A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

Annual Summary Report For The Period
May 4, 1965 To May 3, 1966

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Huntsville, Alabama

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FOREWORD

This report was prepared by Southern Research Institute under Contract NAS 8-20190, "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 Vehicles Engineering Laboratory, Materials Division, of the George C. Marshall Space Flight Center with Mr. James D. Byrd acting as project manager.

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ABSTRACT

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The chemistry of silicon-nitrogen compounds has been studied to find routes to polymers that will be useful in aerospace technology. Two types of silphenylene polymers appear to be promising as sources of elastomers with good stability to heat and radiation. Coatings for titanium that were stable for more than 100 hours at 540°C (1000°F) were made from a silphenylene amine polymer and a methylphenyl silazane pigmented with aluminum. Silylamines also are effective curing agents for epoxy resins to produce polymers with good thermal stability, and they cure organic diisocyanates to resins, probably by a cyclization mechanism. Isocyanate polymers have been made with attractive physical properties at ordinary temperatures, but the combinations tried so far do not look promising for either high- or low-temperature applications. Fundamental studies of silicon-nitrogen bonds have yielded comparative data on the relation of substituents to hydrolytic stability and on the dynamic character or exchange reactions of silicon-nitrogen bonds in simple compounds. Attempts to prepare polymers by brief studies of the following reactions did not produce encouraging results: reactions of amides with silylamines, reactions of cyclic silazanes with dibasic acids, reactions of tetrafunctional silicon compounds, amination of a silicon-nitrogen-aluminum halide, and amination of a silicon-nitrogen-phosphorus halide. The reaction of a cyclic siloxazane with organic diols produced polymers that have unusual ability to remain soft at both high and low temperatures. A methylphenyl silazane primer for aluminum increased the shear strengths of lap joints made with a polyaryloxysilane adhesive.

A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

I. STATUS OF THE RESEARCH PROGRAM

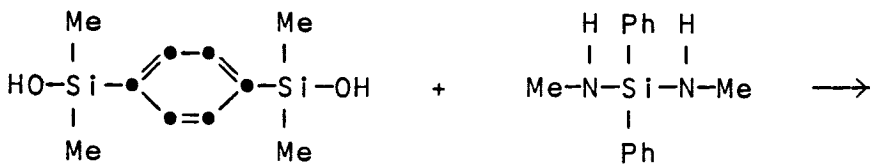
Silicon-nitrogen compounds have been studied as possible sources of polymers that will meet the requirements of aerospace technology. New types of sealants, coatings, lubricants, hydraulic fluids, heat barriers, elastomers, potting compounds, and structural plastics are needed that will have exceptional thermal and radiation stability or perform satisfactorily at extremely low temperatures. This report covers the work done during the past year under Contract NAS 8-20190, which has been a continuation of previous work under Contract DA-01-009-506-ORD-829 with the Army Ballistic Missile Agency[1] and Contract NAS 8-1510.[2,3,4,5]

The study of silicon-nitrogen chemistry was undertaken because theoretical considerations suggested that polymers containing silicon-nitrogen bonds might have exceptional thermal stability. Worldwide interest in silicon-nitrogen chemistry has increased greatly in recent years; but workers, generally, have had discouraging results with polymers containing high proportions of silicon-nitrogen bonds. Silicon-nitrogen polymers are reasonably stable, thermally, but none made so far has had attractive physical properties. On the other hand silicon-nitrogen compounds have been used to form polymers that have desirable characteristics and that cannot be obtained by other methods. The reaction of organic diols with diaminosilanes[6] was initially developed and used to form polymers with high molecular weight and high thermal stability from dianilinodiphenylsilane and a variety of diols. The fundamental reaction was shown to be exceptionally versatile and it has since been used in this program to form elastomers with high thermal stability.[5] Silylamines and oligomers of silylamines have been found to form protective coatings with good adhesion and stability.[1,2,3,4,5] The stability of the coatings is attributed to adherent films that are largely inorganic.

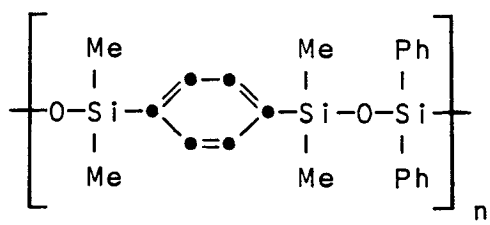
Throughout the program many types of polymer-forming reactions have been tried, and a few have been found that warrant further research. The results of the past year are summarized in Section II.

II. DISCUSSION OF RESULTS

Elastomers with high thermal stability were made by the reaction of 1,4-bis(dimethylhydroxysilyl)benzene and bis(methylamino)diphenylsilane, which produces "silphenylene ethers".



1,4-bis(dimethylhydroxysilyl)benzene bis(methylamino)-diphenylsilane



poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

Compressibility at low temperatures was improved by replacing one of the phenyl groups by methyl and by changing the position of substitution in the silphenylene ring from <u>para</u> to <u>meta.</u> When compared with Viton A and a commercial silicone elastomer that had good thermal stability for a silicone, the silphenylene elastomers had relatively poor physical properties initially, but they retained some compressibility longer than either Viton A or the silicone elastomer when exposed to high temperatures or gamma radiation. They also retained more of their initial compressibility than Viton A but less than the silicone at temperatures down to -78°C.

A silphenylene amine polymer made by amination of 1,4-bis(dimethylchlorosilyl)benzene had a molecular weight of 68,000 and was tough, but it was fluid at 200°C. Because of the low melting point, the polymer did not appear to be useful in itself, but a foam made by crosslinking it with pentaerythritol had attractive thermal stability, and a protective coating formed on titanium also had good thermal stability.

An epoxy resin, Epon 828, filled with glass cloth and cured with bis(methylamino)diphenylsilane formed a composite panel that had good flexural strength and thermal stability. An experimental heat-barrier panel made similarly, but with glass fiber and potassium titanate, performed well enough to justify further investigation.

Silylamines were found to promote polymerization of diisocyanates. The mechanism has not been established, but it is thought to be primarily cyclization of isocyanate groups. The resulting polymers were transparent and tough. Depending on the character of the diisocyanate, they varied from slightly flexible to rubbery, but they did not appear to have outstanding properties at either high or low temperatures.

The reaction of amides with silazanes was studied, and, for a short time, this appeared to be a possible route to polymers with structures that favored high thermal stability. However, the reactions apparently did not go to completion, and the products were not particularly stable, so the work was discontinued.

Cyclic silazanes were copolymerized with dibasic organic acids, and a cyclotrisildiazoxane was copolymerized with organic diols. Both of these reactions formed polymers that contained silicon-nitrogen bonds, and, as such, they offered possibilities of conversion to other materials that might be useful. However, the results obtained in the time allotted were not definitive. Of the products obtained, the polymer made from hexamethylcyclotrisildiazoxane and hydroquinone was the most interesting. This reaction is another example of the versatility of the diol-diaminosilane reaction.[6]) The product was a sticky, elastic polymer with a molecular weight of about 1,000,000, but it was soft enough to flow at 250°C. Efforts to crosslink the polymer by reaction with pentaerythritol did not succeed in making products that were as promising as the silphenylenes. However, the polymer was detectably soft at -78°C, so it appears to merit some additional investigation.

Because of the effectiveness of silazanes as coating agents, methylphenyl silazane was tried as a primer for aluminum in making lap joints with polyaryloxysiloxane as an adhesive. The silazane improved the shear strength slightly.

Attempts to prepare specific types of silaspirane, silicon-nitrogen-phosphorus, and silicon-nitrogen-aluminum polymers were not successful. Excessive crosslinking occurred in the silaspirane reaction and an intractable powder was produced; rearrangement occurred in the silicon-nitrogen-phosphorus reaction and a cyclic phosphorus-nitrogen compound was produced; and the silicon-nitrogen-aluminum reaction failed to produce a polymer.

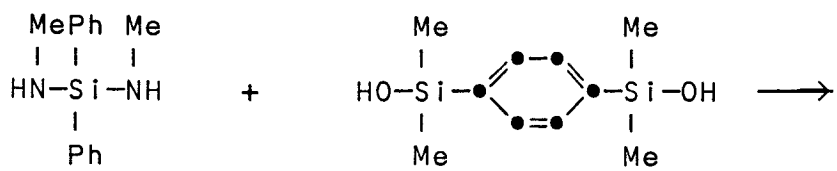
Some fundamental studies were made of the characteristics of silicon-nitrogen bonds. The rates of hydrolysis of several new silylamines were determined and compared with the rates determined previously for other silylamines. The rate of exchange between two diaminosilanes was found to be so high at room temperature that exchange is believed to be one reason why the preparation of silazane polymers has been so difficult.

The publications on silicon-nitrogen compounds that appeared during the contract year were reviewed and are summarized in the last section of this report.

III. POLYMERIC SILPHENYLENE ETHERS

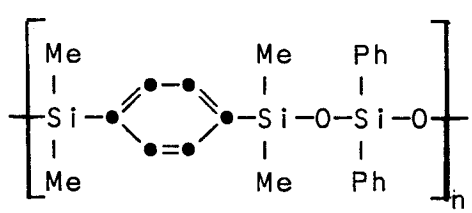
A. Discussion

The reaction of silphenylene diols with diaminosilanes has been used to make elastomers with high thermal stability. The following reaction was used to prepare the polymer that has been studied in greatest detail:



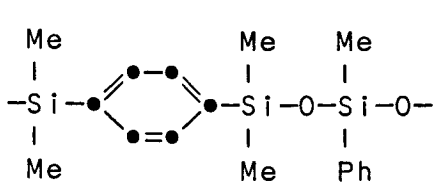
bis(methylamino)-diphenylsilane (BMADPS)

1,4-bis(dimethylhydroxysilyl)benzene



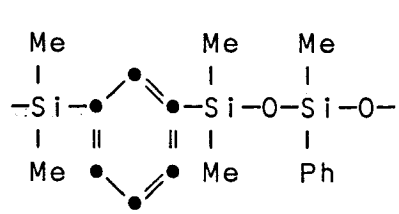
I. poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

This reaction was first studied under the preceding contract.[7] Under the present contract, reaction conditions were studied to find the best methods of obtaining high molecular weights and of crosslinking to form elastomers. Structural variants were also prepared to study the effects of features that would impart low-temperature flexibility and compressibility. The structural formulas for the polymers studied, in addition to Polymer I, are:



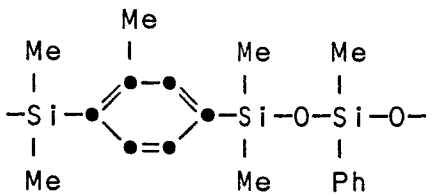
II. poly[1,4-bis(oxydimethylsilyl)benzene methylphenylsilane]

and



III. poly[1,3-bis(oxydimethylsilyl)benzene methylphenylsilane]

In addition, attempts were made to prepare an elastomer with a methyl group attached to the silphenylene ring, as shown below; but the required silphenylene diol was not obtained.



