A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

Progress Report for the Period
November 4, 1964 to December 3, 1964

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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Project 1259, Report 45

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Contract NAS 8-1510

Southern Research Institute
Birmingham, Alabama
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FOREWORD

This Report was prepared by Southern Research Institute under Contract NAS 8-1510, "A Study of Polymers Containing Silicon-Nitrogen Bonds," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch of the George C. Marshall Space Flight Center with Mr. James D. Byrd acting as project manager.

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

ABSTRACT

21333

Studies of diphenylsiloxane—silphenylenesiloxane elastomers and of silphenylene amine polymers were continued. The elastomers were found to have combined thermal and physical properties superior to elastomers prepared previously in this program. meta-Oriented units were found to increase the elasticity and reduce the crystallinity of silphenylene amine polymers without adversely affecting thermal stability. The reactions of carbon disulfide and carbon dioxide with methylaminosilanes and the reactions of Grignard Reagents of cyclic silazanes with silicon halides were investigated for the preparation of polysilazanes, but they were found to be unsatisfactory.

Author

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I. INTRODUCTION AND STATUS

Silicon-nitrogen compounds are being investigated as a source of new liquid and plastic materials that are needed in space and aviation technology for use at extremes of temperature and in intense radiation fields at low pressure. This report covers the seventh month of the contract year.

Polymers made by the reaction of diaminosilanes with 1,4-bis(dimethylhydroxysilyl)benzene were cured by different procedures, and the properties of the resulting elastomers were determined. The elastomers appeared to have a more desirable combination of strength, elasticity, and thermal stability than any of the elastomers prepared previously in this project.

The investigation of the preparation of silphenylene amine polymers was continued. Ammonium sulfate was investigated as a catalyst to increase the molecular weights of the polymers, but it was not effective. A meta-substituted silphenylene amine was investigated as a source of polymers. Alone, it did not produce a polymer with desirable properties; but, in combination with a similar para-substituted amine, without lowering thermal stability, it retarded the crystallization and loss of elasticity of the para-polymer that occurs at room temperature.

The reactions of carbon disulfide and carbon dioxide with methylaminosilanes were investigated briefly for the preparation of polysilazanes. The reactions occurred readily, but yielded only low molecular weight polymers: and, hence, they do not appear to be satisfactory.

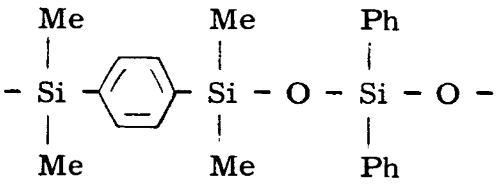
An attempt was made to prepare N-trimethylsilylhexaphenylcyclotrisilazane, by the reaction of the Grignard derivative of hexaphenylcyclotrisilazane with trimethylchlorosilane, but no more than a trace of the desired product was obtained. This and earlier results have led to the conclusion that the Grignard reaction is not satisfactory for the preparation of polymeric cyclic silazanes.

A new series of experiments to investigate the effect of the chemical environment on the reaction of chlorosilanes and ammonia has been started.

II. COPOLYMERIZATION OF DIOLS AND DIAMINOSILANES

A. Discussion

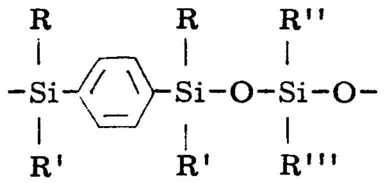
Samples of diphenylsiloxane-silphenylenesiloxane elastomers were prepared by several different curing procedures to obtain information on their potential utility. The polymers have this formula:



They were made by the reaction of 1,4-bis(dimethylhydroxysilyl)benzene with bis(methylamino)diphenylsilane, which was previously described in Report 44.

The raw diphenylsiloxane-silphenylenesiloxane polymers were milled with benzoyl peroxide and with silica or iron oxide, and the mixed samples were cured to form elastic sheets and discs. The samples had excellent thermal stability and were considerably stronger than any elastomers with comparable stability that have been made previously in this program. They can probably be fabricated by molding. One sample had a tensile strength of about 700 psi and an ultimate elongation of 330%. Another sample had a tensile strength of 265 psi and an ultimate elongation of 510%. When they were heated in air at 400°C for 1.5 hours, they became brittle on the surface but remained resilient underneath. When heated in nitrogen at 400°C, one sample lost less than 1% in weight in 1 hour and only 18% in 17 hours. After 17 hours at 400°C in nitrogen, the sample was hard on the surface but resilient underneath.

