reaction.

A more interesting polymer from the standpoint of thermal stability would no doubt be the phenylene-linked polymer prepared as follows:



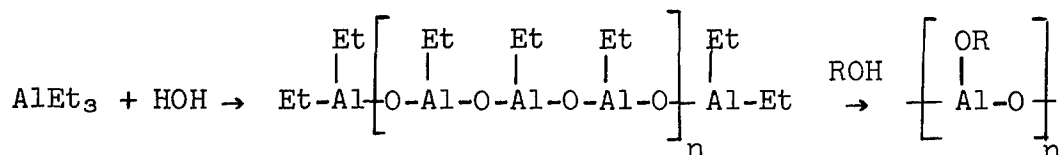
We have observed that reaction does in fact take place between these two reactants. Results were not conclusive.

Difficulties encountered with these reactions have led to more fundamental examination of the method, and have thrown some suspicion on the original mechanism proposed by Kraus¹⁹. Indeed, we have been unable to duplicate his reported synthesis of tetramethyltin by reaction of dimethyltin disodium with methyl iodide. It may well be that the compound "dimethyltin disodium" does not exist at all, or at least does not react as expected with alkyl halides.

E. POLYMERS FROM TRIALKYL ALUMINUMS

The aluminum oxide structure is known to be very stable thermally and should impart similar properties to polymers in which it is incorporated. The accessibility of the aluminum alkyls and hydrides to this laboratory provides convenient starting materials for the preparation of polymers containing an aluminum atom in the backbone of the molecule. The extreme reactivity of the carbon-aluminum bond should also give a facile reaction and aid in the formation of high molecular weight polymers. Such considerations have encouraged us to conduct explorations in this area.

If the reaction of difunctional molecules such as water and diols with triethylaluminum is controlled, a polymer with active ethyl groups is formed. These ethyl groups can then be reacted with an alcohol to give a stable aluminum polymer. It was anticipated

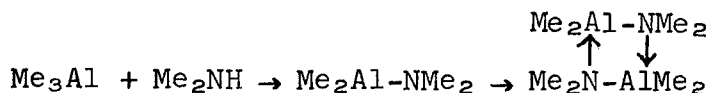


that the ethyl groups along the polymer chain would be relatively less reactive than the two ethyl groups at each end of the growing chain.

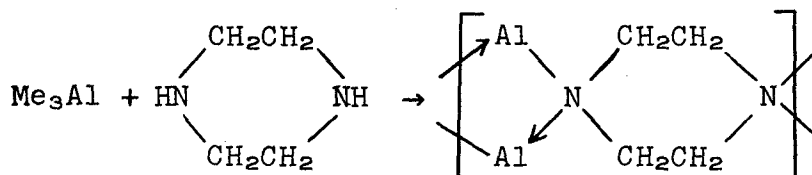
The first step proceeds smoothly, liberating the expected quantity of gas. However, reaction of the formed ethylaluminum oxide polymer with triphenylsilanol or *t*-butanol gave only up to 60% of the theoretical amount of gas evolution. Attempts to account for the other 40% of ethyl groups through the presence of oxygen (requiring over 100 cc) and/or water (0.2 g needed) do not seem logical since extra precautions were taken for the exclusion of air and moisture from the reaction apparatus and materials used.

The formed polymers are insoluble in organic solvents and do not fuse, even at their decomposition points. All are stable up to 250°C and some are stable up to 400°C. These properties are characteristic of a high degree of cross-linking. Since there are two different types of ethyl groups in the linear polymer available for reaction (ethyl groups along the chain, and terminal ethyl groups), it is evident that the statistical probability of an active hydrogen reacting with an ethyl group along the chain quickly overcomes the difference in reactivity of the terminal ethyl groups with the resultant formation of cross-links.

Reactions of amines with trialkyl aluminums has also been explored. The literature²¹ reports that reaction of trimethylaluminum with dimethyl amine first gives a single Al-N bond with the evolution of methane. Upon heating, this material dimerizes to form a stable product.



Applying this idea for use in a polymer might give the desired property of high temperature stability. When trimethylaluminum was reacted with anhydrous piperazine an infusible and insoluble solid was formed having the aluminum content of the expected polymer.



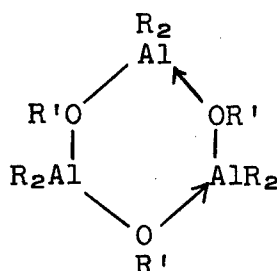
Although the physical properties are similar to those of the previous polymers, there is no proof for linearity or cross-linking. The polymer is not reactive toward water but it decomposes in air at temperatures above 200°C.

F. POLYMERS FROM DIALKYLALUMINUM ALKOXIDES

In an attempt to eliminate cross-linking, dialkylaluminum monomers were used. Such compounds can be readily prepared by reacting a trialkylaluminum with one equivalent of an alcohol. Trimethylsiloxydimethylaluminum was chosen as a starting material because a sample was available in this laboratory. Reaction with molar quantities of diphenylsilanediol gave an infusible solid with a molecular weight of 798. When heated to 180°C, hexamethyldisiloxane and benzene were formed. Similar disproportionation products are obtained from the stannosiloxanes.

Reaction of trimethylsiloxydimethylaluminum with 2,2-dimethyl-1,3-propanediol gave an infusible and insoluble solid which was stable up to 300°C. This material was, in most respects, quite similar to the previous cross-linked polymers.

Molecular weight studies of the dialkylaluminum compounds have led to an explanation of this observed infusibility. Cryoscopic studies of the dimethylaluminum methoxide show that it is a trimer rather than a monomer²¹. The trimer is stable thermally and exists as such in the gas phase. It is also stable towards trimethylamine. A trimeric structure for trimethylsiloxydimethylaluminum readily explains the formation of a three dimensional polymer due to the presence of six reactive sites in the molecule. A check was made by preparing a similar compound, dimethoxyaluminum-*t*-butoxide, which was also a trimer. The general formula for these trimers is believed to be:

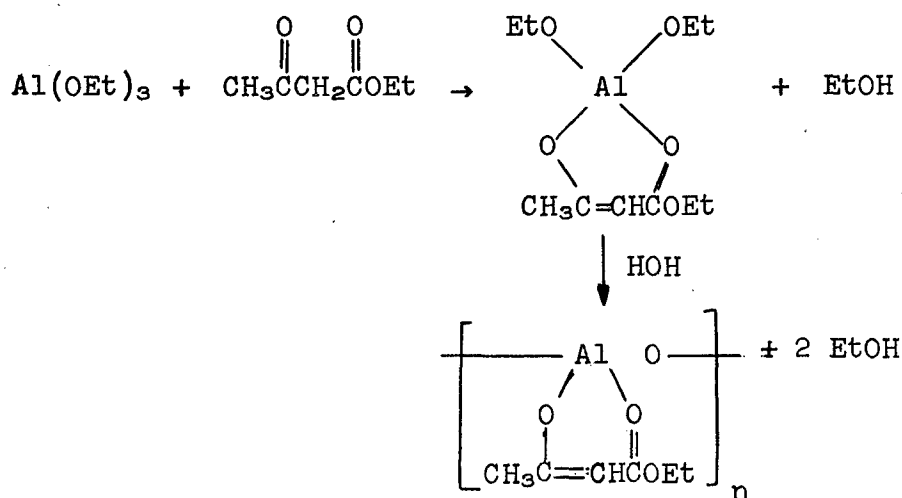


With the object of eliminating cross-linking, it was assumed that the use of a large bulky group for R' might sterically hinder the oxygen and aluminum, thereby eliminating the tendency to form trimers. A highly hindered molecule like 2,6-di-*t*-butylphenol should accomplish this. However, studies showed that the obtained dimethylaluminum-2,6-di-*t*-butylphenoxide was also a trimer. The use of an ether solvent like dioxane in the cryoscopic molecular weight determination still gave a trimeric formula. Hydrolysis of the trimer of dimethylaluminum-2,6-di-*t*-butylphenoxide with 1,5-pentandiol gave an infusible and insoluble polymer consistent with a high degree of cross-linking. This reaction proceeded much slower due to the steric hinderance of the phenol. It is believed that replacement of the methyl groups with larger alkyl groups may give a monomer but the reactivity of the aluminum alkyl bond will be sacrificed.

G. ALUMINUM CHELATE POLYMERS

There is very little known on the chemistry of preparing monochelates of aluminum. The B. F. Goodrich Company has reported their work in this area²², and to date no high molecular weight polymers have been made with good thermal properties. In view of a recent report in the literature²³ on the preparation of diethoxyaluminum ethylacetoacetate, a closer study of these reactions was undertaken.

Aluminum ethoxide reacts with ethyl acetoacetate with the splitting out of one mole of ethanol. The product is reported to be a very viscous material giving the proper aluminum analysis for a 1:1 product. Hydrolysis with water forms a solid with retention of the chelate and liberation of two moles of ethanol.



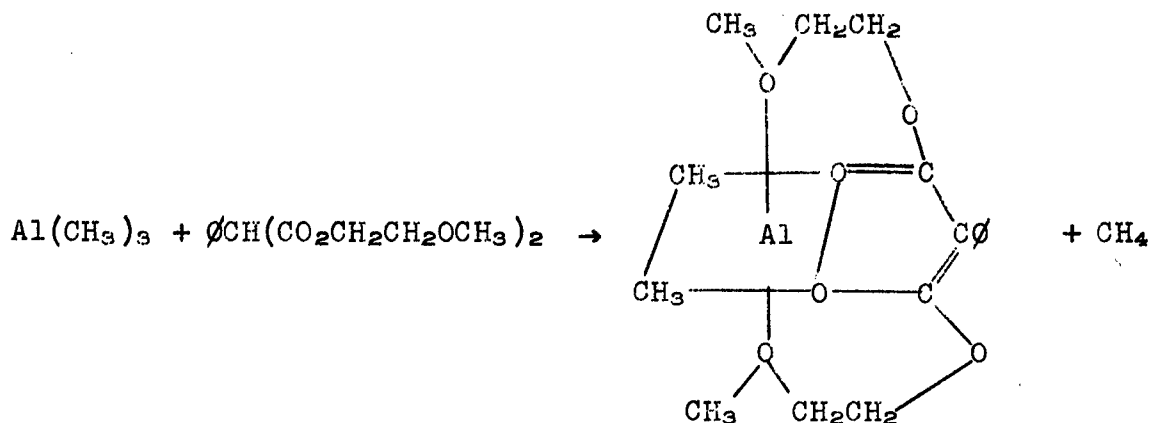
This reaction was repeated except the intermediate chelate was not isolated. Instead, the chelate was reacted with 1,5-pentane-diol to give a yellow brittle solid. A similar reaction using 2,4-pentanedione formed a yellow brittle glass which also gave a brittle solid when reacted with 1,5-pentanediol. Neither resin was fusible or soluble in organic solvents. When both heat and pressure (greater than 10,000 psi) were applied brittle films could be formed. Exposure to moisture in the atmosphere for a few days caused hydrolysis of the resins. If they are heated above 180° the odors of the diketone or ester can be detected.