IV. poly[2,5-bis(oxydimethylsilyl)toluene methylphenylsilane]

Different reaction conditions were tried to find the best method of forming the polymer. The best results were obtained by refluxing the carefully weighed reactants in toluene until reaction became slow, and then removing the toluene and heating the polymer at 200-250°C under reduced pressure. Polymer I was prepared with a molecular weight of 630,000 (Product 4036-47-4) as indicated by light scattering. The polymer, at this stage, was a soft solid. It was crosslinked by heating in air. Heating with oxidizing agents resulted in partial curing, but adequate curing was not obtained except by heating in air. The curing method requires further study.

One batch of polymer was prepared with bis(methylamino)-methylvinylsilane replacing 5% of the BMADPS. No positive beneficial effect of the vinyl group was observed.

Tris(dimethylamino)phenylsilane, $PhSi(NMe_2)_3$, was tried in small amounts as one of the initial reactants to accomplish crosslinking without the need for subsequent oxidation. An intractable elastomer was formed in the initial reaction, and no satisfactory method of making a workable polymer was found.

Bis(dimethylamino)diphenylsilane, $Ph_2Si(NMe_2)_2$, was tried as one of the initial reactants in place of BMADPS; but the reaction then required a higher temperature for initiation, and no beneficial results were observed.

Homopolymerization of the silphenylene diol was thought to be a potentially detrimental side reaction in the diol-diaminosilane reaction that forms the precursor of the elastomer. To the extent that homopolymerization of the diol occurred, BMADPS would be present in excess. In preparing the diol monomer by hydrolysis of 1,4-bis(dimethylchlorosilyl)benzene, formation of the polymer is the chief cause of low yields. Consequently, the tendency of the diol to condense with itself was investigated. The diol underwent no change in melting point in 1 hour in toluene at 60°C, 1 hour in toluene and methylamine at 60°C, or in air at 123°C for 9.75 hours. Hence, homopolymerization was not a problem. During the attempts to cause self-condensation it was observed that, although 0.5 g of the diol failed to dissolve in 10 ml of toluene during an hour of stirring at 60°C, it dissolved very quickly at room temperature when methylamine was introduced. Subsequently, the solution was heated at 60°C for an hour, the toluene was evaporated, and the diol was recovered with its melting point unchanged. The presence of triethylamine also made the diol soluble in toluene. The amine evidently formed a type of bond with the silanol that made it soluble in the non-polar solvent.

Several filling agents were tried for improving the physical properties of the polymers. The agents tried (15% by weight) were zinc oxide, calcium carbonate, ferric oxide, carbon black, and aluminum. The highest elongation, 625%, was obtained with carbon black. The highest tensile strength at break (nominal), 175 psi, was obtained with calcium carbonate.

The appropriate values of the constants in the Mark-Houwink equation,[8]

$$[\eta] = KM^{\alpha}$$

were determined to make it possible to determine the molecular weights of polymers of this group from viscosity measurements in the future. The Mark-Houwink equation expresses the relationship between the intrinsic viscosity, $[\eta]$, and the weight average molecular weight, M, as determined by light scattering measurements. The values determined for the constants were: $K = 5.70 \times 10^{-5}$ and $\alpha = 0.753$.

The compressibilities of cured and filled samples of Polymers I, II, and III were measured at temperatures down to -78°C with a Shore durometer, Type A.[9] Low-temperature compressibility was improved by changing one of the phenyl groups to methyl (Polymer II) and by changing the silphenylene from para to meta (Polymer III). Comparisons were made with Viton A and a methyl silicone rubber, Dow Corning Corporation's Sealant Q-9-0024. As shown in Table I and Figure 1, the silphenylenes ranked between the silicone and Viton A over the temperature range studied. The Viton A was the hardest and the silicone rubber was the softest at all temperatures. The silphenylene that retained the most compressibility at the lower temperatures (4036-119-2, Polymer III) was almost equal to the silicone.

Values for the durometer hardness of Polymer I and two commercial elastomers after exposure to 66 megarads of gamma radiation are shown in Table II and Figure 2. The silphenylene with two phenyl groups and para substitution, Polymer I, was more stable than either the silicone or Viton A.

Table III and Figure 3 show values for the durometer hardness of four different elastomers after exposure to 350°C and 375°C in air and in nitrogen. All of the polymers observed became harder as they were heated in air or nitrogen, except the para silphenylene diphenyl (Polymer I) and the silicone. Polymer I changed very little in nitrogen at 350°C, and the silicone became soft, like putty, in nitrogen at 350°C. Viton A was the hardest at first and remained the hardest throughout the exposure period. The silicone became brittle in 1 hour at 350°C in air and cracked when the durometer was applied. Thus the silphenylenes retained compressibility longer than the Viton A or the silicone, and the difference was more striking in nitrogen than it was in air.

The silphenylenes that have been made to date are inferior to both Viton A and the silicones in strength before they are subjected to thermal and radiation stress. These silphenylenes should be considered for applications in which either thermal stability or radiation stability is needed, and comparatively low strength can be tolerated.

Table I. Hardness of Elastomers at Different Temperatures (by Shore durometer, Type A)

	Hardness at			
	27°C	3°C	-25°C	-78°C
Viton A	75	85	100	100
Polymer I, 4036-35-2, p-silphenylene diphenyl elastomer	35	85	95	100
Polymer II, 4036-101-2, p-silphenylene methylphenyl elastomer	39	60	72	100
Polymer III, 4036-119-2, m-silphenylene methylphenyl elastomer	32	36	51	96
DC Q-9-0024	31	32	35	80

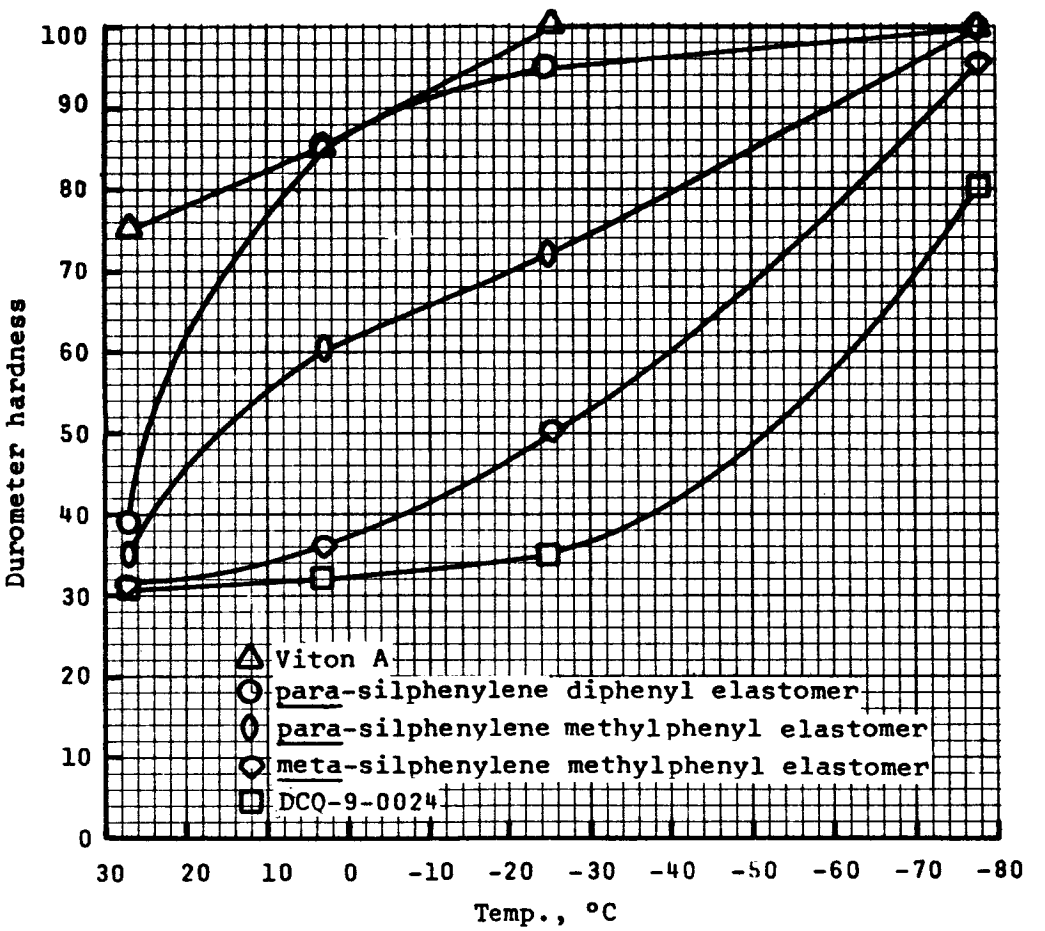


Figure 1. Durometer Hardness of Elastomers at Low Temperatures (Shore durometer "A")

Table II. Hardness of Elastomers Exposed to Gamma Radiation (by Shore durometer, Type A)