The methylphenylsiloxane-silphenylenesiloxane polymers had similar properties, as described in Report 44. Therefore, it is evident that the general formula, (1),



(1)

represents a series of elastomers with high thermal stability. The diol-diaminosilane reaction, by which the polymers were made, is easily controlled and probably is capable of producing polymers with a wide range of molecular weights. Furthermore, the polymers can be cured and fabricated by methods that are commercially feasible.

The time allotted for the current investigation of polymers made from silphenylene diols and diaminosilanes has been spent, and emphasis will now be directed to other subjects. Plans for further study of the effects of different substituent groups and different methods of curing will be suggested in a proposal for later studies.

B. Experimental Details

1. Polymerization of p-bis(dimethylhydroxysilyl)benzene with bis(methylamino) diphenylsilane

The method of preparing the diphenylsiloxane-tetramethyl-p-silphenylenesiloxane polymer was described in Report 44, page 8.

2. Curing the diphenylsiloxane-tetramethyl-p-silphenylene polymer

a. With benzoyl peroxide and silica

A mixture of 6.0 g of the raw polymer, 0.06 g of benzoyl peroxide, and 0.9 g of silica (Cabosil, Cabot Corporation, Boston, Mass.) was milled on a Teflon sheet with a Teflon cylinder, and the milled sheet was divided into six parts for curing experiments.

Sample 3794-3-2: One portion of the milled sheet was compressed manually in a Teflon beaker. The beaker was evacuated to about 0.02 mm pressure and warmed to about 130°C until bubbling of the contents ceased. The viscous liquid in the beaker was then heated in air 2 hours at 190°C, 16 hours at 300°C, and 15 minutes at 400°C. The product was a disc about 5 mm thick that had a tensile strength of approximately 700 psi with 330% elongation at the break point.

Sample 3794-3-3: A portion of the milled sheet was cured at reduced pressure on Teflon as a thin film. The Teflon and film were placed in a glass tube which was evacuated to 0.03 mm pressure and sealed. The sample was heated 0.5 hour at 130°C, 2 hours at 190°C, and 16 hours at 300°C. At the end of the heating period the tube was broken, and the sample was removed. It was sticky and very difficult to remove from the Teflon sheet. After further heating for 15 minutes at 400°C in air, the sample was weak and easily torn.

Sample 3794-3-4: A portion of the milled sheet was cured as a thin film in air on Teflon. It was heated 0.5 hour at 130°C, 2 hours at 190°C, and 16 hours at 300°C. The sheet was cream-colored, flexible, and transparent. It had a tensile strength of 810 psi with 75% elongation at the breaking point.

Sample 3794-3-5: A portion of the milled sheet was compressed and cured as a disc in a Teflon beaker in air. It was heated 0.5 hour at 130°C, 2 hours at 190°C, 19 hours at 300°C, and 15 minutes at 400°C. The sample was a rubbery, non-uniform disc with bubbles throughout.

Sample 3794-7-8-A, A portion of the milled sheet was cured as a thin film on an aluminum panel. To insure adhesion of the silphenylene-siloxane polymer, the methylphenyl silazane - TEA prepolymer (Report 41, page 12) was used as a primer. A 10% solution, 0.2 ml, of the prepolymer was spread over about 8 sq cm of the aluminum strip. After the benzene had evaporated, the portion of the milled sheet was pressed onto the primed surface of the aluminum. The sample was placed in a glass vessel, evacuated to about 0.02 mm pressure, and warmed to about 130°C. The film bubbled slightly. The bubbles did not break, because of the high viscosity of the polymer, and they remained after the sample had been heated in air at 350°C for 10 minutes. The film adhered tightly to the aluminum after 25 minutes at 400°C, but the bubbles detracted from its appearance. The next curing procedure was better.