These results indicate a fair amount of cross-linking. The isolation of the diethoxyaluminum ethylacetoacetate confirmed this. Instead of being a monomer, as reported, the compound is actually a resin with about three times the expected molecular weight of a monomer. Hydrolysis with 1,5-pentanediol gave an infusible and insoluble resin which, when heated, had the odor of ethyl acetoacetate. Hydrolysis with diphenylsilanediol formed a fusible brittle resin with a molecular weight of 1230. Again, when heated the odor of the ester could be detected. Attempts to increase the molecular weight have failed.

Since attempts to get monomeric chelate materials from aluminum ethoxide failed and no high molecular weight polymers were obtained, the use of the trialkylaluminum as a starting material was investigated. The product from the reaction of triisobutylaluminum and 1,3-diphenyl-1,3-propanedione is insoluble in benzene and is presumably the monochelate²⁴. Reaction of trimethylaluminum with 2,4-pentanedione gave a deep red brittle glass.

With ethyl acetoacetate a distillable liquid was obtained. The infrared spectrum showed the characteristic absorption bands for Al-Me and also a band for an Al-O chelate bond. Hydrolysis of this liquid with 1,5-pentanediol gave an insoluble and infusible solid similar to those obtained from the hydrolysis of triethylaluminum.

One possible explanation of the observed cross-linking of the chelate polymers is the fact that aluminum readily forms compounds such as aluminum acetylacetonate where three covalent bonds and three coordinate covalent bonds are formed. A tetradentate molecule could be used whereby the aluminum has only two reactive groups available for formation of linear polymers. Molecular models show that one of the six-membered rings formed from a tetradentate is not stable sterically and that seven-membered rings will most likely be more suitable. A readily available material of this nature can be found in di(methoxyethyl) phenylmalonate. This ester was easily prepared by transesterification of diethyl phenylmalonate with 2-methoxyethanol. Trimethylaluminum should then react with the enolizable hydrogen, liberating one mole of methane, and the remaining oxygens in the diester could then form the octahedral structure.

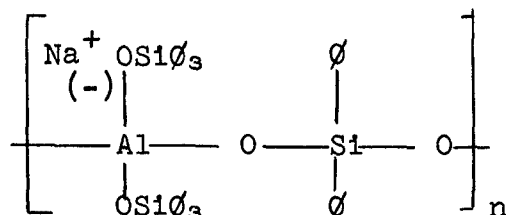


Attempts to carry out this chelation reaction in the laboratory did not give the expected chelate. When the reaction was run in 1:1 mole ratios a viscous liquid was isolated with a molecular weight greater than 500 (calculated molecular weight is 352). Further treatment of this liquid with 1,5-pentanediol gave an infusible and insoluble solid decomposing at a temperature above 230°C. Using two moles of trimethylaluminum and one of the diester gave a similar viscous liquid. However, none of the excess

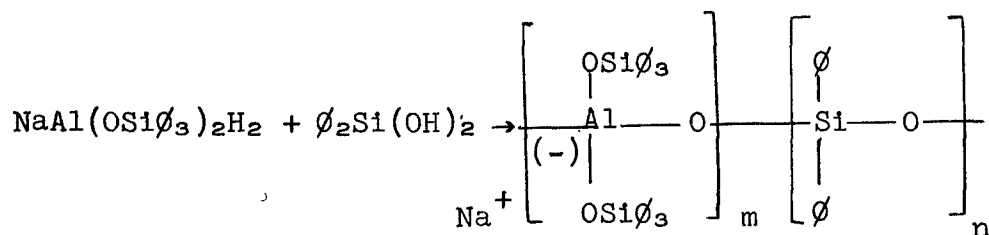
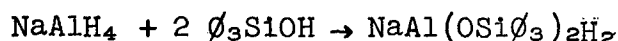
trimethylaluminum could be isolated, indicating that instead of forming a simple chelate intramolecularly, an intermolecular reaction was occurring.

H. ALUMINUM SALT POLYMERS

Chain interaction should be preventable by the elimination of reactive sites along the chain. Thus, if the electron-accepting sites in a chain can be satisfied by groups or structures other than those in a neighboring chain, there will be little interaction. This is, of course, the concept which Ruigh explored in his studies of quadricovalent boronic acids and other chelated structures. Another approach to this problem of neutralization of reactive sites involves use of anions as electron donors, as in the following structure:



While the particular structure indicated might be subject to facile hydrolysis, the analogous polymer using different cations in place of sodium (e.g., Hg^+ , or aluminum) might be quite inert both to hydrolytic and to thermal decomposition. We have attempted the synthesis of the compound represented above by reaction of sodium aluminum hydride with two moles of triphenylsilanol followed by one mole of diphenylsilanediol:



The compound obtained was fairly stable to heat but was easily hydrolyzed.

I. MISCELLANEOUS

Several isolated exploratory reactions have been carried out, including a cohydrolysis of methyl silicate and anhydrous stannous chloride. This gave a polymeric product which was no doubt highly cross-linked. It was quite insoluble and would not soften or melt. Products of this sort, possessing very little organic character, should provide excellent thermal stability. If a way can be found to prepare linear flexible chain polymers of largely inorganic structure, highly stable plastics or elastomers should result.

SECTION III

SUMMARY AND CONCLUSIONS

It is quite likely that stannosiloxane polymers containing methyl or phenyl substituents will not be exceptionally stable materials because of an observed tendency to disproportionate or rearrange. The same phenomenon limits the utility of the siloxane polymers as well. It is believed that incorporation of large organic residues into the polymers might reduce chain interaction and lead to greater stability. So far, the attempted synthesis of tin monomers containing very large groups has been mainly unsuccessful.

Stanthiane polymers, which contain tin-sulfur backbones, have been prepared by a novel synthesis. These provide fluids or very low melting solid resins which might be useful lubricants. Also some of these compounds retain their fluidity at relatively low temperatures (-30 to -40°C).

Organotindisodium preparations have been briefly investigated as a route to tin-carbon polymeric backbones. Some evidence indicates that a phenylene-linked tin polymer can be prepared from diphenyltin disodium and dibromobenzene. Elastomeric compounds have been similarly prepared from dibromobutane, but side reactions such as dehydrohalogenation are probably fairly extensive in this system.

The hydrolysis of trialkylaluminums with one equivalent of water gives an ethylaluminum oxide polymer. Further studies of this reaction using diols such as diphenylsilanediol and neopentyl glycol substantiate the fact that these polymers are not linear. The polymers obtained are infusible, insoluble, and brittle solids, indicative of a high degree of cross-linking.

The ensuing step was then to prepare difunctional aluminum monomers. A study of dialkylaluminum alkoxides also gave cross-linked polymers with diols. From molecular weight studies these compounds were established as hexafunctional trimers instead of difunctional monomers. Even the highly hindered dimethylaluminum-2,6-di-*t*-butylphenoxide was trimeric and gave similar polymers with 1,5-pentanediol.

The initial study of the aluminum chelate polymers indicates that the monomers are actually polymers. The only fusible resin obtained was from the reaction of diphenylsilanediol and diethoxy-aluminum ethylacetoacetate. Attempts to increase the molecular weight above 1230 have failed so far.

The main interest in aluminum oxide types of polymers is the potential heat stability. Although linear polymers have not been made, this one fact has been substantiated: All of the aluminum-containing polymers are stable above 200°C, and some are stable up to 400°C. Once the problem of cross-linking is solved, it is believed that high molecular weight linear aluminum-containing polymers can be made.

SECTION IV

EXPERIMENTAL*

A. TIN OXIDE POLYMERS

Reaction of Triphenylsilanol with Diphenyltin Oxide

This reaction was carried out to study the structure of organotin oxides. Presumably, these compounds are high polymers. That being the case, reaction with less than 2-molar amounts of a monosilanol should lead to stannosiloxanes containing unbroken Sn-O-Sn bonds.

In a 500-ml flask were placed 4.14 g (0.015 mole) triphenylsilanol and 14.4 g (0.05 mole) diphenyltin oxide. Dry dioxane (200 ml) was added and the mixture refluxed. After about 4 hours refluxing, 10.4 g of insoluble white solid was filtered off. The filtrate was concentrated and a large excess of petroleum ether added. A precipitate formed and was removed by filtration. The filtrate was concentrated further and dioxane was removed in a current of air. A viscous syrup remained, weighing 3-4 g.

Anal. Calc. for $(\text{C}_6\text{H}_5\text{Si}-\text{O})_2 \text{SnO}_2$: Sn, 14.4; Si, 6.8.
Found: Sn, 13.3; Si, 8.9.

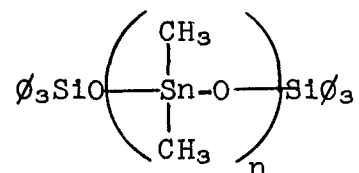
Apparently the product contained a mixture of compounds including $\text{C}_6\text{H}_5\text{Si}-\text{O}-\text{SiC}_6\text{H}_5$ and $(\text{C}_6\text{H}_5\text{Si}-\text{O})_2 \text{SnO}_2$.

Reaction of Triphenylsilanol with Excess Dimethyltin Oxide

Dimethyltin oxide (16.4 g, 0.1 mole) was placed in a flask with 200 ml dry dioxane; 2.8 g (0.01 mole) triphenylsilanol was added and the mixture refluxed. After several hours considerable undissolved solid material was still present; an additional 2.8 g (0.01 mole) of triphenylsilanol was added and refluxing continued. After several more hours a third 2.8 g portion of triphenylsilanol was added. Prolonged refluxing never dissolved all the solid material present. Finally the solids were separated by filtration and the filtrate was concentrated to a thick colorless syrup. This was heated in vacuo to remove traces of solvent. A transparent resin remained, which closely resembled the resins obtained from the silanediol-tin oxide reaction. The product was rather tough and elastic at room temperature. At 130° it was fairly fluid but quite viscous. Cryoscopic molecular weight was

*Temperatures are given in °C; melting and decomposition points are uncorrected.

630, which was surprisingly low. Since the material did not crystallize, it probably contains little $(\phi_3\text{SiO})_2\text{Sn}(\text{CH}_3)_2$, which can be prepared from suitable stoichiometric quantities of the above starting materials. Probably the product is a mixture of low molecular weight polymers of the type



with some $(\phi_3\text{SiO})_2$ and $(\phi_3\text{SiO})_2\text{Sn}(\text{CH}_3)_2$.

Preparation of a (Sn)Dimethyl-(Sn)Diphenyl-(Si)Diphenylstannosiloxane

In a 1-liter resin kettle were placed 46 g (0.28 mole) dimethyltin oxide, 40 g (0.14 mole) diphenyltin oxide, and 116 g (0.538 mole) diphenylsilanediol (Dow Corning "Purified Grade", recrystallized from acetone and chloroform). About 400 ml sodium-dried dioxane was added and the mixture was heated to reflux and maintained at that temperature for about 4 hours. The dioxane solvent was then flash-distilled at reduced pressure to leave a clear, almost colorless, syrup in the reactor. The polymeric material was heated at 120° for 2-3 hours at full oil-pump vacuum (ca. 0.1 mm) and the vessel was then opened. The product possessed a sharp irritating odor like that of the well-known trialkyltin compounds.