Amount of radiation, megarads[b]	Polymer I 4036-70-C[a]	Viton A	DC Q-9-0024
0	54	75	30
2.6	54	83	35
10.5	50	84	38
13.3	52	86	40
21.1	52	86	44
36.9	52	91	53
54.0	-	-	62
59.0	-	-	64
66.0	55	94	66

a. Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] filled with zinc oxide

b. Dose rate, 0.11 megarads per hour with cobalt-60

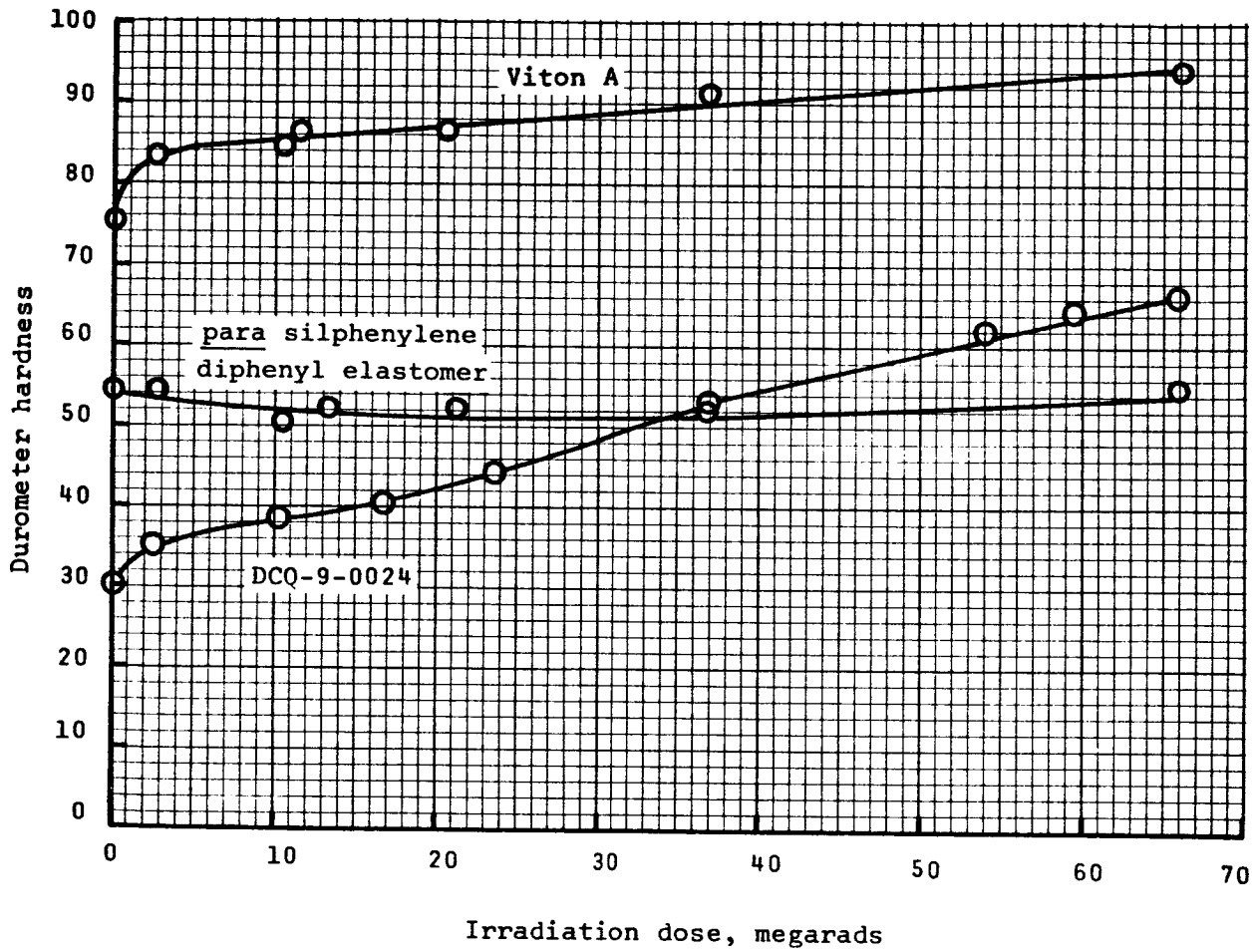


Figure 2. Hardness of Elastomers Exposed to Gamma Radiation (Shore durometer "A")

Table III. Hardness[a] of Elastomers after Heating for Various Times at 350°C and 375°C in Air and in Nitrogen

Heating time, hours	Viton A				Polymer I (4036-59-3)[b]				Polymer I (4036-79-C)[b]	Polymer III (4036-119-2)[c]		DC Q-9-0024	
	Air		Nitrogen		Air		Nitrogen		Nitrogen	Air	Nitrogen	Air	Nitrogen
	350°C	375°C	350°C	375°C	350°C	375°C	350°C	375°C	375°C	350°C	350°C	350°C	350°C
0	75	75	75	75	35	35	35	35	42	32	32	33	33
1	85	99	83	96	68	64	35	40	42	36	36	37	like putty
2	90	100	85	100	78	73	35	41	46	47	40	cracked	in 1 hour
3	90	-	88	-	80	-	35	-	49	51	45	-	-
4	92	-	92	-	80	-	35	46	-	cracked	50	-	-
5	93	-	95	-	87	-	35	-	-	-	split	-	-
6	94	-	96	-	92	-	40	-	61	-	-	-	-
7	96	-	-	-	95	-	-	-	65	-	-	-	-
8	98	-	-	-	96	-	-	-	66	-	-	-	-

a. Measured by Shore durometer type "A"

b. Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

c. Poly[1,3-bis(oxydimethylsilyl)benzene methylphenylsilane]

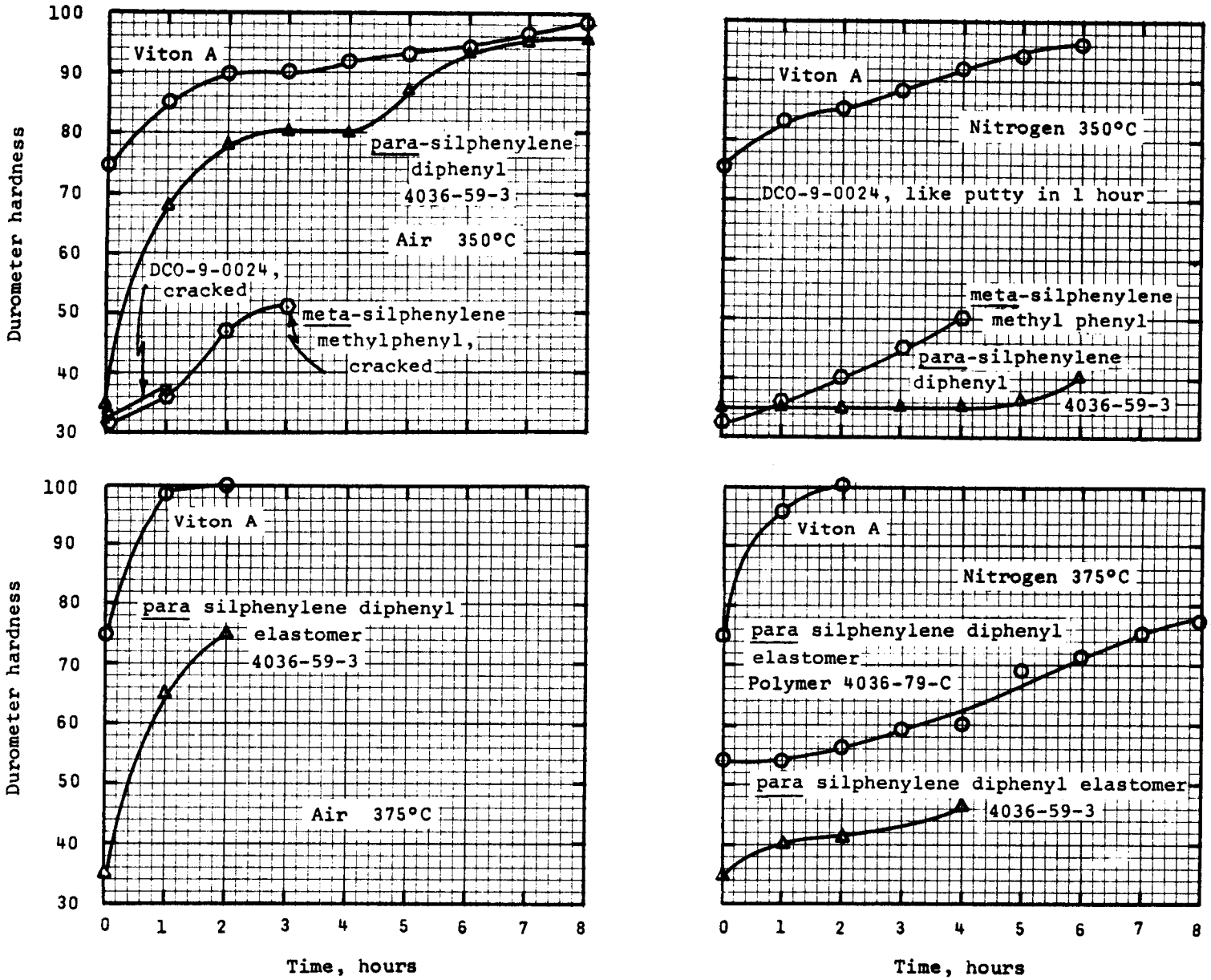


Figure 3. Changes in Hardness of Viton A and Silphenylene Elastomers at 350°C and 375°C (Shore durometer "A")

B. Experimental Details

1. Preparation of monomers

a. 1,4-bis(dimethylhydroxysilyl)benzene

(1) Via 1,4-bis(dimethylhydrogensilyl)benzene

1,4-Bis(dimethylhydrogensilyl)benzene was prepared by the method of Merker[10] as modified during the preceding contract.[11] The yield was 55% of theory. The hydrogen atoms were replaced by hydroxyls as described[11] with a yield of 54%. Thus the overall yield of 1,4-bis(dimethylhydroxysilyl)benzene from dibromobenzene by Merker's method was 30%, m.p. 136-137°C. Dow Corning has recently withdrawn dimethylchlorosilane, Me_2HSiCl, from the market so it is likely that the Merker method will not be used in the future; especially since the Sveda method,[12] which does not require dimethylchlorosilane, is preferred.

(2) Via 1,4-bis(dimethylchlorosilyl)benzene

Sveda[12] described the preparation of 1,4-bis(dimethylchlorosilyl)benzene. His method was used with only slight modifications as described previously.[11] The yield was 46% of theory based on dibromobenzene; dimethyldichlorosilane, the other reactant, was used in excess.

The hydrolysis of 1,4-bis(dimethylchlorosilyl)benzene to the silphenylene diol has been difficult because of the tendency to form polymers rather than the diol monomer. The adoption of ammonium hydroxide instead of sodium hydroxide for the hydrolysis was a significant improvement over Sveda. Yields of 85% or better were obtained when ammonium hydroxide was used in the hydrolysis step as described earlier.[11] The method was improved further by changing the hydrolysis procedure slightly and recrystallizing the crude hydrolysis product from carbon tetrachloride. The following procedure was carried out with a relatively impure distillate fraction of the silphenylene dichloride, which previously would have been discarded because it was not possible to obtain satisfactory diol from it.