Sample 3794-7-8-B: A portion of the sheet was treated in the manner of the preceding sample up to the point of curing. It was not heated at reduced pressure; but after the milled sheet was applied to the primed surface, it was heated in air for 15 minutes at 130°C, 15 minutes at 190°C, 10 minutes at 350°C, and 15 minutes at 400°C. It adhered tightly to the aluminum, was fairly smooth, and contained only a few bubbles. This method could probably be developed to permit application of thick coatings to panels.

b. With benzoyl peroxide and ferric oxide

The raw polymer, 1.7 g, obtained as described in Report 44, page 8, was blended with 0.25 g of ferric oxide (Spanish Red Oxide, C. J. Osborn Company, Linden, New Jersey) and 0.01 g of benzoyl peroxide by milling on a Teflon sheet with a Teflon cylinder. The milled material, designated 3794-7-7, was placed in a Teflon beaker, and the beaker was evacuated to a very low pressure and warmed to about 130°C until bubbling of the contents ceased. It was then heated in air 2 hours at 190°C and 19 hours at 300°C. The product in the beaker was a disc about 5 mm thick that had a tensile strength of 265 psi with 510% elongation at the breaking point. On heating a small piece of the disc 1.5 hours at 400°C, a crust formed on the surface; but it remained rubbery underneath.

c. Tensile measurements

Tensile measurements were made with an Instron Tester, Model TM. Insufficient material was available to prepare samples in the most desirable forms. Consequently, to obtain approximate values of tensile strength and elongation, small strips were cut from the samples and measured to determine their cross-sectional areas. Then they were clamped in the tester and drawn at rates of 200% and 400% per minute. The results are in Table I.

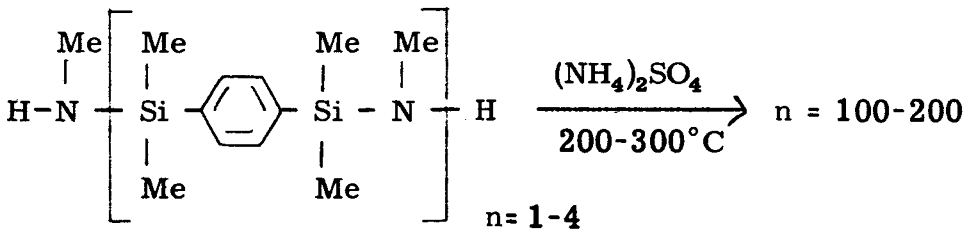
Table I. Tensile Strength and Elongation of Diphenylsiloxane - Silphenylene siloxane Polymers

Sample 3794-	Original cross-section, in.^{2}	Tensile Strength, psi	Elongation at break, %	Elongation % per min
3-4A	0.0041	810	75	200
3-4B	0.0039	735	50	200
7-7	0.013	265	510	400
3-2	0.0044	715	330	400

III. REACTIONS OF PHENYLENE-BRIDGED SILYLAMINES

A. Discussion

Attempts were made to increase the molecular weights and ease of preparation of the p-silphenylene amine polymer by the use of ammonium sulfate as a catalyst for the condensation. (Ammonium



para-MMSP

sulfate had been studied previously as a catalyst for condensation of end-amino groups.[1; 2, 3]) The ammonium sulfate apparently accelerated the reaction; but the product was dark, and it evidently had suffered some decomposition because it was softer at room temperature than the polymer made without ammonium sulfate.

meta-MMSP was investigated for use in making polymers. It was tried both alone and in mixtures with para-MMSP. Earlier[4] para-MMSP was polymerized by heating in air to a tough solid that was soft and elastic at room temperature but that crystallized and became relatively inelastic on standing at room temperature. The drastic change that occurred at room temperature was thought to be a disadvantage, and meta-MMSP was prepared to determine whether it could be used to retard crystallization and prevent hardening at ordinary temperatures. Meta-MMSP was polymerized by heating in air at 250°C for 24 hours. The product was a thick, sticky, grease; whereas the para compound would have become a tough solid under similar conditions. A mixture of 10% meta-MMSP and 90% para-MMSP was converted to a fairly tough, elastic material that crystallized when kept at room temperature overnight and then was flexible but inelastic. A mixture of 50% meta-MMSP and 50% para-MMSP was converted to an elastic red-brown solid that was much like the para polymer but somewhat softer at room temperature. After it had crystallized, it was quite tough. The inclusion of meta-MMSP had little, if any, effect on thermal stability. The all-para polymer retained some resilience after being heated for 30 minutes at 400°C in air, but the polymer made with 10% of meta-MMSP reached a comparable degradation in about 20 minutes. On the other hand, the

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1. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 61.

2. L. W. Breed, R. L. Elliott, and A. F. Ferris, J. Org. Chem. 27, 1114 (1962).

3. E. G. Rochow, Monatsh. Chem. 95, 750-65 (1964).

4. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, May 28, 1964, page 35-39.