Now we have speculated earlier (cf., e.g., WADC TR 58-44, p. 34) that some disproportionation may take place during this reaction of silanols with organotin oxides; if this is the case, some trialkyl (or triaryl) tin derivatives might indeed be formed. These compounds (or the hydroxide, at any rate) are known to be fairly strong bases. A base of moderate strength might catalyze the depolymerization of a stannosiloxane by mechanisms established in the literature¹⁵. Therefore, to lessen the possibility of depolymerization and also to improve the odor of the product somewhat, it was decided to extract a solution of the polymer with water. The material was dissolved in chloroform and extracted in a separatory funnel with water. The separation was slow and required several hours. The chloroform layer was separated and dried over sodium sulfate, filtered, and concentrated. The recovered polymer appeared to be of substantially higher molecular weight than the initial reaction product; the former was soft at 100° but would flow only very slowly, while previous preparations of stannosiloxanes by this reaction have been very mobile at about 90° or below.

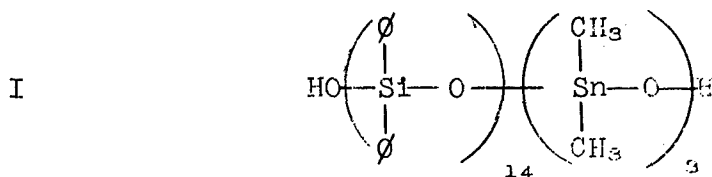
On standing, the aqueous phase from the extraction developed a white solid precipitate, which was filtered off and dried in the vacuum oven. It weighed 12 g and was highly crystalline.

Reaction of Dimethyltin Oxide with Diphenylsilanediol in Refluxing Dioxane

In a 500-ml reaction flask were placed 32.8 g (0.2 mole) dimethyltin oxide, 86.4 g (0.4 mole) diphenylsilanediol, and 250 ml purified dioxane. The mixture was refluxed for several hours. A substantial amount of insoluble white solid was present at all times; this was removed by filtration and the filtrate concentrated under reduced pressure. A clear viscous liquid remained in the flask. A small sample was withdrawn and placed in an Abderhalden pistol under full vacuum at the boiling point of ethanol for several hours; it formed a perfectly clear glass, softening at a low temperature (50-60°) and soluble in several organic solvents.

Anal. Found: Sn, 9.9; Si, 11.4.

This probably represents a structure approximately like I, contaminated with some low molecular weight water-soluble compounds such as Me_3SnOH or perhaps (II).



The bulk of the original reaction product was dissolved in chloroform and extracted three times with water; phase separation became progressively easier. The chloroform layer was drawn off and dried over anhydrous sodium sulfate, filtered, and concentrated at reduced pressure. Finally the product was heated at 150° for several hours at full oil-pump vacuum (ca. 0.2-0.3 mm). The product was a viscous translucent syrup which cooled to a brittle solid.

Anal. Calc. for I: Sn, 10.85; Si, 12.0; mol wt, 3264.
Found: Sn, 11.0; Si, 12.1; mol wt, 2900 (cryo-
scopic in benzene).

The infrared spectrum was consistent with the structure (I) shown. The spectrum showed the presence of Me-Sn, ϕ -Si, and free -OH. There was no ϕ -Sn, no Me-Si, and no bonded OH. On the other hand, the spectrum of the sample before extraction with water indicated the presence of bonded OH; this sample also showed absorption at 11.45 - a peak which disappeared following water extraction.

A similar reaction, carried out in refluxing toluene and using the same starting materials, produced a white, opaque, brittle stannosiloxane resin unlike the translucent glass obtained above. This compound was apparently of comparable structure.

Anal. Found: Sn, 10.6; Si, 11.6.

This is not substantially different from the analysis reported above, and is probably within the limits of the analytical methods used. The infrared spectrum, however, could not be conveniently determined using a film of the material, as apparently some crystallization took place, limiting the transmission of light appreciably. This crystallization was also apparent from the appearance of a microscopic sample of the material. The spectrum showed no free or bonded OH, either as a "film" or in CS_2 solution. The compound is presumably either cyclic or terminated by something other than OH groups.

Reaction of Triphenylsilanol with Dimethyltin Oxide

The desired reaction is $\phi_3\text{SiOH} + (\text{CH}_3)_2\text{SnO} \rightarrow (\phi_3\text{SiO})_2\text{Sn}(\text{CH}_3)_2$.

In a 450-ml beaker were placed 150 ml xylene, 27.6 g (0.1 mole) triphenylsilanol, and 8.2 g (0.05 mole) dimethyltin oxide. The mixture was boiled 20 minutes and filtered, and the filtrate was allowed to stand. Colorless crystals separated. About 50 ml petroleum ether was added and the solution was cooled in ice. The product was separated by filtration and recrystallized from chloroform and petroleum ether. The white finely-divided crystalline product melted at 176°.

Anal. Calc. for $(\phi_3\text{SiO})_2\text{Sn}(\text{CH}_3)_2$: Sn, 16.9; Si, 8.02.
Found: Sn, 15.05; Si, 10.93.

Apparently this compound was contaminated by siloxane compounds. The experiment was like one reported some time ago, but better agreement was obtained the first time.

Reaction of Triphenylsilanol with Diphenyltin Oxide

The desired reaction is $\phi_3\text{SiOH} + \phi_2\text{SnO} \rightarrow (\phi_3\text{SiO})_2\text{Sn}\phi_2$. The reaction was carried out as above, but 14.4 g diphenyltin oxide was substituted for the dimethyltin oxide. The product was precipitated as an oil by addition of petroleum ether; on standing, the product crystallized. It was recrystallized from chloroform and petroleum ether, and observed to melt at 163° . It was extracted with ethyl ether; the insoluble portion melted at 156° .

Anal. Calc. for $(\phi_3\text{SiO})_2\text{Sn}\phi_2$: Sn, 14.38; Si, 6.82.
 Calc. for $(\phi_3\text{SiO})_4\text{Sn}$: Sn, 10.5; Si, 10.0.
 Found: Sn, 9.13; Si, 8.49.

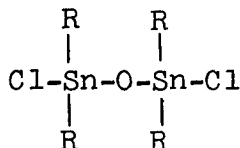
The analysis obviously checks more close for tetrakis (triphenylsiloxo)tin; however, it is hard to visualize a mechanism of formation of this compound.

Reaction of Dimethyltin Dichloride with Dimethyltin Oxide

Dimethyltin dichloride (21.9 g, 0.1 mole) and 16.4 g (0.1 mole) dimethyltin oxide were placed in 200 ml benzene and the mixture was refluxed. After several hours the white solid present in the reaction mixture appeared somewhat different from the starting material; it was separated, boiled with 2B ethanol, and filtered. A fine powdery solid separated from the filtrate on cooling.

Anal. Calc. for $\text{Me}_2\text{SnO} \cdot \text{Me}_2\text{SnCl}_2$: Sn, 61.6; Cl, 18.5.
 Found: Sn, 61.0; Cl, 15.5.

It has been suggested that these compounds might have the structure:



The low chlorine content might be the result of some trimer or polymer formation.

Reaction of Diphenyldichlorosilane with Dimethyltin Oxide

A mixture of 200 ml benzene, 25.3 g (0.1 mole) diphenyldichlorosilane, and 16.4 g (0.1 mole) dimethyltin oxide was refluxed for about 30 minutes. The resulting clear solution was concentrated at reduced pressure to a gelatinous mass. When this was shaken vigorously with petroleum ether, a granular product weighing 28 g separated. The compound melted at 96°.

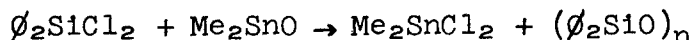
Anal. Calc. for $\begin{array}{c} \phi_2 \quad \text{Me}_2 \\ | \quad | \\ \text{Cl-Si-O-Sn-Cl} \end{array}$: Si, 6.72; Sn, 28.4.

Found: Si, 7.0; Sn, 29.7; Cl, 19.5.

Since the results did not check perfectly, the compound was recrystallized from carbon tetrachloride and dried in the vacuum oven and reanalyzed:

Anal. Calc. for Me_2SnCl_2 : Sn, 54; Cl, 32; mol wt, 219.
Found: Sn, 42.6; Si, 2.3; Cl, 25.2;
mol wt, 233.

Apparently the CCl_4 recrystallization had separated a rather weakly bound complex so that effectively the following reaction had taken place:



An analogous reaction between octadecyltrichlorosilane and dimethyltin oxide produced a white crystalline product which melted over a wide range (96-118°).

Anal. Found: Sn, 40.8; Si, 1.59; Cl, 27.3; mol wt 207.

This is also believed to be substantially dimethyltin dichloride contaminated with a silicone polymer.

Thermal Degradation of Stannosiloxane Polymers

A small sample of (Sn)dimethyl(Si)diphenylstannosiloxane polymer was heated at 300° by means of a molten bath for several hours without extensive decomposition; the fluid turned yellow-brown

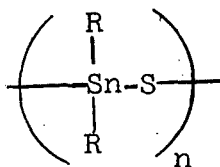
in color, but remained transparent and did not char. Upon being heated to 400°, however, the fluid decomposed appreciably, with considerable blackening and charring. A more quantitative study was therefore made as follows:

A small sample of the same stannosiloxane polymer was heated in an oven at 120° for several hours; it then weighed 3.0186 g. The sample was heated to 320-325° in a small "molecular still" apparatus at atmospheric pressure for 18-20 hours. After the first 2-3 hours of heating, the liquid polymer had become yellow-brown in color and a few drops of liquid distillate had collected. After 18-20 hours of heating, 4 or 5 drops of distillate had collected, and some long (10-15 mm) crystals had collected in a relatively cool part of the apparatus. The crystals were washed with petroleum ether, and observed to melt at 228-230°; the mixture melting point with authentic tetraphenylsilane was 227-230°. Therefore, it seems clear that one of the decomposition products is tetraphenylsilane.

The polymer sample had lost 0.94 g in weight, or approximately 30% of its initial mass. The residue was a glassy resin, soluble in benzene, but containing some black insoluble material superficially resembling carbon. None of these products have been identified. The several drops of distillate, which appeared to account for the remainder of the weight-loss incurred by the sample, had a powerful organotin odor, but were not identified.

B. TIN SULFIDE POLYMERS

Earlier work on stannoxane polymers led us to investigate the analogous stanthianes:



The simple "organotin sulfides" were prepared by Harada¹⁷ from the dihalides and sodium hydrogen sulfide. We have discovered an alternate preparation involving reaction of sulfur with divalent organotin compounds; this is in many respects more convenient.

Reaction of Dimethyltin with Sulfur

This reaction was investigated as a route to the dimethyltin sulfide, and eventually to copolymeric stanthianes. The reaction

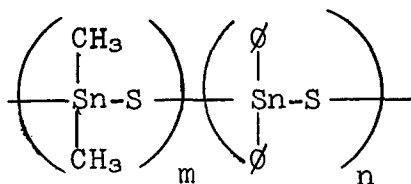
is based on the reported analogous oxidation of dimethyltin to dimethyltin oxide, by oxygen.

Dimethyltin dichloride (21.9 g, 0.1 mole) was placed in a 1-liter 3-necked flask fitted with a high-speed stirrer, a solid CO₂ condenser, and a dropping funnel. About 200 ml liquid ammonia was condensed onto the organotin salt, and 4.6 g (0.2 g-atom) sodium was added in small successive portions with vigorous stirring. A yellow precipitate appeared, but continued stirring resulted in the formation of a brown mixture which did not appear homogeneous. Sulfur (3.2 g, 0.1 g-atom) was added in successive small portions. An obvious reaction took place at once, with various changes in color and appearance manifesting themselves in the reaction mixture. Eventually an all-white mixture resulted. The ammonia was evaporated and the residue extracted with chloroform and filtered. Concentration of the chloroform solution left a small amount of crystalline dimethyltin sulfide, mp 148°.