1,4-Bis(dimethylchlorosilyl)benzene, b.p. 80-93°C at 0.5 mm, 42.33 g (0.16 mole), was dissolved in 450 ml of dry ether and added dropwise with vigorous stirring to 2 liters of a mixture of cracked ice and water that contained 205 ml (3.2 moles) of concentrated ammonium hydroxide. The ice mixture was in a 5-liter, 3-neck flask. The addition required about 30 minutes, and frost remained on the outside of the flask throughout the addition. Then the ether layer was removed in a separatory funnel. The water layer was extracted again with 500 ml of ether, and the combined ether layers were washed with 150 ml of water. The ether solution was then allowed to evaporate overnight in an evaporating dish. The crude diol, m.p. 122-128°C, was recrystallized once from 2 liters of carbon tetrachloride to give 19.48 g (0.086 mole) of 1,4-bis(dimethylhydroxysilyl)-benzene (54% yield), m.p. 136-137°C. One additional recrystallization of a 0.50-g sample from 40 ml of carbon tetrachloride yielded 0.47 g that melted sharply at 136°C. During recrystallization the solution was usually cooled to about 20°C. On one occasion the mother liquor was cooled to 1°C and allowed to stand overnight. The small amount of crystalline material that separated melted at 132-134°C. Consequently, 20°C is the crystallization temperature recommended for purification.

b. Preparation of bis(methylamino)diphenylsilane

Bis(methylamino)diphenylsilane was first prepared by the method of Larsson and Bjellerup.[13,14] A similar method was used for the present work, but the yield was much higher. In a 2-liter, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel was placed 500 ml of anhydrous ether. The ether was cooled to -15°C. Methylamine was drawn as a liquid from a cylinder into a 500-ml Erlenmeyer flask which was filled to a mark at the 325-ml level, and three pea-size pieces of sodium were added. A small amount of reaction with the sodium was detected, but it subsided quickly. The methylamine, estimated 250 g (8.0 moles), was decanted into the cooled ether. Then diphenyldichlorosilane, 166 ml (202 g, 0.8 mole), was added dropwise with stirring while the reaction mixture was kept below -15°C. The addition required 2.5 hours. The mixture was allowed to warm to room temperature, then it was refluxed for 1 hour. The salts were filtered off and washed with benzene. The benzene and ether solutions were combined, and the solvents were removed by distillation. Distillation of the product through a 30 x 1.2-cm packed column produced 159.3 g of material with a boiling point of 103-104°C at 0.2 mm (82% of theory). Gas chromatographic analysis indicated 99+% purity.

c. Bis(dimethylamino)diphenylsilane

Bis(dimethylamino)diphenylsilane was prepared in the manner just described for the bis(methylamino) compound. A 78% yield was obtained of material boiling at 138°C at 0.1 mm. Pmr spectra showed the ratio of methyl to phenyl protons to be 6:5.1 (theory 6:5).

Anal. Calculated for $C_{16}H_{22}N_2Si$: C 71.06, H 8.20, N 10.36, Si 10.38.

Found: C 71.16, H 8.19, N 10.17, Si 10.28.

Mol. wt. Calculated: 270.45.

Found (vapor osmometry): 265, 270.

d. Bis(methylamino)methylvinylsilane

Bis(methylamino)methylvinylsilane was prepared in the manner described for bis(methylamino)diphenylsilane but starting with methylvinyldichlorosilane. The product was obtained in 30% of the theoretical yield, and it boiled at 129-130°C. Zhinkin[15] reported a boiling point of 131°C at 743.5 mm.

e. Tris(dimethylamino)phenylsilane

Tris(dimethylamino)phenylsilane was prepared in the manner described for bis(methylamino)diphenylsilane but with phenyltrichlorosilane and dimethylamine. In the first distillation, a fraction boiling at 58-59°C at 0.2 mm (71% of theory) was obtained. This was judged to be 94% pure by gas chromatography; redistillation produced a fraction that was judged to be 99% pure (45% yield). Pmr spectra showed the ratio of methyl to phenyl protons to be 18:5 (theory, 18:5).

Anal. Calculated for $C_{12}H_{23}N_3Si$: C 60.71, H 9.76, N 17.70, Si 11.83.

Found: C 61.00, H 9.74, N 17.89.

Mol. wt. Calculated: 237.4.

Found (vapor osmometry): 254.

f. Bis(methylamino)methylphenylsilane

An earlier attempt to prepare bis(methylamino)methylphenylsilane[16] was reported to have been unsuccessful because the molecular weight did not agree with the calculated value even though the analysis was acceptable. Recent work with pmr spectra, which indicated high rates of exchange in silylamines, has suggested that the apparent high molecular weights were manifestations of intermolecular bonding in solution. Gas chromatography, which probably causes dissociation back to the monomer, indicated that a recent preparation was 98% pure.

The new preparation was carried out as follows:

Methylphenyldichlorosilane, 191.1 g (1.0 mole), was dissolved in 1000 ml of benzene and stirred under an atmosphere of methylamine for 3 hours. The resulting mixture was refluxed for 3 hours and filtered. The filtrate was freed of solvent by evaporation at reduced pressure, and the product was distilled at 57-58°C at 1.0 mm pressure. The yield was 50.6 g (0.281 mole), 28% of theory.

Anal. Calculated for $C_9H_{16}N_2Si$: C 59.94, H 8.94, N 15.54, Si 15.58.

Found: C 60.05, H 9.03, N 15.41, Si 15.83.

Mol. Wt. Calculated: 180.33.

Found (vapor osmometry): 350

Gas chromatography revealed three peaks. Two peaks having shorter retention times than the main component accounted for 2% of the total, and the main component was the remainder. Thus it is believed that pure bis(methylamino)methylphenylsilane was prepared and that it was partly dimerized (see Section XIV).

g. 1,3-Bis(dimethylhydroxysilyl)benzene

Four unsuccessful attempts were made to prepare 1,3-bis-(dimethylhydroxysilyl)benzene from m-dibromobenzene before it was finally obtained. In the first, magnesium was treated with m-dibromobenzene in tetrahydrofuran. Formation of the Grignard Reagent appeared to have been satisfactory by visual inspection,

so it was added to a 5% excess of dimethyldichlorosilane and refluxed for 1 hour. The salts were filtered off, and the product was distilled at 50-80°C at 0.5 mm. The product was hydrolyzed with dilute ammonium hydroxide, and a non-crystallizable oil was obtained. Pmr spectra indicated no Si-OH content. If any silphenylene dichloride was present, it evidently polymerized during hydrolysis. In the second attempt, diethyl ether was used as the solvent, and the product was found to contain 28.2% of bromine. The third attempt was made by the method described above in Section III.B.1.a.(2), except that only a 5% excess of magnesium was used. Pmr spectra of the product indicated that only half of the expected Si-Me and Si-OH groups were present. In the fourth attempt, the method described in Section III.B.1.a.(2) was followed closely, and a product that distilled at 75-95°C at 0.4 mm was obtained. Two-thirds of this product was dissolved in toluene and treated with methylamine to form the methylamino derivative, which was then added dropwise with rapid stirring to a large excess of water. The product formed an oil that crystallized partially in several hours, but efforts to separate the silphenylene diol from it were not successful. The other third of the product, 3.8 g, was dissolved in 50 ml of ether and added dropwise with rapid stirring to a mixture of 100 ml of crushed ice, 50 ml of water, and 100 ml of concentrated ammonium hydroxide. The organic material was extracted from ether and recrystallized three times from carbon tetrachloride to yield 1.6 g (7.1 millimoles, 20% of theory) of 1,3-bis(dimethylhydroxysilyl)benzene, m.p. 78-79°C. This material was used to make a polymer for the study of low-temperature resilience.

h. Attempts to prepare 2,5-bis(dimethylhydroxysilyl)-toluene

2,5-Dibromotoluene was treated with magnesium and dimethyldichlorosilane by methods that paralleled those just described. No silphenylene diol could be isolated from any of the products. Apparently the reactions failed because of incomplete formation of the -MgBr derivatives or polymerization during hydrolysis of the silphenylene chloride.

2. Homopolymerization of the silphenylene diol

The tendency of the monomer, 1,4-bis(dimethylhydroxysilyl)-benzene, "the silphenylene diol", to condense with itself was investigated because of the possibility that homopolymerization was a detrimental factor in the diol-diaminosilane reaction. The silphenylene diol, 0.5 g, m.p. 137-138°C, was stirred with toluene, 10 ml, for 1 hour at 60°C. The crystals did not dissolve completely. The toluene was evaporated in a stream of nitrogen, and the residue was found to melt at 137-138°C. Evidently no polymerization occurred. The diol was again mixed with 10 ml of toluene, and methylamine was passed over the surface of the liquid while the liquid was being stirred. The solution became clear within a minute after the amine was first introduced, and the temperature rose to 35°C. The solution was stirred for 1 hour at 60°C, then the solvent and methylamine were removed by evaporation in a stream of nitrogen. The residue melted at 137-138°C.

The diol was placed in an open beaker in an oven at 123°C for 9.75 hours. Some sublimation occurred, but the remainder melted at 137-138°C. Evidently homopolymerization does not occur readily without a catalyst.

3. Preparation of polymers

a. Polymerization to Polymer I

Polymerization 3794-151-1 was typical of the preparations of Polymer I, poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane], that are summarized in Table IV.

In a 100-ml, 3-neck flask fitted with a thermometer, magnetic stirrer, and reflux condenser was placed 5.52 g (0.0228 mole) of bis(methylamino)diphenylsilane. To this was added 5.00 g (0.0228 mole) of 1,4-bis(dimethylhydroxysilyl)benzene slurried and largely dissolved in 50 ml of dry toluene. No increase in temperature was observed. As the mixture was heated, gas bubbles appeared, and the undissolved solid disappeared when the temperature reached about 60°C. The mixture was refluxed for 2 hours, during which time gas evolution became progressively slower, and then the toluene was distilled off while the pot temperature rose to 200°C. The pressure was reduced to 1 mm to remove the last traces of toluene. In about 5 minutes the melt became so viscous that stirring could not be continued, so the reaction was terminated. The product was a cloudy, rubbery solid at toom temperature.