50-50 mixture retained some resiliency after 45 minutes at 400°C in air. A crystallized sample of the 50-50 polymer had a tensile strength of 1800 psi with 365% elongation at break.

The meta-MMSP also was polymerized by heating at 300°C at 0.02 mm pressure as described for the para-MMSP in Report 44, page 20. Whereas the para compound was converted to a tough, elastic solid that flowed slowly at about 200°C, the meta compound flowed very slowly at room temperature.

No further work is planned for the silphenylene amine polymers in this contract period. The time allotment has been spent, and the polymers have had melting points that are too low for practical use. It would be fruitful, however, to find a cross-linking reaction that would convert the soft polymers to elastomers and make them infusible.

B. Experimental Details

1. Polymerization of para-MMSP with ammonium sulfate

The para-MMSP was made by the method previously reported.[4] The model for the polymerization was Reaction 3640-33-2 (Report 44, pages 20-21), but ammonium sulfate was added. The para-MMSP, 1.8 g, was placed in a small distilling flask with a Teflon-covered magnetic stirrer. Ammonium sulfate, 0.02 g, was added, and the pressure was reduced to 0.02 mm. A small amount of frothing occurred, but it stopped in a few seconds. The temperature was raised to 300°C, and maintained for 6 hours. The rate of gas evolution decreased over a 3-hour period while the viscosity increased. The viscosity seemed to increase faster than it did in a comparable reaction without the ammonium sulfate. However, the polymer never reached a state where it could not be stirred, and after 6 hours the reaction was stopped. The cooled product was a soft, dark-brown, sticky paste.

2. Investigation of meta-MMSP

a. Preparation of 1,3-bis(dimethylchlorosilyl)benzene and meta-MMSP

The method of Sveda[5] which has been described previously[4] was used to prepare 1,3-bis(dimethylchlorosilyl)benzene.

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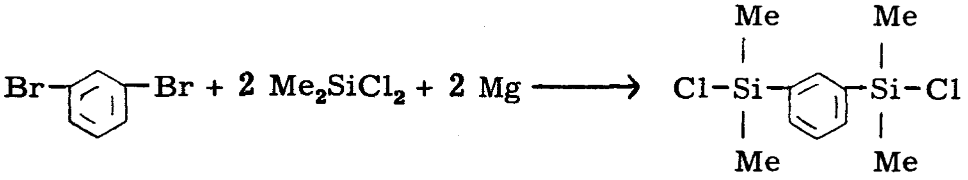
[5] M. Sveda, U. S. Patent 2,561,429 (assigned to E. I. du Pont de Nemours and Company, Inc.), July 24, 1951.



The product was a colorless liquid, b.p. 90-92°C at 0.2 mm, and it had a neutral equivalent of 144 (theory, 132). The product was treated with methylamine as described previously,[4] and a pale yellow oil, "meta-MMSP" was obtained.

Anal. Calcd. for $C_{11}H_{19}NSi_2$[a]: C, 59.66; H, 8.65; N, 6.32; Si, 25.37.

Calcd. for $C_{12}H_{24}N_2Si_2$[b]: C, 57.08; H, 9.58; N, 11.09; Si, 22.25.

Found: C, 54.88; H, 8.86; N, 9.74; Si, 19.84.

meta-MMSP was polymerized by the procedure that was used to make a polymer of 52,000 molecular weight from para-MMSP (Report 44, pages 20-21). meta-MMSP, 5.0 g, was placed in a 10-ml distilling flask, then it was heated and stirred at 300°C at 0.1 mm pressure for 8 hours. About 20% of the total amount distilled, and the remainder was a viscous liquid at room temperature. An additional 8 hours of heating at 300°C at 0.01 mm failed to increase the viscosity or cause any other visible change. Two additional experiments under similar conditions but with 1% ammonium sulfate failed to produce any higher viscosity polymers.

b. Thermal condensation polymerization of meta-MMSP in air

meta-MMSP was treated by the method that converted para-MMSP to an elastic red-brown solid.[4] During the investigation of para-MMSP several different curing procedures were used. Simple heating at 250°C for 24 hours invariably produced a solid, but frequently produced wrinkling on the surface. Longer heating at a lower temperature