Reaction of Sulfur with Mixed Dimethyltin and Diphenyltin

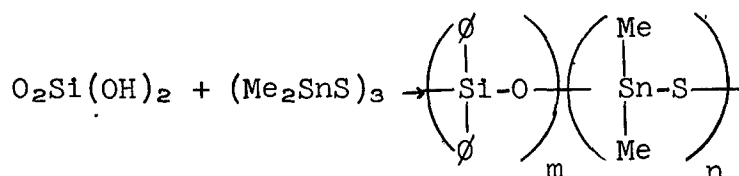
A mixture of 17.2 g (0.05 mole) diphenyltin dichloride and 10.9 g (0.05 mole) dimethyltin dichloride was placed in a 1-liter 3-necked flask with about 100 ml petroleum ether. About 100 ml liquid ammonia was placed in the flask. Sodium metal (4.6 g, 0.2 g-atom) was added in small successive portions. When all the sodium had been added, a yellow and white precipitate was present. Continued stirring resulted in the separation of a brown-black precipitate; a brown solution appeared to form. After about an hours stirring, 5 g (0.156 g-atom) sulfur was added in small portions. The dark color immediately began to fade, and after an hour or so had disappeared, leaving a yellow to tan heterogeneous reaction mixture. The ammonia was vented to the atmosphere, and 250 ml toluene was added to the mixture. The resulting solution was filtered; the clear pale-yellow solution was concentrated by reduced-pressure distillation to leave a thick yellow syrup. This was placed in the vacuum oven overnight. It was then stirred and heated with petroleum ether, which left a solid material undissolved. The mixture was filtered, the insoluble material melted over a wide range in the neighborhood of 150°.

The petroleum ether filtrate was found to contain a yellow oil, which was heated in vacuo overnight to remove traces of solvent. The product was a thick viscous oil, presumably the copolymeric stanthiane:



Reaction of Dimethyl Sulfide with Diphenylsilanediol

In a small beaker were placed 15.0 g (0.08 mole) dimethyltin sulfide and 17.6 g (0.08 mole) diphenylsilanediol. The mixture was heated on a hot plate; it melted to a liquid and was stirred and heated to about 300°. Bubbles of gas, presumably water, were eliminated as the diol condensed. The desired reaction was:



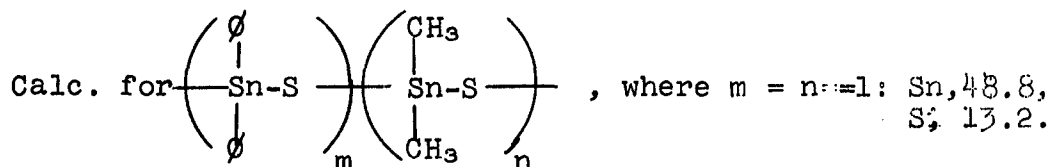
This apparently did not take place to a large extent. As the liquid cooled it set to a white partly-crystalline mass. This was divided into two parts and heated respectively with solid KOH and concentrated sulfuric acid; this treatment did not produce observable results. All the mixtures described above fumed vigorously above about 250° and gave off irritating vapors, presumably organotin sulfides or oxides. The experiment was abandoned.

Reaction of Divalent Organotin Compounds with Sulfur

A mixture of 10.95 g (0.05 mole) dimethyltin dichloride, 51.6 g (0.15 mole) diphenyltin dichloride, and 6.4 g (0.2 g-atom) sulfur was placed in liquid ammonia and allowed to react with 9.2 g (0.4 g-atom) sodium, added in small successive portions with vigorous stirring. The ammonia was vented and the reaction mixture was extracted with toluene and filtered; 39.1 g of a white solid (largely sodium chloride) was separated. The filtrate contained diphenyltin sulfide (75863C), 178°, and a polymer (75863D) which contained tin and sulfur and formed a glassy resin.

Anal. Calc. for $(\phi_2\text{SnS})_n$: Sn, 38.8; S, 10.5.

Found for 75863C: Sn, 37.75; S, 10.94.



Found: for 75863D: Sn,
45.18; S, 14.16.

This agreement is probably close enough for a compound of this sort.

C. STERICALLY HINDERED MONOMERS

Preparation of Neophyltin Dichloride

By Sodium Condensation. The procedure employed was basically that of van der Kerk and Luijten²⁶ Sodium "sand" (20 g, 0.87 g-atom) was prepared by stirring in boiling dioxan and allowed to cool to room temperature. The dioxane was removed by forcing it through a fritted glass filter stick, and about 300 ml sodium-dried petroleum ether was added to the sodium in a 3-necked flask fitted with a stirrer, condenser, and addition funnel. A mixture of 57.2 g (0.22 mole) stannic chloride, 72.5 g (0.44 mole) neophyl chloride, and 200 ml petroleum ether was placed in the addition funnel and added dropwise to the sodium with vigorous stirring. A white waxy deposit appeared on the sides of the reaction flask (presumably the addition product formed by stannic chloride with residual dioxane) and a gray-black precipitate formed. No heat was generated, so a heating mantle was employed to maintain reflux temperature. Refluxing and stirring were continued for about 2 hours after the addition of reagents was complete. The mixture was then filtered (fluted paper) and the filtrate distilled. The black precipitate on the paper contained considerable active sodium which was destroyed with alcohol and benzene. This mixture was filtered and the solid material extracted with a further portion of hot benzene, which was added to the filtrate; this solution was concentrated to a heavy oil which could not be induced to crystallize. The oil was dissolved in 2B ethanol and ammonium hydroxide was added; a copious white precipitate appeared. This was dissolved in concentrated hydrochloric acid by heating. Subsequent cooling deposited a white crystalline compound of very limited solubility and very high melting point.

By the Grignard Route. An attempt was made in the usual manner to prepare a Grignard reagent from 33.9 g (0.2 mole) neophyl chloride and 4.86 g (0.2 g-atom) magnesium in 400 ml tetrahydrofuran. The reaction proceeded very slowly, and it was necessary to heat the mixture externally throughout the entire reaction period in order to dissolve the magnesium. After about six hours reaction time, a sample of the reaction mixture was treated with excess standard acid and back-titrated with base; no Grignard reagent was present. Apparently, the magnesium had reacted by reduction, coupling, or dehydrohalogenation reactions. Apparently the Wurtz reaction described above is a more promising possibility for this synthesis.

By Reaction of Diphenyltin Disodium with Neophyl Chloride. Dineophyldiphenyltin would provide an excellent route to dineophyltin dichloride, for the phenyl groups should be readily cleaved by treatment with halogen or hydrogen halide.

Diphenyltin disodium was prepared by addition of 9.2 g (0.4 g-atom) sodium metal in small portions to 34.3 g (0.1 mole) diphenyltin dichloride in about 200 ml liquid ammonia. The mixture became brown, then reddish, next deep red-brown, and eventually black. A solution of 33.7 g (0.2 mole) neophyl chloride in about 100 ml benzene was added; not all the color disappeared, the mixture remaining light brown. Additional benzene was added and the ammonia was allowed to evaporate. The benzene solution resulting from filtration of this mixture was concentrated by distillation to leave a yellow opaque liquid. Some unreacted neophyl chloride was recovered by subjecting this material to distillation at about 0.2 mm pressure; a soft waxy yellow-colored bottoms remained, which is probably the desired product. It weighed 18-20 g.

Ten grams of this material was dissolved in about 100 ml 2B ethanol. A small amount of insoluble white precipitate was discarded. About 30 ml concentrated hydrochloric acid was added to the alcohol solution and the mixture was boiled 15-20 minutes and allowed to stand. A clear colorless oil separated but could not be induced to crystallize. An alcoholic solution was treated with excess concentrated ammonium hydroxide and filtered to remove a small amount of white insoluble solid. Concentration of the filtrate produced a white crystalline solid which weighed 5 g and melted at 132°. Recrystallization from ethanol gave a product melting at 120-121°.

Anal. Calc. for $[\text{C}(\text{CH}_3)_2\text{CH}_2]_2\text{SnOH}_2$: Sn, 28.3; C, 57.3;
H, 6.7.
Found: Sn, 31.4; C, 50.2;
H, 5.9.

This agreement is not good, but it is closer for the expected compound than for any other likely compound.

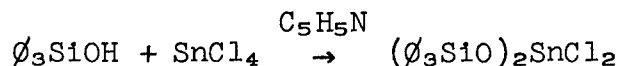
Reaction of Dimethyltin Disodium with Neophyl Chloride.

It was thought that a convenient method of synthesis of dineophyltin dichloride would involve preparation of dimethyldineophyltin by reaction of neophyl chloride with dimethyltin disodium followed by cleavage of the methyl groups, which should be split off preferentially by either HCl or chlorine.

Dimethyltin disodium (0.1 mole) was prepared as described above. A benzene solution of 33.7 g (0.2 mole) neophyl chloride was added in successive small portions over about an hour. Stirring was continued for another hour, and then the ammonia was evaporated from the mixture. The mixture was filtered to remove sodium chloride and the filtrate was concentrated to leave a yellow semi-solid wax which could not be induced to crystallize.

Reaction of Triphenylsilanol with Stannic Chloride.

The desired reaction is



Stannic chloride (13.0 g, 0.05 mole) and 27.6 g (0.1 mole) triphenylsilanol were dissolved in 50 ml dry benzene; 7.9 g (0.1 mole) pyridine was added, whereupon a white precipitate appeared. The mixture was refluxed 15-30 minutes and filtered; the white precipitate weighed 24 g, which is about twice as much as the desired pyridine hydrochloride should have weighed. The filtrate was concentrated to a low volume by distillation, and the resulting colorless oil was left to stand overnight, during which time it crystallized. The product weighed 11 g; mp 47-49°. The compound was recrystallized from 2B ethanol and dried in vacuo; it melted over the range 67-71°. Another recrystallization left a product melting at 69-71°.

Calc. for $(\text{O}_3\text{SiO})_2\text{SnCl}_2$: Si, 7.6; Sn, 16.0; Cl, 9.6.

Found: Si, 12.97; Sn, 0.2; Cl, 0.5.

This product is obviously not the desired bis-(triphenyl-siloxy)tin dichloride. The identity of the compound is not known. However, only 2-3 g of this compound was obtained. More of the reaction product probably ended up in the insoluble product described above.

Evaporation of the combined mother liquors from the above recrystallization left a colorless oil; final traces of solvent were removed in vacuo to leave a viscous transparent fluid. Analyses are not available on this compound.

D. TIN ALKYLENE POLYMERS

Reactions of Difunctional Halides with Metallated Organometallics

An excellent method for preparing polymers containing organometallic backbones involves reaction of a difunctional halide with a "metallated" organometallic, such as dimethyltin disodium. Reactions of the latter with a series of halides were studied - not only to produce polymers but also in some cases to synthesize monomeric tin derivatives containing bulky groups. Throughout these experiments the dimethyltin disodium was prepared in liquid ammonia, by a technique analogous to that employed above for the preparation of dimethyltin.