Table IV. Preparation of Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] (Polymer I)

Starting material	Solvent	Method: Time, hr[a]	Temp, °C	Press, mm	Product: MW	State	Polymer number
Me vinyl[b]	THF	2.0 3.0	200 210	atm 0.03	27,000[c]	visc. liq.	3794-141-1
3794-141-1		4.0	255	0.03	31,000[c]	visc. liq.	3794-141-2
Normal[d]	THF	1.0 2.0 0.2	200 260 310	atm 0.03 0.03	-	visc. liq.	3794-143-1
Normal[d]	none	2.0 2.5	200 260	atm 0.02	43,000[c]	rub. solid	3794-147-A
Normal[d]	toluene	0.1	200	1.0	51,000[c]	rub. solid	3794-151-1
Normal[d]	toluene	1.0	255	0.02	-	soft solid	3794-159-1
Normal[e]	toluene	2.0 2.5	200 250	atm 0.02	260,000[c]	rub. solid	4036-13-1
XS diol[f]	toluene	2.0 2.5	200 250	atm 0.02	32,000[c]	visc. liq.	4036-15-1
XS amine[g]	toluene	2.0 2.5	200 250	atm 0.02	82,000[c]	soft solid	4036-17-1
Normal[e]	toluene	2.0 2.5	200 250	atm 0.02	-	visc. liq.	4036-35-1
Diamine[h]	toluene	2.0 2.5	200 250	atm 0.02	-	visc. liq.	4036-27-1
Tris[j]	toluene	0.5	75	0.03	-	visc. liq.	4036-39-1
Normal[h]	toluene	2.0 2.5	200 250	atm 0.02	-	rub. solid	4036-41-1
Normal[e]	toluene	2.0 0.16	200 240	atm 0.02	610,000[c]	rub. solid	4036-47-1
Repptd[k]	benzene	-	-	-	630,000[c]	rub. solid	4036-47-4
Normal[e]	triethylamine	2.0 2.5	200 250	atm 0.02	140,000[m]	rub. solid	4036-59-1
Tris[n]	toluene	-	-	-	-	visc. liq.	4036-61-1
Amine deficient[p]	toluene	2.0 2.5	200 250	atm 0.02	40,000[m]	visc. liq.	4036-63-1
Normal[e]	toluene	2.0 2.5	200 250	atm 0.04	130,000[c]	rub. solid	4036-65-1
Repptd[k]	benzene	-	-	-	150,000[m]	rub. solid	4036-65-3
Normal[e]	toluene	0.5 0.5	200[q] 250	atm 0.02	-	rub. solid	4036-75-1
Normal[e]	toluene	0.5	200	atm	260,000[m]	rub. solid	4036-79-1

See the following page for footnotes

Footnotes for Table IV.

a. Time at 200°C or above after the initial rapid reaction or after removal of solvent

b. 5% of the stoichiometric amount of bis(methylamino)diphenylsilane was replaced by bis(methylamino)methylvinylsilane

c. By light scattering

d. Stoichiometric amounts of bis(methylamino)diphenylsilane and 1,4-bis(dimethylhydroxysilyl)benzene weighed to 1% accuracy

e. Same as d but to 0.01% accuracy

f. 5% excess 1,4-bis(dimethylhydroxysilyl)benzene

g. 5% excess bis(methylamino)diphenylsilane

h. Bis(dimethylamino)diphenylsilane as the silylamine reactant - weighed to 0.01% accuracy

j. 7.25% of stoichiometric amount of bis(methylamino)diphenylsilane replaced by tris(dimethylamino)phenylsilane

k. Preceding polymer dissolved in benzene and reprecipitated with methyl alcohol

m. Molecular weight estimated from solution viscosity measurements

n. Same as j but 2%

p. 2% of the equivalent amount of silylamine was left out to provide silanol end groups. The triaminosilane curing agent was added later to form the elastomer

q. Filler, calcium carbonate, added before heating. See Table VI for additional treatment

Other reactions were conducted in the manner described but with the variations indicated in Table IV. In the experiment without solvent, 3794-147-A, no reaction was detected when the reactants were mixed at room temperature. Gas evolution began and the melt became uniform when the temperature reached about 60°C. The temperature was further increased and held at 200°C for 2 hours at atmospheric pressure. The time after the reaction temperature reached 200°C is shown in Table IV.

At attempt was made to purify one polymer by the following method: Polymer 4036-47-1, 6.0 g, was dissolved in 50 ml of benzene by stirring and warming slightly. After the solution was cooled to room temperature, methanol (about 50 ml) was added until no more precipitation occurred. Polymer 4036-47-4 settled out, and the cloudy supernatant solution was decanted to yield 1.2 g of a polymer that was slightly softer and stickier than the original. The molecular weight determined by light scattering was 630,000; for the starting polymer, 4036-47-1, the molecular weight was 610,000.

Polymer 4036-61-1 (Table IV) was prepared with the intention of introducing the triaminosilane cross-linking agent into the initial reaction mixture and stopping the polymerization while the polymer could still be molded. 1,4-Bis(dimethylhydroxysilyl)-benzene, 2.1057 g (0.0186 equivalent), was treated with 2.2260 g (0.0183 equivalent) BMADPS and 0.0296 g (0.0003 equivalent) of tris(dimethylamino)phenylsilane in 20 ml of toluene. The solution was refluxed for 2 hours, and then the toluene was removed at reduced pressure while the temperature was kept below 40°C. The polymer was a viscous liquid.

b. <u>Polymerization to Polymer II</u>

Poly[1,4-bis(oxydimethylsilyl)benzene methylphenylsilane] was prepared by refluxing 2.151 g (0.0095 mole) of 1,4-bis-(dimethylhydroxysilyl)benzene with 1.713 g (0.0095 mole) of bis(methylamino)methylphenylsilane in 20 ml of toluene for 2 hours. The toluene was distilled off, and the partly polymerized material was heated at 200°C for 2 hours and 250°C for 2.5 hours at 0.04 mm pressure. The product was a clear, slightly viscous liquid, 4036-101-1. It had a molecular weight of 20,000 by light scattering.

c. Polymerization to Polymer III

Poly[1,3-bis(oxydimethylsilyl)benzene methylphenylsilane] was prepared by refluxing 0.8387 g (0.0037 mole) of 1,3-bis-(dimethylhydroxysilyl)benzene with 0.6676 g (0.0037 mole) of bis(methylamino)methylphenylsilane in 10 ml of toluene for 2 hours. The solvent was distilled off, and the partly polymerized material was heated at 200°C for 2 hours and at 250°C for 2.5 hours at 0.04 mm pressure. The product was a clear, slightly viscous liquid (4036-119-1).

4. Curing of polymers

The method of curing Elastomer 3794-151-B illustrates the general method used for the entire group of elastomers prepared from Polymer I as described in Table V. The rubbery solid, 3794-151-1, 1.5 g was stirred with 3.0 ml of tetrahydrofuran (THF) to form a viscous liquid. To this was added 0.015 g (1% of the polymer) of dicumyl peroxide (from K and K Laboratories, Inc., Plainview, New York). The polymer-peroxide mixture appeared homogeneous after being stirred for about 10 minutes in a Teflon beaker. The mixture was placed in a mold, which was a 2 x 0.5 x 0.125-inch recess machined in a Teflon bar. The filled mold was placed in a vacuum desiccator, and the pressure was reduced slowly to 0.04 mm to remove the solvent. Foaming occurred, and the result was a rounded mass in the mold. Heating to 200°C did not cause the bubbles to collapse, and so the sample was placed in an oven at 250°C for 41 hours. After this time the product was a smooth, tacky, elastic solid. Further heating for 2 hours at 350°C produced a smooth, slightly cloudy, orange elastomer. Tensile measurements on strips cut from the product showed it to have a tensile strength at break (nominal)[17] of 72 psi, an elongation at break of 112%, and a modulus of elasticity[17] of 104 psi when elongated at 20% per minute.

The other polymers were sufficiently soft that THF was not needed to make them pliable. However, benzoyl peroxide (Distillation Products Industries, Rochester, N. Y.) did not dissolve in any of the polymers at room temperature to form homogeneous masses. The other peroxides appeared to blend satisfactorily. 2,4-Dichlorobenzoyl peroxide was obtained from Wallace and Tiernan, Inc., Buffalo, New York as a 50-50 blend with dibutyl phthalate. Di-*tert*-butyl peroxide was also obtained from Wallace and Tiernan, and 2,5-dimethyl-2,5-di-*tert*-butyl-peroxyhexane was obtained from K and K Laboratories, Inc.

Table V. Preparation of Unfilled Elastomers from Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] (Polymer I)

Polymer	Peroxide, %	Curing method (in open mold) Time in air, hr at 125°C	200°C	250°C	350°C	Elastomer number	Elastomer Modulus,[a] psi	Elongation at break, %	Ten. str.[b] psi	Thickness, in.	Appearance[c]	Recovery when stretched
3794-141-1	benzoyl, 1	-	4.0	25	2	3794-141-A	-	-	-	-	lumpy	slow
3794-141-2	-	-	2.5	41	2	3794-141-B	110	100	50	0.105	smooth	fast
	-	-	2.5	41	2	3794-141-D	130	90	90	0.032	smooth	fast
3794-143-1	benzoyl, 3	-	2.5	41	2	3794-141-D	-	-	-	-	bubbles	slow
	dicumyl, 3	-	2.5	63	2	3794-143-C	100	80	50	0.073	smooth	fast
3794-147-A	-	-	0	17	2	3794-147-C	60	180	60	0.078	smooth	fast
	di-t-but,[d] 3	-	2.5	41	2	3794-153-A	-	-	-	-	bubbles	fast
3794-151-1	-	-	2.5	41	5	3794-151-A	210	60	80	0.063	smooth	slow
	dicumyl, 1	-	0	41	2	3794-151-B	100	110	70	0.036	smooth	fast
3794-159-1	-	-	2.5	41	2	3794-159-A	50	170	40	0.058	smooth, tacky	slow
	dichlbenz.[e] 1	-	2.5	41	2	3794-159-B	-	-	-	-	bubbled, tacky	v. slow
	di-t-but,[d] 1	-	2.5	41	2	3794-159-C	-	-	-	-	wrinkled, tacky	v. slow
	2,5-dimet,[f] 1	-	2.5	41	2	3794-159-D	30	320	20	0.056	rough, tacky	v. slow
4036-13-1	-	-	2.0	41	2	4036-13-2	70	100	90	0.055	smooth	fast
4036-15-1	-	-	2.0	41	2	4036-15-2	-	-	-	-	bubbled, tacky	slow
4036-17-1	-	-	2.0	41	2	4036-17-2	70	90	40	0.061	smooth	fast
Q-9-0024[g]	-	-	-	-	0	4036-3-A	70	500	1400	0.082	smooth	v. fast
	-	-	-	-	2	4036-3-E	15	70	15	0.081	tacky, friable	slow
4036-27-1	-	-	2.0	72	2	4036-27-2	60	110	60	0.053	smooth	fast
4036-35-1	-	-	2	72	2	4036-35-2	25	120	20	0.067	smooth	slow
4036-41-1[h]	-	-	-	149	2	4036-41-2	150	80	100	0.040	smooth	fast
4036-47-4	-	-	0.25	18	2	4036-53-1	70	170	70	0.065	smooth	fast
4036-47-4	-	-	0.25	24	6	4036-53-2	2400	100	280	0.075	smooth	slow
4036-59-1[j]	-	-	-	28	2	4036-59-2	80	150	90	0.050	smooth	fast
4036-61-1[k]	-	18	-	48	2.5	4036-61-2	30	470	30	0.061	smooth	fast
4036-61-1[k]	-	18	-	48	5	4036-61-3	100	150	190	0.057	smooth	slow
4036-63-1[m]	-	24	-	48	3.5	4036-63-2	2400	60	250	0.046	smooth	slow
4036-65-1	-	-	-	48	4.5	4036-65-7	380	80	110	0.068	smooth	fast
4036-65-3	-	-	-	48	3.5	4036-65-6	110	170	140	0.065	smooth	fast