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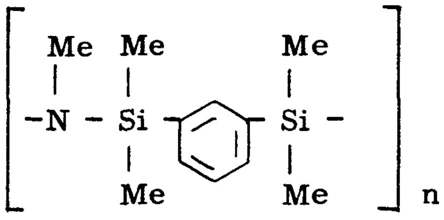
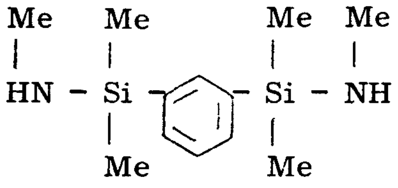
[a] $C_{11}H_{19}NSi_2$



[b] $C_{12}H_{24}N_2Si_2$



produced a smoother surface. meta-MMSP was placed in a layer 2 mm deep in a 10-ml Teflon beaker and heated at 250°C for 24 hours. The product was a thick, dark-yellow grease at room temperature.

A mixture of 50% meta- and 50% para-MMSP was placed in a Teflon beaker and heated 48 hours in air at 190°C. A soft, clear, sticky solid was formed. It was removed from the beaker and heated for 24 hours at 250°C. The product was a disc about 1 mm thick, and it was highly elastic. After about 4 hours at room temperature, it could not be torn or stretched by hand, but it was quite flexible. The crystallized sample was cut into a strip that had a cross-sectional area of 0.0016 square inches. On the Instron Tensile Tester, it broke at 0.97 pound after an elongation of 280%. Thus its tensile strength was 1800 psi. A similar sample was heated to remove its crystallinity, and it had a tensile strength of 230 psi with 365% elongation.

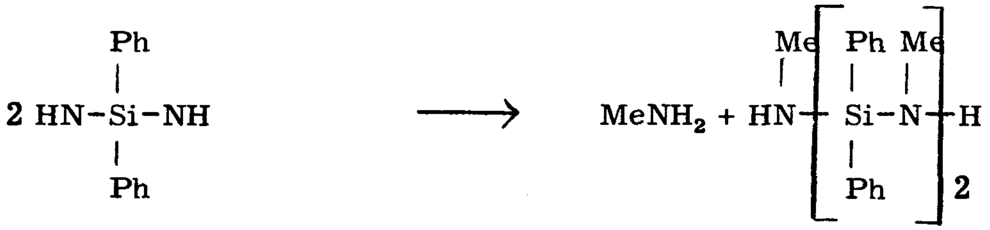
A mixture of 10% meta- and 90% para-MMSP was heated 8 hours at 190°C and 24 hours at 250°C. The product was dark brown and elastic immediately after being cooled to room temperature. After standing at room temperature overnight, it was still flexible but relatively inelastic. When heated 20 minutes in air at 400°C, it lost most of its strength but was still resilient. Heating an additional 10 minutes at 400°C made it friable.

IV. REACTIONS OF SILYLAMINES WITH CARBON DISULFIDE AND CARBON DIOXIDE

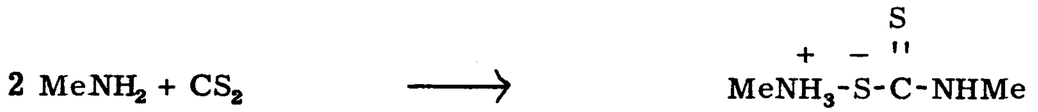
A. Discussion

Silylamines react rapidly at room temperature with carbon disulfide and carbon dioxide. The reaction was discovered during studies of NMR spectra when an attempt was made to use carbon disulfide as a solvent for bis(methylamino)dimethylsilane. A solid formed immediately when the two chemicals were mixed, and it appeared to have some polymeric character. Accordingly, the investigation was extended to determine whether a means of polymerization had been found.

It now appears that carbon disulfide causes condensation of end-amino groups in bis(methylamino)diphenylsilane to release methylamine, which forms methylammonium N-methyldithiocarbamate.



$$2\,\mathrm{HN}-\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{NH} \longrightarrow \mathrm{MeNH_2} + \overset{\mathrm{Me}}{\mathrm{HN}}\left[\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}-\overset{\mathrm{Me}}{\mathrm{N}}\right]_2\mathrm{H} \tag{2}$$



$$2\,\mathrm{MeNH_2} + \mathrm{CS_2} \longrightarrow \overset{+}{\mathrm{MeNH_3}}-\overset{-}{\mathrm{S}}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{NHMe} \tag{3}$$

The reaction is capable of producing polymers if sufficient carbon disulfide is used. According to the equation, a mole of dithiocarbamate is expected for each mole of carbon disulfide. Actually less than half of the expected dithiocarbamate was isolated when the ratios of aminosilane to carbon disulfide were 1:2.25, 4:1, and 2:1. When a large excess of carbon disulfide was used, half of the total available methylamine was isolated as the dithiocarbamate, but the resulting silicon-containing polymer apparently contained some carbon disulfide. The polymer was pale yellow even though it was obtained in approximately the theoretical yield; elemental compositions and molecular weights are being determined.