Reactions of Dimethyltin Disodium with 1-Bromo-4-Chlorobenzene.

Sodium metal (9.2 g, 0.4 g-atom) was added to 21.9 g (0.1 mole) dimethyltin dichloride in liquid ammonia. A deep red - almost black - color was formed when all the sodium had been added. 1-Bromo-4-chlorobenzene (19.1 g, 0.1 mole) was dissolved in about 100 ml benzene and added dropwise to the stirred reaction mixture. The red color was gradually discharged as the reaction proceeded; finally an additional 100 ml benzene was added and the ammonia was allowed to evaporate. The resulting mixture was filtered, and the cake was washed with hot benzene. The benzene filtrate was concentrated by distillation to leave finally a brown tar or wax. This material was cleaned up to some degree by trituration with petroleum ether, which produced a light colored insoluble solid.

The filter cake was dissolved in water and found to contain halogen. A bromine test, carried out by addition of carbon tetrachloride and chlorine water to the solution, was positive, indicating that the bromine end, at least, of the starting material had reacted. This is interesting as it had been strongly suggested to us that aromatic halides would not react with the disodium derivative. The actual identity of the product, however, was not ascertained.

Reaction of Diphenyltin Disodium with 1,4-Dibromobenzene.

Diphenyltin disodium was prepared by addition of 9.6 g (0.4 g-atom) sodium metal to 34.3 g (0.1 mole) diphenyltin dichloride in about 250 ml liquid ammonia. A solution of 24.6 g (0.104 mole) p-dibromobenzene in 250 ml petroleum ether was slowly added via an addition

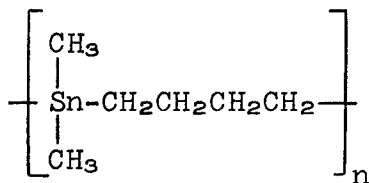
funnel.. Reaction proceeded vigorously, with discharge of the deep red color. When all reagents had been added a little yellow-brown color still remained. Addition of a small amount of dibromobenzene did not remove the color. The ammonia was vented and 300 ml toluene and 250 ml water were added. Addition of the water resulted in reaction - possibly hydrolysis of Sn-Na end groups. A thick stable emulsion resulted, which was gradually separated into a clear organic phase, an aqueous phase, and a stable emulsion. The aqueous phase was discarded. Evaporation of the solvents from the organic solution and from the emulsion left tan-colored powders which would not melt but which decomposed on the hot plate at a high temperature with a resulting irritating organotin odor.

Reaction of Dimethyltin Disodium with Methyl Bromoacetate.

This reaction should give rise to dimethyl-bis-carbomethoxymethyltin. Such compounds have been reported to be unstable but it was thought worthwhile to carry out the reaction in case the relatively mild conditions might permit isolation of the compound. The reaction was carried out using 0.05 mole dimethyltin disodium and 15.7 g (0.1 mole) methyl bromoacetate dissolved in 100 ml or so of benzene. The resulting reaction was quite vigorous. The mixture was filtered and the solid precipitate discarded. The filtrate was concentrated at reduced pressure to leave a yellow solid. This was found to contain 72% Sn and is presumably dimethyltin contaminated with a small amount of dimethyltin oxide.

Reaction of Dimethyltin Disodium with 1,4-Dibromobutane.

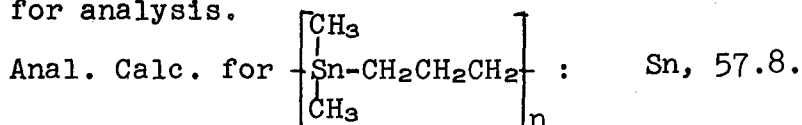
The reaction of 1,4-dibromobutane with dimethyltin disodium would be expected to produce a polymeric tin-alkylene structure:



Dimethyltin disodium (0.1 mole) was prepared in liquid ammonia in the usual manner. To this was added a solution of 21.6 g (0.1 mole) 1,4-dibromobutane in about 100 ml petroleum ether (bp 30-60°). (This is a vastly more suitable solvent than the benzene used previously because of its much lower freezing point; some difficulty was experienced in working up the benzene-containing mixtures because of freezing.) The deep red color was essentially all gone when only about 20% of the dihalide had been added; this is difficult to explain. When all the reagent had been added, the mixture was white in appearance. The mixture was stirred for about half an hour, and

the the ammonia and petroleum ether were driven off on a water bath. The remaining solid mass was extracted with water; this left a two-liquid phase system. About 500 ml ether was added and the mixture was shaken and separated. The ether solution was dried over sodium sulfate, filtered, and concentrated by distillation. When all the solvent had been evaporated a light oil, almost clear and colorless remained. On standing, this material separated into two phases - the lower being quite viscous and the upper fairly mobile. On further standing, however, the upper layer also became quite viscous and after several days would not flow appreciably.

A sample of the upper layer was separated mechanically and submitted for analysis.



Found: Sn, 54.4.

Reaction of Dimethyltin Disodium with α,α -Dichlorotoluene.

This reaction was carried out in a manner analogous to that described above using 0.1 mole dimethyltin disodium and 16.1 g (0.1 mole) α,α -dichlorotoluene in about 100 ml petroleum ether. The red color of the disodium reagent was partially discharged, indicating that a reaction was taking place, but when all the dichlorotoluene had been added the reaction mixture was still decidedly red in color. This discrepancy has not been accounted for unless, perhaps, the toluene was impure (no effort was made to purify it before reaction). The reaction mixture was worked up by addition of water and ether. Subsequent evaporation of the layer left a mobile yellow oil.

Reaction of Dimethyltin Disodium with Methyl Iodide. Dimethyltin disodium was prepared by reaction of 9.2 g (0.4 g-atom) sodium metal with 21.9 g (0.1 mole) dimethyltin dichloride in liquid ammonia. A solution of 29 g (0.2 mole) methyl iodide in 100 ml petroleum ether was added slowly with vigorous stirring. The deep red-black color of the sodiostannane was readily discharged. The reaction mixture was distilled through a small helices-packed fractionating column, and the fraction boiling at 74-78° was collected. Only a few milliliters of product was obtained; n_D^{20} 1.3842. The refractive index for tetramethyltin is reported to be 1.5201, so that obviously this product is not tetramethyltin. Another run using slightly different conditions gave similar results. It is apparent that the reaction is not so clear-cut as the literature would lead one to believe. Further investigation is necessary.

Reaction of Sodium Metal with Dimethyltin Dichloride in Diglyme

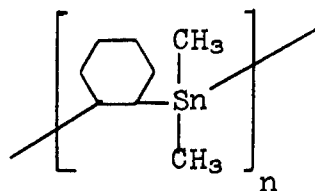
The reaction of sodium with dimethyltin dichloride in liquid ammonia solution is well known; however, there would be some advantage

to the use of ether solvents. We have previously investigated the use of toluene as a solvent, but without success. The fact that sodium appears to be somewhat soluble in diglyme led us to speculate that this solvent might serve in the indicated reaction.

In a 1-liter 3-necked flask fitted with a condenser, stirrer, and dropping funnel were placed 10.9 g (0.05 mole) dimethyltin dichloride and about 200 ml dry diglyme. The mixture was stirred and 4.6 g (0.2 g-atom) sodium added in small pieces. No reaction took place until the mixture was heated, whereupon a rapid reaction took place, apparently involving reduction of the tin compounds present. A black precipitate appeared; this material was quite active with water, liberating a gas, and was probably a sodium-tin alloy. The experiment was abandoned.

Reaction of Dimethyltin with Cyclohexene in Liquid Ammonia

The dialkyltins are polymeric materials which are quite reactive to halides, oxygen, and certain other reagents (although not particularly to water or alcohols). It was thought that in a monomeric state, as a sort of reactive intermediate, these dialkyltins should be extremely reactive - similar, in fact, to the carbenes, whose structure they resemble in a formal sense. It was decided to study the reaction of dimethyltin in a nascent state with olefins, the most available of which was cyclohexene. A carbene would form a substituted cyclopropane; this would not be so likely for the corresponding tin compound, which might on the other hand form a linear polymer of the type:



Dimethyltin dichloride (21.9 g, 0.1 mole) was placed in a 1-liter 3-necked flask and about 200 ml ammonia condensed onto it. About 9 g (0.11 mole) cyclohexene was added, and 4.6 g (0.2 g-atom) sodium metal was added with vigorous stirring in successive small portions. A yellow precipitate formed. When all the sodium had been added a small amount of red color appeared, which was slowly discharged as stirring was continued. (This was due, no doubt, to the formation of small amounts of dimethyltin disodium.) After about 2 hours additional stirring, 100 ml 2B ethanol was added to the mixture to destroy any excess sodium or other active compounds. The ammonia was allowed to evaporate, leaving an alcoholic system containing a yellow precipitate. The yellow solid was separated by

filtration, boiled with water to remove sodium chloride, washed with alcohol, and allowed to dry in the air. A sample left on filter paper overnight charred the paper and itself; it apparently oxidizes slowly but generates considerable heat. This behavior is characteristic of polymeric dimethyltin. Thus, there was probably very little reaction with the olefin under the conditions stated.

E. POLYMERS FROM TRIALKYL ALUMINUMS

Reaction of Triethylaluminum with Triphenylsilanol

Triethylaluminum (3.4 g, 0.03 mole) was dissolved in 100 ml benzene in a dropping funnel and added to a solution of 27.6 g (0.1 mole) triphenylsilanol in 250 ml benzene. The reaction was carried out in a 1-liter 3-necked flask fitted with a high-speed stirrer and a condenser. About half the triethylaluminum solution was added with evolution of only a small amount of gas. A gas burette was connected to the system and the mixture was warmed; gas was evolved more rapidly, and heat was generated. About an hour was required for total addition of reagents. Two liters of evolved gas was measured, and a little was lost at the beginning of the reaction; theoretical gas evolution was 0.1 mole or about 2300 ml. The clear solution was filtered to remove traces of solids, and concentrated to a low volume by distillation. Final traces of solvent were removed at reduced pressure. A viscous syrup was left, which cooled to a brittle resin.

Anal. Calc. for $\text{Al}(\text{OSi}\phi_3)_3$: Si, 9.86; Al, 3.17.
Found: Si, 13.77; Al, 2.76.

The actual structure and the course of the reaction have not been determined.

Reaction of Ethylaluminum Oxide with Triphenylsilanol

Another reaction which should have produced tris(triphenylsiloxy)aluminum was that of triphenylsilanol with ethylaluminum oxide. Ethylaluminum oxide (3.5 g or 0.05 mole) was placed in 50 ml ethylene glycol dimethyl ether and 41.4 g (0.15 mole) triphenylsilanol was added. A vigorous evolution of gas, undoubtedly ethane, immediately took place. The mixture was then refluxed about 24 hours and concentrated partially by distillation. The viscous mixture was diluted with benzene and filtered. The filtrate was poured into excess petroleum ether; a white semi-solid precipitation appeared. By repeated solution in benzene and reprecipitation from petroleum ether, a white powdery solid (7 g) was obtained; this was soluble in organic solvents and insoluble in water. It did not melt, but charred on heating in a direct flame. The expected product was $(\phi_3\text{SiO})_3\text{Al}$.