See following page for footnotes

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Footnotes for Table V.

a. Modulus of elasticity. For definition, see Reference 17

b. Tensile strength at break (nominal). For definition, see Reference 17

c. All samples were softer in the center than on the surface

d. Di-*tert*-butyl peroxide

e. 2,4-Dichlorobenzoyl peroxide used as 50-50 blend with dibutyl phthalate, but the 1% figure is based on the weight of peroxide

f. 2,5-Dimethyl-2,5-di-*tert*-butylperoxylhexane

g. Dow Corning Sealant Q-9-0024 cured at room temperature 3 days

h. Tris(dimethylamino)phenylsilane, 5% by weight, stirred in before curing

j. Triethylamine as solvent

k. Polymer cured in nitrogen until it was heated at 350°C for 2.5 hr in air

m. Same as h, but 2%

Polymer 4036-61-1, which had been made with a small amount of the triaminosilane crosslinking agent, was processed by heating in a Teflon mold in a nitrogen atmosphere as described in Table V. It did not lose its tackiness in 48 hours at 250°C in nitrogen, so it was heated 2.5 hours at 350°C in air.

The preferred method for preparing the elastomers was to heat the polymers in cylindrical aluminum dishes 3/16-inch deep and 1 inch or 2 inches in diameter. The cured elastomers were removed by cooling the dishes in dry ice, cutting the sides, and peeling off the aluminum.

A sample of Polymer II (4036-101-1) was cured in an aluminum planchet by heating in air for 162 hours at 250°C and 3.5 hours at 350°C. The resulting clear, yellow elastomer, 4036-101-2, appeared to recover faster when deformed than the diphenyl elastomers. The modulus of elasticity was 450 psi, the tensile strength at break (nominal) was 52 psi, and the elongation at break was 36%. Another portion of 4036-101-1 was mixed with 30% by weight of Spanish red oxide and cured in a planchet at 250°C for 96 hours and at 350°C for 3.5 hours. The red elastomer, 4036-101-3, also recovered quickly after deformation; it had a modulus of elasticity of 770 psi, a tensile strength at break (nominal) of 76 psi, and an elongation at break of 36%.

A sample of Polymer III (4036-119-1) was cured in an aluminum planchet by heating in air for 164 hours at 250°C and 2.5 hours at 350°C. The resulting clear, yellow elastomer, 4036-119-2, had good recovery.

5. Filling the polymers

The following is an example of the method of filling the polymers to form the elastomers listed in Table VI. Polymer 4036-75-1, 3.51 g, was stirred with 8 ml of toluene to form a viscous solution. Precipitated calcium carbonate, Purecal-O, Wyandotte Chemical Corp., 0.52 g, was stirred into the solution for 30 minutes with a magnetic stirrer, and then the solvent was removed at reduced pressure. The sample was heated at 200°C for 0.5 hour and at 250°C at 0.02 mm pressure for 0.5 hour. The resulting polymer was white, sticky, and elastic. A 1.5-g portion of the white, sticky polymer was heated in a Teflon mold (0.5 x 2.0 x 0.125 in.) at 250°C for 69 hours and at 350°C for 4 hours. The resulting smooth strip had good recovery when stretched.

Table VI. Preparation of Filled Elastomers from Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] (Polymer I)

Polymer	Curing method (in open mold) Time in air, hr at 250°C	350°C	Filler	Elastomers: Elastomer	Modulus, psi	Elongation at break, %	Tenacity, psi	Thickness, in.	Appearance	Recovery when stretched
4036-39-1	32	2	ferric[a] oxide	4036-39-2	461	38	49	0.1073	smooth	slow
4036-75-1[b]	93	3.5	calcium[c] carbonate	4036-75-2	50	167	49	0.1251	smooth	fast
4036-75-1[b]	69	2	calcium[c] carbonate	4036-75-3A	38	192	45	0.0725	smooth	fast
4036-75-1[b]	69	4	calcium[c] carbonate	4036-75-3B	225	168	175	0.0583	smooth	fast
4036-79-1[b]	41	6	aluminum[d] pigment	4036-79-B	140	464	37	0.0967	smooth	fast
4036-79-1[b]	20	5	zinc[e] oxide	4036-79-C	252	176	110	0.0975	smooth	fast
4036-79-1[b]	92	3	carbon[f] black	4036-79-D	98	626	50	0.1236	grainy	fast
4036-79-1[b]	43	3	ferric[a] oxide	4036-79-E	33	176	48	0.0795	smooth	fast

a. 15% ferric oxide by weight (Spanish Red Oxide, C. J. Osborn Company, Linden, New Jersey)

b. Polymer dissolved in 5-10 ml of toluene before filler added

c. 15% calcium carbonate by weight (Purecal-O, Wyandotte Chemical Corp., Wyandotte, Mich.)

d. 15% aluminum pigment by weight (No. 322, Aluminum Company of America, Pittsburgh, Pa.)

e. 15% zinc oxide by weight (No. 505XX New Jersey Zinc Company, New York, New York)

f. 15% carbon black by weight (SRF carbon black, Cabot Corporation, Boston, Mass.)

6. Hardness of elastomers

The hardnesses of Viton A, Dow Corning sealant Q-9-0024, and the silphenylene elastomers were compared at low temperatures, at elevated temperatures, and after they were exposed to gamma radiation. Hardness was measured with a Shore durometer, Type A.[9] Data on hardness at 27°C, 3°C, -25°C, and -78°C are in Table I and Figure 1.

The elastomers were exposed at 20°C to gamma radiation from cobalt-60 at a dose rate of 0.11 megarads per hour, and hardness was measured at frequent intervals for 25 days until 66 million rads had been received. The results are in Table II and Figure 2.

The elastomers were heated in air and nitrogen at 350°C and at 375°C, and measurements of hardness were made each hour. The data are in Table III and Figure 3. DC Q-9-0024 cracked when the attempt was made to measure hardness after an hour at 350°C in air, and it was soft like putty at the end of an hour at 350°C in nitrogen. Consequently, no measurements were attempted at 375°C.

7. Relationship between molecular weight and viscosity

To facilitate the determination of molecular weights of samples of Polymer I in future studies, the values of constants for the Mark-Houwink equation were determined so that the molecular weights could be calculated from intrinsic viscosity values. The Mark-Houwink equation,[8] a general empirical relationship between intrinsic viscosity, $[\eta]$, and the weight-average molecular weight, M, has the form $[\eta] = KM^{\alpha}$, in which K and α are constants for a given polymer, solvent, and temperature. To determine K and α, it is necessary to have intrinsic viscosity data on at least two polymers of known molecular weights. The weight-average molecular weights of several specimens of Polymer I were determined by light scattering, and the intrinsic viscosities of the same polymers were determined at 30°C in tetrahydrofuran. The values of K and α were found to be 5.70×10^{-5} and 0.753, respectively, by determining the best fit of the data by the least-squares method.

Table VII lists the data on the inherent and the intrinsic viscosities and molecular weights. Figure 4 is a plot of the intrinsic viscosities and molecular weights.

Table VII. Viscosities and Molecular Weights of Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] (Polymer I)

Polymer	Viscosity		Molecular weight[b]
	Inherent[a]	Intrinsic	
4036-13-1	0.62	0.700	260,000
4036-15-1	0.15	0.154	32,000
4036-17-1	0.25	0.250	82,000
4036-47-1	1.06	1.334	610,000
4036-65-1	0.37	0.392	130,000

a. Determined at 30°C at a concentration of 1.00 g per deciliter in tetrahydrofuran

b. Weight average, by light scattering

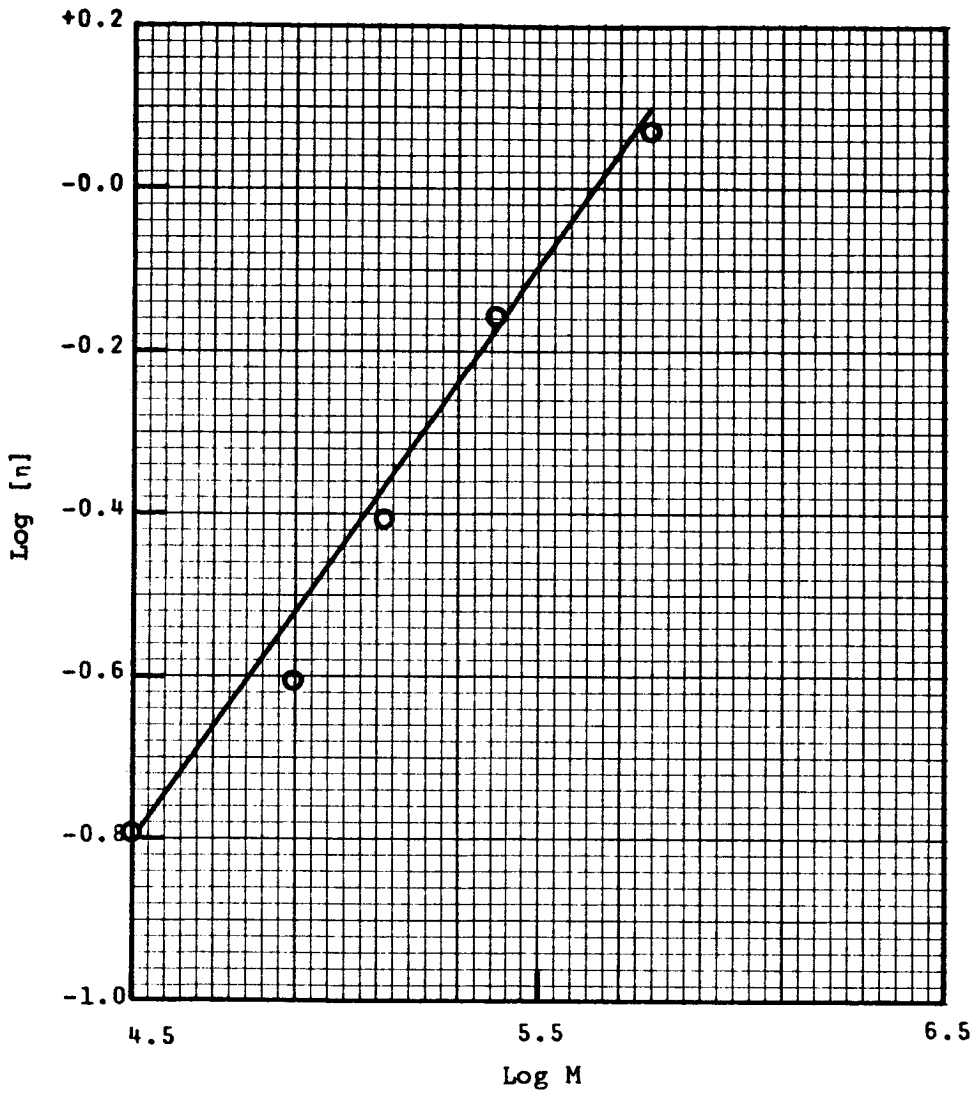
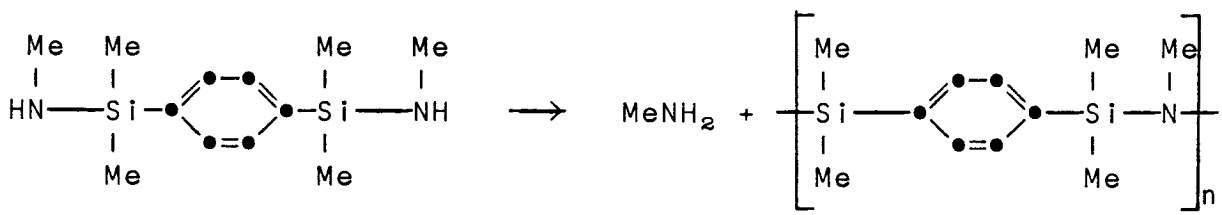