Trials of the polymer as a coating agent were not encouraging. Earlier work on an N-methyl-Si-phenyl coating agent resulted in coatings that had outstanding thermal stability but that required curing at unusually high temperatures.[7] Accordingly, the polymer from the carbon disulfide reaction was tried as a coating agent, but it adhered poorly.

No reaction was detected between carbon disulfide and hexamethylcyclotrisilazane when they were mixed and held at room temperature.

A single simple trial showed that carbon dioxide reacted with bis(methylamino)diphenylsilane to form a crystalline compound. This reaction will be investigated briefly to determine whether it is promising as a source of useful products.

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7. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 60 and 66.

B. Experimental Details

1. Preliminary experiment

To 2.0 g (4 millimoles) of bis(methylamino)diphenylsilane dissolved in 10 ml of benzene was added 0.3 g (9 millimoles) of carbon disulfide. The solution was allowed to stand at room temperature for 16 hours in a stoppered flask. Filtration yielded 0.3 g of a white crystalline material with a melting point of 112 to 120°C that was tentatively identified as methylammonium N-methyldithiocarbamate. Thus, the yield was 2.3 millimoles, 25% of theory. The elemental composition was:

Anal. Calcd for $C_3H_{10}N_2S_2$: C, 26.07; H, 7.27; N, 20.27; S, 46.39.

Found: C, 26.76; H, 7.00; N, 19.20; S (by difference) 47.04.

Bodendorf[8] reports the melting point of methylammonium N-methyldithiocarbamate, $C_3H_{10}N_2S_2$, to be 114-115°C (with decomposition).

2. With silylamine to carbon disulfide mole ratio of 4:1

If the reaction proceeded according to this equation,

$$4\ (HNMe)_2SiPh_2 + CS_2 \longrightarrow 2\ HNMe(SiPh_2NMe)_2H + MeNH_3SCSNHMe$$

the stoichiometric ratio for dimerization of the silane would be 4:1. In a 25-ml Erlenmeyer flask was placed 1.94 g (8 millimoles) of bis-(methylamino)diphenylsilane and 10 ml of dry benzene. To this was added 0.15 g (2 millimoles) of carbon disulfide, which was added as a benzene solution that contained 0.1 g of CS_2 per milliliter of solution. After the reaction had stood at room temperature for 16 hours, the white precipitate was filtered off and washed with benzene. It amounted to 113 mg and melted at 116-117°C. The crystalline product was water soluble, and the solution gave a characteristic brown precipitate when dilute aqueous copper sulfate solution was added. Methylammonium N-methyldithiocarbamate behaves in a similar manner. Thus, the yield was 41% of theory.

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[8] K. Bodendorf, J. prakt. Chem. 126, 233-40 (1930); C. A. 24, 3993^8 (1930).

The filtrate was evaporated in a stream of dry nitrogen and evacuated to 0.05 mm pressure. Two immiscible liquids, 1.70 g, remained. They were shaken with 10 ml of hexane and centrifuged into two layers. One of the layers, after evaporation, yielded a clear liquid, m.p. 15-17°C. It was 56% of the original silylamine. The second fraction was a yellow gum that weighed 0.61 g, which was 34% of the theoretical yield calculated as the dimer, 1,3-bis(methylamino)- 1,1,3,3-tetraphenyl-2-methyldisilazane.