Anal. Calc. for $(\phi_3\text{SiO})_3\text{Al}$: Al, 3.1; Si, 9.9.
Found: Al, 7.94; Si, 11.08.

Obviously the compound was not tris(triphenylsiloxy)aluminum. Evidently these reactions of ethylaluminum compounds with silanols form complex products, and may well follow an entirely different course than that anticipated.

Evaporation of the combined mother liquid left 22 g of a brown resin which melted at 140-150° and decomposed below 250°

It is interesting to compare these results with those recently reported by Goodrich (WADCTR 55-453), who prepared tris (triphenylsiloxyaluminum) by reaction of sodium triphenylsilanolate with aluminum chloride. They report a white solid, melting ca. 485°, soluble in benzene but insoluble in ether. Our product was soluble in both ether and benzene (and other solvents) but would not melt. Both compounds showed considerable thermal stability. It might be wise to prepare the compound from triphenylsilanol and triethylaluminum, for comparison purposes.

Reaction of Triphenylsilanol and Diphenylsilanediol with Ethylaluminum Oxide.

In a 250-ml flask in a nitrogen box were placed 100 ml dioxan, 3.6 g (0.05 mole) ethylaluminum oxide, and 13.8 g (0.05 mole) triphenylsilanol. When reaction had subsided, 21.6 g (0.1 mole) diphenylsilanediol was added and the mixture refluxed for 8-10 hours. The resulting clear solution was concentrated by distillation to a heavy syrup; this was dissolved in benzene and added to an excess of petroleum ether, which precipitated a white solid.

Anal. Calc. for $(\text{Al-O})_2\text{Si-O-}$: Al, 6.48; Si, 10.08.
 $\begin{array}{c} \phi \\ | \\ \text{OSi}\phi_3 \\ | \\ \phi \end{array}$

Found: Si, 13.34; Al, 6.34.

This compound is probably contaminated with a siloxane resin, as no combination of the possible groups permits as much silicon as the analysis indicates.

Evaporation of the petroleum ether solution left a resin which was not analyzed.

Reaction of Ethylaluminum Oxide Polymer with Triphenylsilanol.

The apparatus, consisting of a 300-ml 3-necked flask equipped with a condenser, stirrer and side-arm addition funnel, was dried by heating with a gas flame while passing through a stream

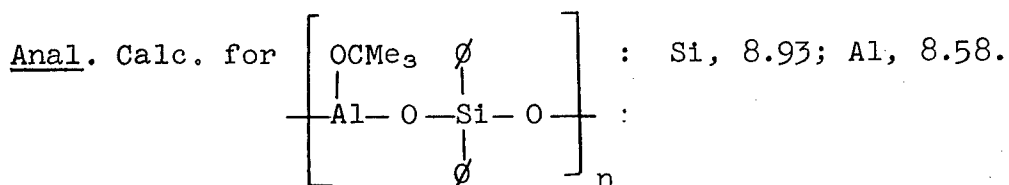
of dry nitrogen. A solution of 10 ml (8.40 g, 0.0736 mole) of triethylaluminum in 50 ml of anhydrous 1,2-dimethoxyethane was added to the reaction flask and heated to reflux temperature. A wet test meter was connected to the condenser and 1.32 g (0.0733 mole) of distilled water (degassed by bubbling nitrogen through) in 100 ml of anhydrous 1,2-dimethoxyethane was added dropwise, while stirring and refluxing, over a period of 1.2 hours. A total of 0.111 cu ft of gas (98% of theoretical) was evolved. To the solution was added 20.3 g (0.0733 mole) of triphenylsilanol. The resulting solution was refluxed and stirred for 20 hours. (Unfortunately, the connection to the test meter developed a leak so an accurate gas measurement was not obtained.) The solvent was distilled and the residue dried at reduced pressure to give 23.4 g of white powder. The solid was dissolved in benzene and filtered to remove some aluminum oxide. Three fractions of precipitate were obtained by adding portions of petroleum ether (60-70°): (1) 12.30 g of white powder; (2) 3.25 g of solids; and (3) after reducing the volume of the mother liquor to about 20 ml and adding 20 ml of petroleum ether, 4.00 g of solid was obtained. The first fraction was mainly triphenylsilanol by infrared analysis and decomposition at 250°). The second fraction decomposed around 270°, and the third at greater than 400°. The last fraction was fairly stable toward acid and base (qualitative, not quantitative).

Anal. Calc. for $\left[\begin{array}{c} \text{OSi}\phi_3 \\ | \\ \text{Al-O} \end{array} \right]_n$: Si, 8.82; Al, 8.470.

Found: Si, 13.82; Al, 8.93.

Hydrolysis of Triethylaluminum with Diphenylsilanediol and t-Butanol.

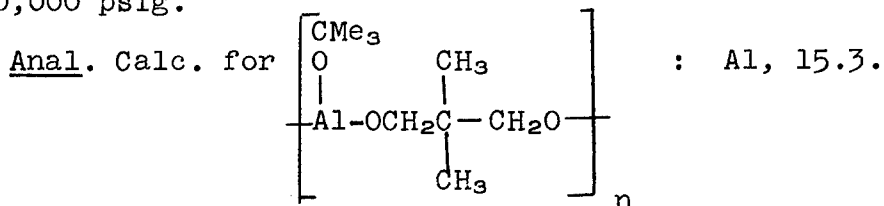
The same apparatus and precautions to insure dryness and exclusion of oxygen were used as described above. A solution of diphenylsilanediol (15.8 g, 0.0731 mole) in 50 ml of 1,2-dimethoxyethane was added dropwise over a period of 45 minutes to a stirred solution of triethylaluminum (10 ml, 8.40 g, 0.0736 mole) in 25 ml of 1,2-dimethoxyethane at reflux temperature. A total of 0.120 cu ft of gas was evolved (103% of theoretical) at the end of 130 minutes. Anhydrous t-butanol (6.0 g, 0.081 mole) was added dropwise and the heating and stirring was continued for 2.5 hours. A 105% gas evolution was measured but it is believed that a fair amount of solvent was entrapped. The solvent was distilled and the residue was dried in vacuo. A small portion dissolved in acetone evolved a gas when water was added. In order to insure complete reaction, the residue was heated with 100 ml of freshly distilled t-butanol and 50 ml of 1,2-dimethoxyethane for 18 hours. The solvent and excess t-butanol were distilled and the residue was dried in vacuo to give a white powder, decomposing at 250° without melting.



Found: Si, 11.87; Al, 10.81.

Reaction of Triethylaluminum with 2,2-Dimethyl-1,3-Propanediol and t-Butanol.

The same apparatus and precautions described above were followed except a Dry-Ice trap was inserted between the apparatus and test meter. A solution of 2,2-dimethyl-1,3-propanediol (7.65 g, 0.0735 mole) in 30 ml of anhydrous 1,2-dimethoxyethane was added to a stirred solution of triethylaluminum (10 ml, 0.0736 mole) in 50 ml of 1,2-dimethoxyethane to give a 96% gas evolution. Then dry t-butanol (7.9 g, 0.107 mole) was added dropwise. After this addition was complete the resulting solution was heated at reflux temperature for 17 hours to give a 55% gas evolution. Most of the solvent was distilled and 50 ml of t-butanol was added. The solution was heated to about 90° and stirred for 4.5 hours to give 7% more gas evolution. The solvent was evaporated in a nitrogen atmosphere and the residue dried in vacuo. The formed polymer was stable up to 300° and did not fuse, even at 40,000 psig.

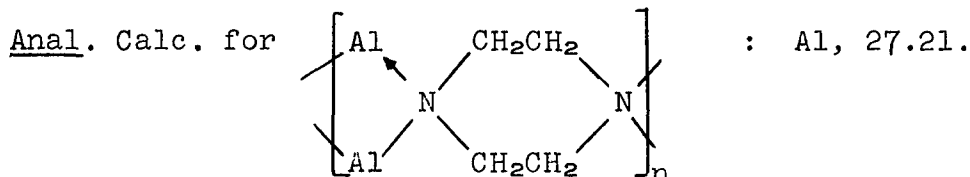


Found: Al, 14.32.

Reaction of Trimethylaluminum with Piperazine.

A mixture of anhydrous piperazine (8.6 g, 0.1 mole), trimethylaluminum (7.44 g, 0.103 mole) and 50 ml of dry xylene was charged in a 100-ml round bottomed flask in a dry box with a nitrogen atmosphere. The reaction flask was connected to a condenser with nitrogen purge. The flask was heated in an oil bath at 126° for 4 hours and then at 100° for 16 hours. At the start everything went into solution and then a solid slowly formed. The reaction flask was transferred to the dry box and the solid was filtered on a sintered glass funnel. After washing three times with dry xylene and drying in a vacuum desiccator, 7.8 g of product was obtained. It did not fuse when heated

on a spatula with a flame. After the spatula turned red the material decomposed. It is insoluble in hydrocarbon solvents, acetone, alcohol and ether.



Found: Al, 26.43.

F. POLYMERS FROM DIAKYLALUMINUM ALKOXIDES

Preparation of Monomers

Preparation of Dimethylaluminum-*t*-Butoxide. The reaction was carried out in a dry box with a nitrogen atmosphere. A solution of anhydrous *t*-butanol (37.30 g, 0.503 mole) in 30 ml of 1,2-dimethoxyethane was added dropwise, with swirling, to trimethylaluminum (36.25 g, 0.503 mole) over a period of 8 hours. The solvent was distilled in a nitrogen atmosphere and the residue was heated to 210° with an oil bath. Nothing distilled, so the bath was cooled to 140° and the pressure was reduced to 20 mm. The material distilled at 100° but solidified in the condenser. The apparatus was changed to a Claisen-type head with an elbow leading to a 3-necked flask and the material was quickly distilled at 15 mm to give 60.1 g of waxy solid (94.5% yield).

Anal. Calc. for $[\text{Me}_2\text{AlO}(\text{t-Bu})]_3$: Al, 20.76; mol wt, 390.
Found: Al, 20.76; mol wt, 397.

Preparation of Dimethylaluminum-2,6-di-*t*-Butylphenoxide. In a dry box with a nitrogen atmosphere a solution of 2,6-di-*t*-butylphenol (21.9 g, 0.102 mole) in 30 ml of dry heptane was added, with swirling, to trimethylaluminum (25 ml, 18.6 g, 0.257 mole). The solvent and excess trimethylaluminum was distilled and the residue was heated at 1 mm with an oil bath temperature of 150° to remove residual unreacted material. Nitrogen was bled into the flask and upon cooling a very viscous material was obtained. Attempts to distill this material gave decomposition.

Anal. Calc. for $[\text{Me}_2\text{AlOC}_6\text{H}_3(\text{t-Bu})_2]_3$: Al, 10.30; mol wt, 786.
Found: Al, 8.86; mol wt, (cryoscopic from benzene 854, from dioxane, 727).