Figure 4. Relation of Intrinsic Viscosity to Molecular Weight of Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

IV. POLYMERIC SILPHENYLENE AMINES

A. Discussion

In earlier work, silphenylene amine polymers were prepared with molecular weights up to 50,000, and they were found to have excellent thermal stability.[18] The investigation was continued to improve the methods of preparation and to find means of crosslinking with the expectation that the products might be useful in laminates, adhesives, or structural resins.



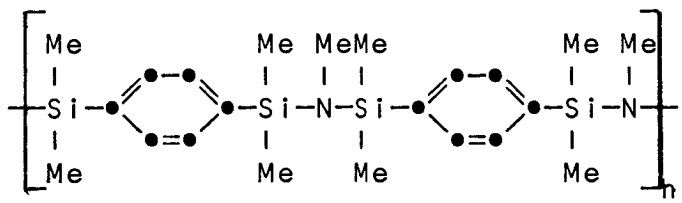
1,4-bis(methylaminodimethylsilyl)benzene poly(tetramethyl-p-silphenylene methylamine)

1,4-Bis(methylaminodimethylsilyl)benzene is polymerized by heat, and the reaction proceeds faster and to higher molecular weights if a small amount of anhydrous magnesium chloride is present. An apparent catalytic effect of magnesium in the thermal condensation reaction was later shown to be more likely a result of interaction of magnesium with the silphenylene chloride to form magnesium chloride. In the earlier work,[18] the highest molecular weight, 52,000, was obtained by heating at 300°C for 8 hours at pressures of 0.01-0.1 mm. Recently a silphenylene amine polymer was prepared with a molecular weight of 68,000. It was a tough solid that resembled nylon in appearance, but it was soft enough to flow at 200°C. The two most interesting products made from the silphenylene amines were a resilient foam with good thermal stability that was made by crosslinking with pentaerythritol, and a protective coating that is described in Section V.

Pentaerythritol was the only successful one of many potential crosslinking agents that were tried. The unsuccessful agents were phloroglucinol, p,p'-biphenol, hexaphenylcyclotrisilazane, and a silphenylene polymer made by the reaction of 1,4-bis(dimethylchlorosilyl)benzene with ammonia. When these latter agents were

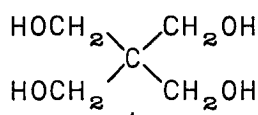
heated with the polymeric silphenylene amine for long periods at 400°C, some crosslinking apparently occurred, but it was found that the same effect was obtained by heating without the agent and with or without air. The products did not soften enough to flow at 400°C. They were relatively weak, resilient polymers that could be molded under pressure at 200°C to form discs. The nitrogen contents were 2.4-3.1%, 37-50% of theoretical for the silphenylene amine polymer shown above. The discs lost 8-10% in weight when heated for 1 hour at 400°C in nitrogen, and 13-17% when heated for 1 hour at 400°C in air. Although this behavior constitutes worthwhile thermal stability, the polymers were relatively weak; and they appeared to consist partly of decomposition products, so investigation of these products was discontinued in favor of the products made with pentaerythritol.

The reaction with pentaerythritol to form resilient polymers is believed to be this:

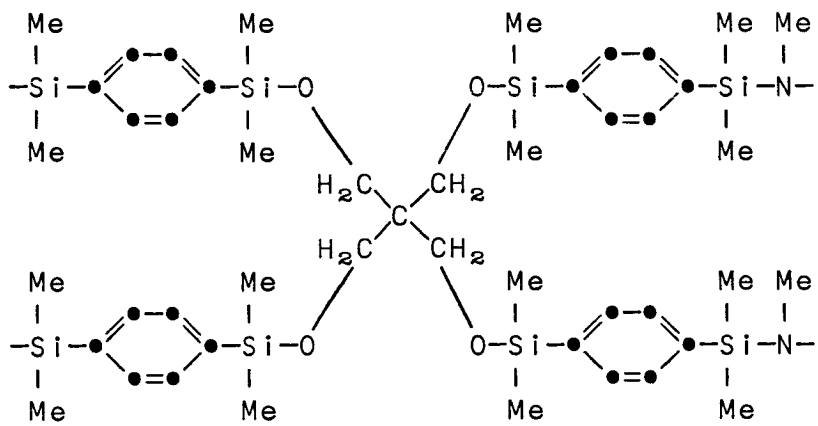


poly(tetramethyl-p-silphenylene methylamine)

+



pentaerythritol



The silphenylene amines crosslinked with pentaerythritol are interesting for several reasons in addition to their thermal stability and resilience. They can be cured at relatively low temperatures, 125-250°C, and they can be cured in the absence of air, which makes it possible to form them in molds. When the reaction is conducted under conditions that permit the polymer to expand, the product is an infusible foam. When the reaction is conducted in a piston mold that permits the escape of gas but not polymer, the product is a solid elastomer. Many, but not all, of the crosslinked silphenylene amines have crystallized on standing at room temperature with resultant loss in compressibility and an increase in toughness. One explanation is that the various polymers had undergone different degrees of exposure to oxygen or moisture which resulted in varying degrees of conversion of silphenylene-N-silphenylene units to silphenylene-O-silphenylene units. The latter are known to exhibit the crystallization phenomenon observed in our original "aromatic bridged" polymer,[19] which contained only 0.1% nitrogen, and in the Merker-Scott polymer,[10] which was made by self-condensation of the silphenylene diol. It is significant that the silphenylene-O-Si-O-silphenylene units of the polymers described in Section III, above, do not crystallize on standing at room temperature.

The silphenylene amines crosslinked with pentaerythritol are lively enough to bounce when dropped, and they do not become soft enough to flow even when heated to red heat. However, they are swollen by benzene.

To crosslink the silphenylene amine polymer, it was heated with amounts ranging from 8.5% to 60% of the stoichiometric amount of pentaerythritol. When the amount of pentaerythritol was 45% or more, the cured polymer contained visible crystals of pentaerythritol. When curing was done in a piston mold that permitted leakage of gas, the product was a solid disc with only a few bubbles at the outer edges. One solid disc that had been allowed ample time at room temperature to undergo its hardening processes had the following strength properties: modulus of elasticity, 1400 psi; tensile strength at break (nominal),[17] 420 psi; elongation at break, 60%.

In one series of experiments, a silphenylene amine polymer, (3640-127-2, molecular weight 45,000) was crosslinked with pentaerythritol while between aluminum plates spaced about 0.25-inch apart. The mixture was then cured at 250°C for 1 hour to form a foamed elastomer that was well-bonded to the two plates. This sandwich sample, designated 3640-125-1, was sent to Marshall Space Flight Center for examination. The elastomer did not harden at room temperature during several weeks.

The relationship of the weight-average molecular weight, M, to intrinsic viscosity, [η], for the linear silphenylene amine polymer described above was determined to facilitate estimations of molecular weights. The equation: $[\eta] = 13.0 \times 10^{-6} M^{0.96}$ was derived from the data.

B. Experimental Details

1. Preparation of monomers or oligomers for polymerization

a. Preparation of 1,4-bis(methylaminodimethylsilyl) benzene

The method of Breed and Elliott was used.[20] In a 2-liter, 3-neck flask fitted with a stirrer, thermometer, gas-inlet tube, and a condenser cooled with dry ice were placed 200 ml of dry toluene and 12.61 g (0.047 mole) of 1,4-bis(dimethylchlorosilyl)-benzene.[11] The solution was stirred, cooled to 0°C, and methylamine gas was passed in above the surface of the solution. The temperature was kept below 3°C, and introduction of methylamine was stopped after about 1.5 hours when methylamine began to reflux. The cold solution was filtered, and most of the solvent was evaporated in the filter flask by lowering the pressure with a water aspirator. The concentrated product was distilled, and a fraction, 5.53 g (46% of theory), b.p. 87°C at 0.5 mm, was obtained.

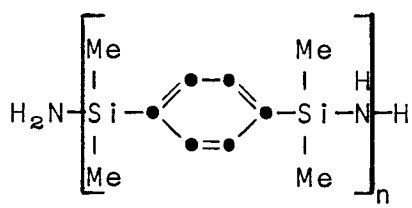
Anal. Calculated for $C_{12}H_{24}N_2Si_2$: C 57.08, H 9.58, N 11.09, Si 22.25.

Found: C 57.38, H 9.21, N 11.57.