3. With silylamine to carbon disulfide mole ratio of 2:1

According to the equation, 2.0 moles of silylamine should react with 1.0 mole of carbon disulfide to produce 1.0 mole of dithiocarbamate and either a cyclic silazane or a polymer of such length that the end groups would be insignificant.

$$n\ \mathrm{MeHNSiPh_2NHMe} + \frac{n}{2}\mathrm{CS_2} \longrightarrow (\mathrm{-MeNSiPh_2-})_n + \frac{n}{2}\mathrm{MeNH_3SCSNHMe}$$

In a 25-ml Erlenmeyer flask was placed 1.45 g (6 millimoles) of the silylamine and 10 ml of dry benzene. To this was added 0.23 g (3 millimoles) of carbon disulfide as a benzene solution containing 0.1 g of CS_2 per milliliter of solution. After the solution stood 16 hours at room temperature, the precipitate was removed by filtration. This precipitate was washed with benzene and then dried. It weighed 171 mg (41% of theory), and melted at 117-119°C.

4. With silylamine to carbon disulfide ratio of 2:5

In one reaction, an excess of carbon disulfide was added in increments to a benzene solution of the silylamine until no more dithiocarbamate was produced. The final amounts of reactants were 12.12 g (50 millimoles) of silylamine and 9.52 g (125 millimoles) of carbon disulfide. After the final addition, the reaction was refluxed for 3.5 hours. The solvent was evaporated, and the residue was fractionated by solution in hot hexane. The insoluble portion was 12.0 g of an orange solid that melted at 115-130°C (114% yield for $-SiPh_2NMe-$). The soluble portion was 2.28 g of a yellow gum that had the odor of carbon disulfide.

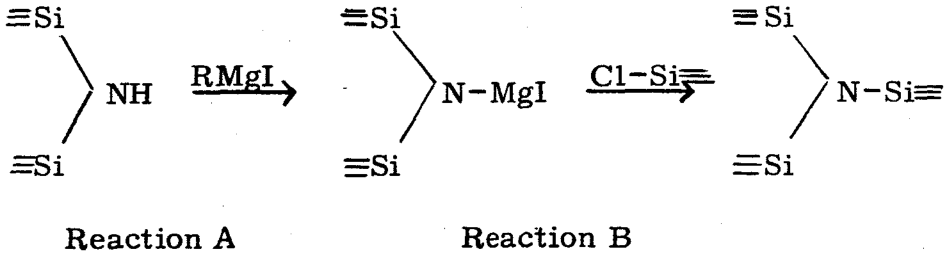
5. With a large excess of carbon disulfide

Carbon disulfide, 152 g (2.0 moles), was added dropwise with stirring to 6.06 g (25 millimoles) of bis(methylamino)diphenylsilane at 1-8°C over an hour. The reaction mixture was then stirred at 33°C for 2 hours. The mixture was cooled, allowed to stand overnight, and filtered to yield 1.74 g of dithiocarbamate (101% yield). The carbon disulfide was removed by evaporation at reduced pressure with the temperature being kept below 40°C. The residue was dissolved in benzene, a small amount (36 mg) of solid was filtered off, and the benzene was removed by evaporation at 50°C at reduced pressure. The product was 5.02 g of a pale yellow solid that melted at 155-161°C. The yield was 95% of theory for a cyclic compound or polymer of infinite chain length (– $SiPh_2NMe$ –). The crystalline product evaporated slowly when heated on a stainless steel spatula over a flame and finally formed a solid coating. However, it was less stable to heat than a similar coating made from methylphenyl silazane — TEA.

V. POLYMERIZATION OF SILAZANES THROUGH GRIGNARD REAGENTS

A. Discussion

Previous work on the use of the Grignard Reagent for making derivatives of cyclic silazanes showed that silicon halides did not react readily with halomagnesium derivatives of cyclic silazanes.



(4)

Reaction A proceeded satisfactorily with hexamethylcyclotrisilazane, but Reaction B did not. The last reaction of the series planned was an attempt to form N-trimethylsilylhexaphenylcyclotrisilazane by the reaction of trimethylchlorosilane with the Grignard derivative of hexaphenylcyclotrisilazane. Most of the hexaphenylcyclotrisilazane, 58%, was recovered unchanged. In addition, a mixture was obtained that accounted for 28% of the yield and was mostly liquid with a small amount of unidentified crystalline material. Even if some of the desired product were present, the reaction could not be considered satisfactory for polymerization. The potassium route[9] gave a 63% yield of the N-trimethylsilyl derivative of hexaphenylcyclotrisilazane, and almost quantitative yields are needed for successful polymerization reactions.