Hydrolysis of Monomers

Hydrolysis of Trimethylsiloxydimethylaluminum with Diphenylsilanediol. The entire reaction was carried out in a nitrogen atmosphere. A solution of diphenylsilanediol (10.6 g, 0.0495 mole) in 40 ml of 1,2-dimethoxyethane was added dropwise to a stirred solution of trimethylsiloxydimethylaluminum (7.23 g, 0.0495 mole) in 30 ml of 1,2-dimethoxyethane over a period of 1.5 hours to give a 103% gas evolution. The solvent was distilled and the residue was dissolved in benzene. A white flocculent precipitate was obtained when the benzene solution was diluted with petroleum ether (30-60°). The solution was suction filtered and dried in a vacuum desiccator to give 2.5 g of white solid. The mother liquor was evaporated and the solid was dried in vacuo to give 11.3 g of white solid. A solution of the solid petroleum ether left a brittle film. When some powder was heated to 250° no apparent decomposition took place and the material was no longer soluble in petroleum ether. At 300° the sample decomposed with the formation of hexamethyldisiloxane and benzene.

Anal. Found: Al, 7.13; Si, 17.00; mol wt, 798.

Hydrolysis of Trimethylsiloxydimethylaluminum with 2,2-Dimethyl-1,3-Propanediol. A solution of 2,2-dimethyl-1,3-propanediol (5.00 g, 0.048 mole) in 20 ml of anhydrous 1,2-dimethoxyethane was added dropwise to a stirred solution of trimethylsiloxydimethylaluminum (7.00 g, 0.048 mole) in 20 ml of 1,2-dimethoxyethane in a nitrogen atmosphere to give a 96% gas evolution. The reaction mass was a gel. The solvent was removed by heating the pot and passing through a stream of dry nitrogen and then it was further removed in a vacuum desiccator. The polymer was a white powder stable up to 300°. It was infusible (even at 300° and 40,000 psig) and insoluble in organic solvents.

Anal. Found: Al, 11.88; Si, 15.10.

Hydrolysis of Dimethylaluminum-2,6-di-t-butylphenoxide with 1,5-Pentanediol. In a dry box with a nitrogen atmosphere, a 300-ml 3-necked flask was charged with a dimethylaluminum-2,6-di-t-butylphenoxide (10 g, 0.0381 mole) in 100 ml of dry xylene, and a side-arm addition funnel with 1,5-pentanediol (3.96 g, 0.0381 mole) in 50 ml of xylene and 25 ml of 1,2-dimethoxyethane. The apparatus was transferred to the hood and connected to a condenser. A wet-test meter was joined to the condenser through a Dry-Ice trap. The pot was heated to reflux while stirring with a magnetic stirrer and the meter was adjusted to zero. The diol was added dropwise and the solution was refluxed for 16 hours. A total of 0.020 cu ft (37% yield) of gas evolved. About half of the solvent was distilled, leaving a gelatinous material. The excess xylene was decanted and the residue was dried at

85° (1 mm) in an evacuated oven. Every 30 minutes nitrogen was bled into the oven and the oven was re-evacuated. A white powder remained which evolved some gas when a drop of water was added to an acetone solution.

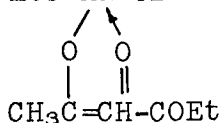
G. ALUMINUM CHELATE POLYMERS

Preparation of Chelates

Reaction of Aluminum Ethoxide with 2,4-Pentanedione. The aluminum ethoxide was purified by distillation according to Org. Syn., Col. Vol. II, 599. A gas chromatogram of the 2,4-pentanedione showed a purity of 99.5%. The reaction was carried out in a nitrogen atmosphere. A mixture of aluminum ethoxide (47.8g, 0.299 mole) and 2,4-pentanedione (29.0 g, 0.290 mole) was charged in a flask fitted with a 12-inch Vigreux column with a condenser and receiver. The flask was heated to 140° with an oil bath and 12.4 g of distillate was collected rapidly, bp 79-82°. A gas chromatogram of the distillate showed it to contain 96 mole % ethane, 3 mole % ethylacetate, and 1.0 mole % of an unidentified component. The residue was heated to 165° at 1 mm pressure but nothing distilled. Upon cooling, an orange glass formed. Exposure to moisture caused decomposition.

Preparation of Diethoxyaluminum Acetoacetate. In a nitrogen atmosphere, aluminum ethoxide (64.4 g, 0.398 mole) and 30 ml of dry xylene were heated at 150° with an oil bath until homogeneous. Then ethyl acetoacetate (51.7 g, 0.397 mole) in 20 ml of dry xylene was added dropwise. The alcohol was distilled and the pot was heated to 185° and about 10 ml of xylene was collected. The pressure was reduced and the remaining xylene was removed. The residue distilled at 167-171° (0.2 mm) with a pot temperature of 210° to give 46.1 g of a very viscous pale yellow material which set to a brittle glass upon cooling. The cryoscopic molecular weight determination from benzene gave values of 667 and 703 while the calculated value is 246.

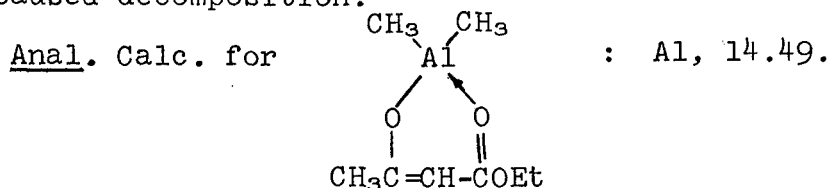
Anal. Calc. for EtO-Al-OEt : Al, 10.95.



Found: Al, 10.86.

Reaction of Trimethylaluminum with Ethyl Acetoacetate. The experiment was conducted under anhydrous conditions in a nitrogen atmosphere. A mixture of ethyl acetoacetate (6.50 g, 0.05 mole) and 75 ml of heptane was added dropwise to 25 ml of trimethylaluminum

(14.9 g, 0.20 mole) while stirring with a magnetic stirrer. The solvent and excess trimethylaluminum were removed at reduced pressure and the residue was distilled to give 4.3 g of a colorless liquid, bp 35-37 (1 mm). Exposure to light, air, or moisture caused decomposition.



Found: Al, 13.80.

Reaction of Trimethylaluminum with 2,4-Pentanedione. The experiment was conducted under anhydrous conditions in a nitrogen atmosphere. A solution of 2,4-pentanedione (20.0 g, 0.2 mole) in 30 ml of 1,2-dimethoxyethane was added dropwise, with stirring, to 50 ml of trimethylaluminum (37.2 g, 0.515 mole). The excess trimethylaluminum and solvent were removed at reduced pressure, leaving a dark red residue. Upon cooling, the residue solidified to a brittle glass.

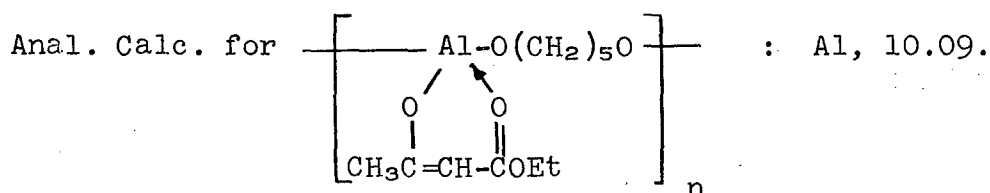
Preparation of (2-Methoxyethyl) Phenylmalonate. A solution of diethyl phenylmalonate (70.8 g, 0.3 mole), 2-methoxyethanol (69.4 g, 0.9 mole), p-toluenesulphonic acid monohydrate (5 g), and 20 ml of benzene was refluxed in a 4-foot column. Distillate was collected until the head temperature reached 124°. The pot was extracted with a saturated sodium chloride solution (ether was added to break an emulsion). The ether was distilled and the residue distilled to give 69.4 g (78% yield) of product, bp 165-167 (0.25 mm).

Reaction of Trimethylaluminum with Di(2-Methoxyethyl) Phenylmalonate. A solution of diester (15.2 g, 0.0514 mole) in 20 ml of benzene and 100 ml of petroleum ether (30-60°) was added dropwise over a period of 10 hours to trimethylaluminum (5 ml, 3.72 g, 0.051 mole) in 300 ml of petroleum ether. After stirring for 16 hours, the solvent was distilled with an oil bath temperature of 90°. The residue was heated to 95° at 0.6 mm to remove traces of solvent, leaving a viscous yellow liquid with a molecular weight from benzene of 541 and 513.

Reaction of Trimethylaluminum (excess) with Di(2-Methoxyethyl) Phenylmalonate. A solution of diester (15.2 g, 0.0514 mole) in 100 ml of benzene was added dropwise to trimethylaluminum (10 ml, 7.44 g, 0.103 mole) while stirring with a magnetic stirrer. The benzene was distilled at reduced pressure and the residue was heated at 50° at 0.8 mm for three hours. None of the excess trimethylaluminum was detected in the distillate or Dry Ice traps. The residue was a yellow viscous material.

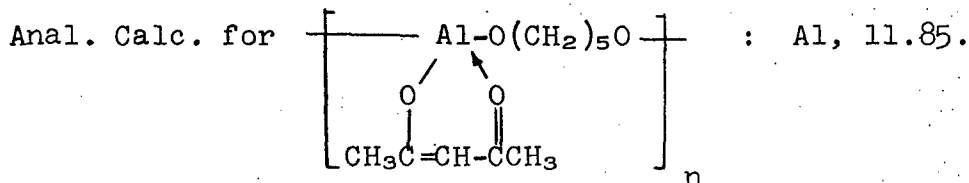
Hydrolysis of Chelates

Reaction of Aluminum Ethoxide with Ethyl Acetoacetate and 1,5-Pentanediol. A mixture of 40 ml of dry xylene and aluminum ethoxide (46.0 g, 0.284 mole) was heated in a nitrogen atmosphere until homogeneous and then a solution of ethyl acetoacetate in 20 ml of dry xylene was added dropwise. A total of 14.0 g (theoretical, 13.1 g) of distillate was collected (some xylene was included), bp 78-82°. About 10 ml of xylene was distilled and 1,5-pentanediol (29.6 g, 0.284 mole) was added dropwise. A total of 22.1 g of alcohol was collected, bp 78-81°, and then 10 ml of xylene. The remaining xylene was removed at reduced pressure and the residue was dried in a vacuum oven by alternately bleeding in dry nitrogen and evacuating the oven.



Found: Al, 10.67.

Reaction of Aluminum Ethoxide-2,4-Pentanedione Product with 1,5-Pentanediol. The glass obtained was melted and then pentanediol (26 g, 0.255 mole) was added and the mixture was stirred. A total of 18.5 g of alcohol distilled (theoretical, 23.4 g). Dry xylene (40 ml) was added and the mixture was heated, with stirring, until about 10 ml of xylene had distilled. The liquid was decanted and the solid dried in a vacuum oven at 90° (2 mm) to give 6.5 g of yellow solid. Evaporation of the liquid under reduced pressure left a yellow solid which was dried in the vacuum oven at 110° to give 40.1 g of solid. Heat alone did not cause the material to soften but by applying 35,000 psig at 270°F, a brittle film could be formed. Once the film is formed, the temperature requirements for fusing are increased. A sample left exposed to the atmosphere slowly formed a gummy material.