B. EXPERIMENTAL DETAILS

Hexaphenylcyclotrisilazane, 11.84 g (0.02 mole), was dissolved in 150 ml of dry benzene at 40°C in a 500-ml, 3-neck flask. To this, 0.02 mole of methylmagnesium iodide in 100 ml of dry ether was added dropwise with stirring. No reaction occurred at 40°C, and so the temperature was raised to 65°C, whereupon gas was evolved for 1 hour. The total gas evolved amounted to 93% of the theoretical amount of methane. The flask was cooled to 30°C, and 2.55 ml (2.17 g, 0.02 mole) of trimethylchlorosilane was added from a pipette. The mixture was stirred at 55°C for 1 hour and stored at room temperature overnight. The ether and the chlorosilane that had not reacted were removed by distillation, and a solid that was insoluble in benzene was removed by filtration at 40°C. The benzene-insoluble matter was almost completely soluble in water; it weighed 3.64 g, which was 98% of the theoretical weight of magnesium chloroiodide. The benzene was removed by evaporation at reduced pressure, and a white crystalline powder remained. Previous work showed that N-trimethylsilylhexaphenylcyclotrisilazane[8] could be recrystallized from hexane. Accordingly, the crystalline powder was extracted with 250 ml of hexane at 35-40°C, and the residue weighed 6.80 g, m.p. 209-211°C. Thus, 58% of the starting material was recovered. On evaporation, the hexane yielded 3.44 g of an oil that contained a small amount of a crystalline solid. If the oil had been entirely the trimethylsilyl derivative, which melts at 155-156°C, the yield would have been 26%; but the actual yield was doubtless much less.

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9. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 91.

VI. THE EFFECT OF THE CHEMICAL ENVIRONMENT ON THE AMMONIA-CHLOROSILANE REACTION

Triethylamine was shown previously to be capable of retarding cyclization in the reaction of chlorosilanes with ammonia, but high polymers were not produced.[10] Study of the reaction has been resumed in a search for more effective agents to prevent cyclization.

A reaction between diphenyldichlorosilane and ammonia was run in the presence of N,N, N', N'—tetramethylethylenediamine, and the product was an oil. This result was similar to that obtained with triethylamine, but characterization of the product has not been completed.

A series of experiments is in progress to screen a number of compounds to find those that form complexes with silicon halides. The compounds are being stirred with silicon halides under conditions that will reveal heats of reaction during mixing, if any heat is released. Details will be given in the next report.

VII. FUTURE WORK

The investigation of environmental factors to inhibit cyclization of silazanes has been started. Tertiary amines were shown to be beneficial, and more effective materials are being sought. A variety of tertiary amines and other possible complexing agents are being screened for activity.

An investigation of cyclization inhibition by means of steric effects is being started. Large diamines with stiff structures that appear unlikely to cyclize will be tried.

The use of silylamines to initiate polymerization of epoxy compounds will be studied. The object is to increase the thermal stability of epoxies by incorporation of the thermally stable silylamines.

VIII. TIME EXPENDITURE

In November, 673 man-hours were expended on the project. The total in the current contract year has been 4, 505. 5 man-hours.

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[10] Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, May 28, 1964, pages 10-19.

ACKNOWLEDGMENTS

Dr. Richard S. Johnson, Senior Chemist; Mr. Thomas W. Ray, Assistant Chemist; Mr. Robert E. Lacey, Senior Chemical Engineer; and Mr. Charles L. Christy, Jr., Chemical Technician, assisted with the work discussed in this report. Studies of NMR spectra were made by Mrs. Martha C. Thorpe.

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PROGRAM PLANNING CHART

Item No.	Topic	Alotted time, man-hours	1964								1965			
			May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
A.	Synthesis of Si-N Compounds													
	1. Polymerization through Grignard reagents	450				X	X	X						
	2. Polymers with aromatic bridges	1,750	X	X	X	X	X	X	X					
	3. Cyclization inhibition, effect of complexing agents	400							X	X	X			
	4. Reactions of diaminosilanes	2,200	X	X	X	X	X	X	X					
	5. Polymers also containing B, Ti, or Al	450									X	X	X	
	6. Cyclization inhibition, steric effects	1,300								X	X	X	X	
	7. Reactions involving epoxy compounds	400								X	X	X		
	8. Comparison of silicon-nitrogen and siloxane polymers	350						X	X	X				
B.	Evaluation of polymer stability (hydrolytic, radiation, thermal)	550	continuous											
C.	Applications and preparation of samples for NASA	500	at time designated by NASA											
D.	Literature survey	100	continuous											
E.	Preparation of final report	250												X