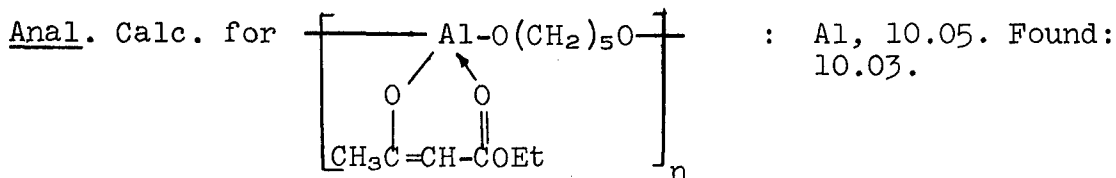


Found: Al, 10.94.

This material resembles the one prepared from 2,4-pentanedione except its initial softening point is 350°F (30,000 psig). About half of the sample was heated at 210° in vacuo with a slow nitrogen bleed for 3 hours. No fusion was noted, so an open flame

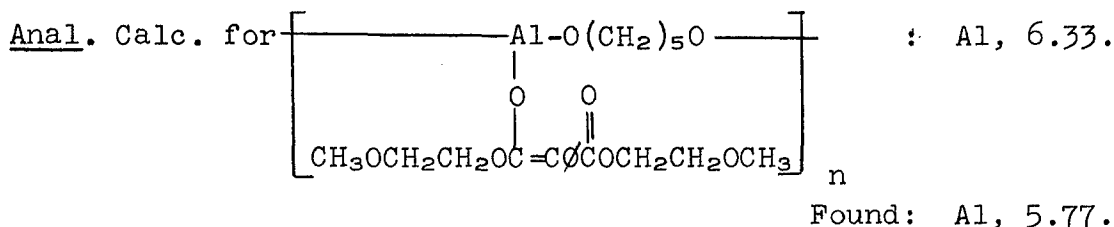
was used. No softening was noted even at the point where decomposition started. However, the heat-treated polymer could be fused at 450°F and 40,000 psig.

Reaction of Diethoxyaluminum (Ethyl Acetoacetate) with 1,5-Pentanediol. A mixture of 1,5-pentanediol (1.90 g, 0.01825 mole) and the chelate (4.18 g, 0.01825 mole) was placed in a flask with a capillary tube extending down into the mixture. Nitrogen was slowly bubbled into the mixture and the temperature was raised to 150° in an oil bath. After 2 hours the temperature was increased slowly. At 230° the solid began to turn yellow and the odor of ethyl acetoacetate could be detected. A characteristic infusible and insoluble solid was obtained.



Reaction of Diethoxyaluminum (Ethyl Acetoacetate) with Diphenylsilanediol. A mixture of the aluminum chelate (4.36 g, 0.0167 mole) and diol (3.60 g, 0.0167 mole) and 20 ml of benzene was heated in an oil bath at the boiling point. As the benzene distilled the oil bath temperature was raised to 150°. A slow stream of dry nitrogen was bubbled through and the temperature was raised to 180°. The strong odor of ethyl acetoacetate could be detected. The resin formed was a brittle glass which could be fused and had a molecular weight of 1230 (from benzene).

Reaction of 1,5-Pentanediol with the Product of Trimethylaluminum and Di(2-Methoxyethyl) Phenylmalonate. A mixture of the chelate material (1.85 g, 0.0526 mole based on the expected product) and 1,5-pentanediol (5.46 g, 0.00526 mole) was heated in an oil bath while passing a stream of nitrogen through the mixture. About 10 ml of benzene was added and the mixture was boiled. After the benzene had evaporated the temperature was raised to 150°. The residue was heated to 230° at 0.6 mm and at 250° decomposition began to occur. The residue was an insoluble and infusible solid.



H. ALUMINUM SALT POLYMERS

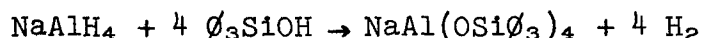
Reaction of Triphenylsilanol and Diphenylsilanediol with Sodium Aluminum Hydride.

In a 1-liter 3-necked creased flask fitted with a high-speed stirrer, a condenser and a dropping funnel were placed 27.6 g (0.1 mole) triphenylsilanol, 10.8 g (0.05 mole) diphenylsilanediol, and 500 ml dry benzene. A solution of sodium aluminum hydride in diglyme was obtained, containing 0.239 mole NaAlH_4 in 250 ml solution. This solution (52 ml, 0.05 mole) was added over about an hour to the silanol solution. Evolution of gas was immediate and rapid. About 5 liters of gas was collected during the addition of reagents; the mixture was then heated to reflux and an additional 1500 ml gas collected. (The theoretical volume of hydrogen was only 4800 ml; it is difficult to account for the excess of gas over this volume.) The reaction mixture formed a clear colorless solution, which was filtered with suction and concentrated under reduced pressure to a low volume. Benzene was added, and 3 g of a white crystalline precipitate formed: this material did not melt below 300° . On heating on a hot plate, it softened to a paste between 300 - 350° .

When the filtrate was added to a large volume of petroleum ether, an oil separated. This oil was heated in vacuo to remove solvent. A white friable solid product was obtained. No analyses are available.

Reaction of Triphenylsilanol with Sodium Aluminum Hydride.

The desired reaction is :



About 0.01 mole sodium aluminum hydride in diglyme was placed in a 250 ml Erlenmeyer flask in the dry box. A solution of 11 g (0.04 mole) triphenylsilanol in about 50 ml dry diglyme was added to the sodium aluminum hydride solution. Vigorous reaction took place. When the reaction subsided, the mixture was heated to 100° or so, allowed to cool, and diluted with an equal volume of petroleum ether. An oil separated, which crystallized on standing overnight. The product was recrystallized from benzene and petroleum ether; a salt-like product was obtained which would not melt below 290° . On a hot plate at about 300° the compound softened and then changed to a brittle solid.

Anal. Calc. for $\text{NaAl}(\text{OSi}\phi_3)_4$: Si, 9.75; Al, 2.3.
Found: Si, 10.30; Al, 3.32.

Although the product is certainly impure, it is probably substantially the desired compound, so that the reaction of silanols with sodium aluminum hydride will produce aluminosiloxanes.

I. MISCELLANEOUS REACTIONS

Preparation of Hexamethyldisiloxane.

In a 3-liter 3-necked creased flask were placed 1-liter of water and 5-10 ml sulfuric acid. The flask was fitted with a stirrer, condenser, and dropping funnel containing 100 ml Me_3SiCl , which was added to the aqueous solution with vigorous stirring over about 1/2 hour. After about 45 minutes total reaction time the upper layer was separated, dried over calcium chloride, and distilled. About 75 ml hexamethyldisiloxane, bp 100° , was obtained.

Reaction of Hexamethyldisiloxane with Lead Oxide.

In a small flask were placed 25 ml hexamethyldisiloxane and 5 g PbO . The mixture was agitated by a magnetic stirrer for 5 days. There was no evidence of reaction.

Patnode and Schmidt²⁷ reported the reaction of triphenylsilanol with PbO to give lead (II) triphenylsilanolate. The reaction conditions were substantially the same as those reported above. This was surprising, as we could observe only very limited reaction of diphenylsilanediol with PbO . We speculated therefore that Patnode's trimethylsilanol might have condensed to the disiloxane, and that the observed reaction actually took place between the disiloxane and the PbO . Since we did not observe such a reaction, however, it is assumed that Patnode and Schmidt actually observed a reaction with the silanol.

Reaction of Anhydrous Stannous Chloride with Methyl Silicate

Into 200 ml benzene in a flask were placed 30.4 g (0.2 mole) methyl silicate and 18.9 g (0.1 mole) anhydrous stannous chloride, dried azeotropically by heating in benzene. The mixture was refluxed several hours without change. Addition of a little concentrated sulfuric acid did not catalyze reaction. No methyl chloride was split out over 24-30 hours refluxing. The method is apparently unsuitable for polymerization.

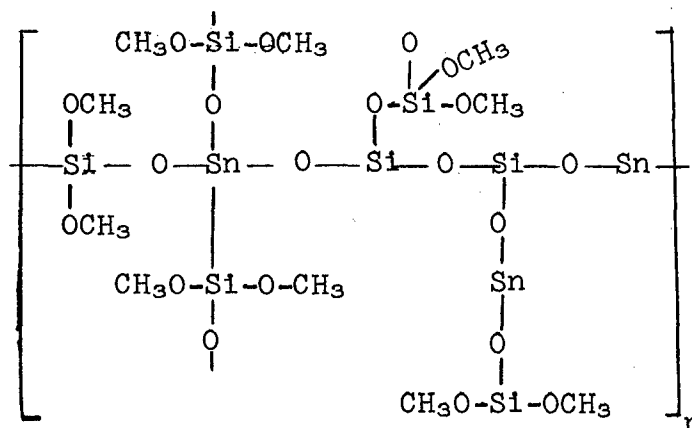
Simultaneous Hydrolysis of Methyl Silicate and Stannous Chloride.

In a 1-liter, 3-necked creased flask were placed 30.4 g (0.2 mole) methyl silicate and 18.9 g (0.1 mole) anhydrous stannous

chloride in about 300 ml anhydrous ethyl ether. A solution of 100 ml methanol, 50 ml water, and 10 ml concentrated ammonium hydroxide was added slowly with vigorous stirring. A white solid precipitate appeared, which was separated and dried. It weighed 30.5g. It would not melt, but decomposed at some high temperature (above 300°).

Anal. Found: Sn, 36.4; Si, 20.2.

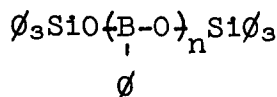
This composition corresponds to a polymer containing seven Si atoms to three Sn atoms in the repeating unit. The polymer would probably be highly cross-linked:



This material could be pressed to form a very hard but quite brittle mass. Structures of this general sort may serve as "synthetic mica".

Reaction of Triphenylsilanol with Phenylboronic Anhydride.

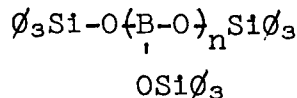
Three grams (0.013 mole) phenylboronic anhydride was placed in a flask with 22.0 g (0.080 mole) triphenylsilanol and 100 ml dioxane. The mixture was refluxed and rapidly formed a clear solution. After about 2 hours refluxing the mixture was cooled and added to excess petroleum ether; 11 g of unreacted triphenylsilanol was recovered. The mother liquor was concentrated to a heavy syrup, which gradually solidified when placed in a vacuum oven for several hours. The product was triturated with petroleum ether and recovered as a white powder with a wide melting range (110-125°), melting to a viscous fluid. The expected product is



Anal. Calc. for above (n = 1): B, 1.7; Si, 8.8.

Found: B, 2.02, 2.28; Si, 10.45.

It may be that some ϕ -B cleavage occurred also, to give something like



Such a compound (with $n = 2$) contains 1.9% B and 9.86% Si.

The idea of ϕ -B cleavage by silanolysis is supported by another run like the above which was carried out for a longer time (24 hours) to effect more complete silanolysis of the boroxane bonds. The reaction mixture was concentrated to about half its volume and repeatedly extracted with petroleum ether. This treatment left a relatively insoluble oil which was placed in the vacuum oven for several hours and finally crystallized. It was triturated with petroleum ether and found to melt at 95-98°.

Evaporation of the petroleum ether extract left another oil which eventually crystallized in vacuo to melt at 101°.

Anal. Calc. for $(\phi_3\text{SiO})_3\text{B}$: Si, 10.02; B, 1.3.
Found: Si, 11.46; B, 0.97

SECTION V

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