The reaction reported above was one of six. One was run in ether, one in benzene, and four in toluene. The yields from the reactions in toluene ranged from 22-46% of theory. The reactions in ether or benzene yielded no monomer. It was important to keep the temperature as low as possible until the final distillation. In one case, an attempt was made to redistill the monomer; but condensation occurred, and the monomer was lost. Still residues were oligomers of 1,4-bis(methylaminodimethylsilyl)-benzene.

b. 1,4-Bis(aminodimethylsilyl)benzene oligomer

The reaction between 1,4-bis(dimethylchlorosilyl)benzene and ammonia was first described in a preceding report.[19] 1,4-Bis-dimethylchlorosilyl)benzene,[11] 21.75 g, was dissolved in toluene and cooled to 0°C. The solution was stirred and kept at 0-3°C while dry ammonia was passed over the surface for 3 hours. The solution was filtered, the precipitate was washed with toluene, and the clear filtrate was freed of solvent by evaporation at reduced pressure. The product was a white, waxy solid. Earlier preparations[19] yielded similar products having n = 1 to 3 in the formula:



This composition is called the silphenylene-ammonia oligomer.

2. Polymerization reactions

The reactions listed in Table VIII were designed to determine the effectiveness of catalysts and to prepare polymers for subsequent studies of crosslinking reactions. The reactions were conducted in pairs so parallelism in pressure, temperature, and time of heating could be maintained closely. In each pair of reactions, equal amounts of starting material were placed in 50-ml, 3-neck flasks fitted with thermometers, magnetic stirrers, and connections to vacuum lines. Heat was applied with electrical heating mantles. Viscosities were measured in tetrahydrofuran. Two specific polymerizations are described below.

The oligomer of 1,4-bis(methylaminodimethylsilyl)benzene, 3640-127-1, was polymerized by heating 15.0 g with 0.02 g of anhydrous magnesium chloride at 300°C for 8 hours at 0.04 mm pressure. When cool, the product, poly(tetramethyl-p-silphenylene methylamine), 3640-127-2, was a tough, white solid that had an inherent viscosity of 0.35 deciliters per gram. Based on previous data, this viscosity indicated the molecular weight to be about 45,000.

Table VIII. Preparation of Poly(tetramethyl-p-silphenylene methylamine)

Starting material	Polymerization conditions				Weight loss,[a] % of theory	Inherent viscosity, dl/g	Phys. state	Molecular weight, estd.[b]	Polymer 3640-
	Temp., °C	Press., mm Hg	Time, hr	Catalyst, weight %					
Monomer 3640-97-1	250	0.1	2	Mg, 6	-	0.13	visc. liq.	13,000	99-1
Monomer 3640-97-1	250	0.1	2	-	-	0.19	visc. liq.	18,000	99-2
Oligomer 3640-97-2	200 250	0.01 0.01	2 2	Mg, 2	47	0.071	visc. liq.	9,000	105-1
Oligomer 3640-97-2	200 250	0.01 0.01	2 2	-	63	0.066	visc. liq.	8,000	105-2
Monomer 3640-97-1	200	ambient	4	Mg, 1	120	-	visc. liq.	-	109-1
Monomer 3640-97-1	200	ambient	4		134	-	visc. liq.	-	109-2
Polymer 3640-109-1	200	-[c]	2	Mg + diCl[d]	164[e]	-	grease	-	109-1A
Polymer 3640-109-2	200	-[c]	2	diCl[d]	136[e]	-	visc. liq.	-	109-2A
Oligomer 3640-97-2	200	0.1	6	Mg + diCl[d]	14	0.14	visc. liq.	14,000	113-1
Oligomer 3640-97-2	200	0.1	6	$MgCl_2$, 0.04	160	0.23	soft solid	26,000	113-2
Oligomer 3640-97-2	200	0.1	6	$MgCl_2$, 0.03	57	0.21	soft solid	25,000	115-1
Oligomer 3640-97-2	200	0.1	6	Mg, 0.3	8	-	visc. liq.	-	115-2
Polymer 3640-115-1	330	0.1	0.5	$MgCl_2$, 0.03	57[e]	0.26	solid	30,000	115-1A
Polymer 3640-115-2	330	0.1	0.5	Mg, 0.3	8[e]	-	visc. liq.	-	115-2A

a. Weight loss assumed wholly due to evolution of methylamine

b. Estimated from solution viscosity in THF

c. Pressure periodically reduced as far as practical without excessive frothing. Polymers 109-1A and 109-2A were subjected to identical pressures, -1A was frothy and -2A was not

d. diCl is 1,4-bis(dimethylchlorosilyl)benzene; about 1 mg, or less than 0.1% of the weight of starting material

e. Cumulative weight loss based on original starting material

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In another polymerization, the oligomer, 3640-127-1, 33.0 g, was stirred at 300°C with 0.04 g of anhydrous magnesium chloride for 1 hour. At this time the melt became too viscous to be stirred, and 50 ml of o-dichlorobenzene was added to dissolve the polymer. Stirring was continued with refluxing at 180°C for 8 hours. The solvent was distilled off, and the residue, when cool, was a tough, cream-colored solid that resembled nylon in appearance. It was designated 3640-127-3.

Anal. Calculated for the polymer, $-C_{11}H_{18}NSi_2-$:
C 59.66, H 8.65, N 6.32, Si 25.37.

Found: C 56.13, H 7.63, N 1.12, Si 27.82.

Mol. wt. (by light scattering): 68,000

Inherent viscosity (THF): 0.49 deciliters per gram

3. Cross-linking with various agents

Several polyfunctional hydroxy compounds and silylamines were tried as crosslinking agents for poly(tetramethyl-p-silphenylene methylamine).

a. Control (polymeric silphenylene amine without cross-linking agent)

Several polymers were combined and mixed in the molten form to provide a uniform batch of starting material. At room temperature the mixture was a light tan, slightly sticky, tough solid. The mixture was placed in a glass tube sealed at one end and measuring 14 x 250 mm. The tube was swept with dry nitrogen and the open end was capped with a balloon filled with nitrogen. The polymer-containing end of the tube was then placed in a furnace at 400°C so the capped end was outside the furnace. The polymer darkened gradually and became solid in 48 hours at 400°C. An appreciable amount of a dark solid collected in the tube above the polymer. The polymer, when cool, was solid, rubbery, infusible, dark brown, and easily torn with the fingers. On being left in benzene or tetrahydrofuran for 5 hours the polymer swelled and broke into fragments.

b. Phloroglucinol, 1,3,5-trihydroxybenzene

The polymeric silphenylene amine mixture described in the preceding paragraph, 2.21 g (0.01 mole of repeating unit), was mixed with 0.162 g (0.0001 mole) of phloroglucinol, and heated in a glass tube as described in the preceding paragraph. The mixture became homogeneous without evolution of gas at about 200°C. During 22 hours at 400°C, the mixture became progressively thicker and finally solidified. A dark solid collected in the tube above the polymer. The polymer resembled the one described in the preceding paragraph.

c. Hexaphenylcyclotrisilazane

The polymer (0.01 mole) was mixed with 0.06 g (0.0001 mole) of hexaphenylcyclotrisilane and heated at 400°C for 24 hours with results similar to those just described.

d. p,p'-Biphenol

An attempted crosslinking with p,p'-biphenol gave results in 50 hours essentially the same as those just described.

e. The silphenylene-ammonia oligomer

The silphenylene-ammonia oligomer described above (Section IV.B.1.b.) was also tried as a crosslinking agent. Reaction was expected between the NH groups of the ammonia oligomer and the Si-Me groups of the polymeric silphenylene amine, but the same results were obtained in 50 hours at 400°C as with the other agents described above.

f. Molding of products from crosslinking reactions

Each of the products from the attempted crosslinking reactions with phloroglucinol, p,p'-biphenol, and the ammonia oligomer was placed in a circular steel mold, 0.75-in. in diameter, and compressed between pistons. On heating with compression, material flowed around the pistons at a fairly low temperature, until the disc was 0.125-in. thick (the limit of travel of the pistons). A temperature of 400°F (204°C) was maintained for 1.5 hours. The resulting discs were resilient solids that could be torn easily

by hand. When the molded samples were heated 1 hour at 400°C in air, they all became friable. When they were heated 1 hour in nitrogen, the sample made with phloroglucinol was still resilient, the sample made with p,p'-biphenol became rigid, and the sample made with the ammonia oligomer was much harder than originally but it was still slightly flexible.

4. Crosslinking with pentaerythritol

Pentaerythritol was tried as a crosslinking agent, but difficulty was encountered at first in getting a homogeneous mixture. When pentaerythritol, 0.014 g (0.0001 mole), was mixed with 2.21 g of the polymeric silphenylene amine and warmed to melt the polymer, reaction started almost immediately. When the polymer became fluid, solid particles were distributed non-uniformly throughout the mass. Subsequent heating at 400°C led to solidification in 60 hours with results similar to those described above for the various crosslinking agents. Later, a better procedure, which is described below, was found.

Since the equivalence values of the polymer vary slightly with the molecular weight, the values below are given to facilitate appraisal of the data. The formula weight of the repeating unit of poly(tetramethyl-p-silphenylene methylamine) is 221.45, and it is difunctional with respect to alcohols, R-OH. Thus the equivalent weight of polymer is 110.73. The equivalent weight of monomer is 126.25, of oligomer with two repeating units is 118.49, and of oligomer with three repeating units is 115.90. Pentaerythritol has a molecular weight of 136.15 and is tetrafunctional as ROH, so its equivalent weight is 34.04. One-half mole of pentaerythritol is equivalent to 1 gram formula weight of $-SiMe_2C_6H_4SiMe_2NMe-$. A series of crosslinking experiments was conducted with different ratios of pentaerythritol to polymer and oligomer, under the conditions given in Table IX.

Poly(tetramethyl-p-silphenylene methylamine), 3640-127-2, 1.00 g (9.05 milliequivalents), was mixed with 0.025 g (0.74 milliequivalents) of pentaerythritol. Thus the stoichiometric ratio of polymer to cross-linking agent was 12:1. To permit mixing, the polymer was warmed to about 190°C in a small beaker with nitrogen passing over it, and the pentaerythritol was stirred in rapidly with a spatula as the mass cooled. Before the mixture became too tough to handle, it was transferred to a small aluminum Teflon-coated planchet (a cylindrical dish 1" diam. x 3/16" deep).

Table IX. Cross-Linking Silphenylene Amines[a] with Pentaerythritol

Starting material		Curing			Product	
Amine	Stoichiometric ratio, amine:penta[b]	Time, min	Temp., °C	Container	Character	No. 3640-129-
Polymer	12:1	45	225	clamped planchets	dense, resilient foam	10
Polymer	12:1	60	204	piston mold	resilient solid[c]	9
Polymer	12:2	60	204	piston mold	sim. to 129-9 but weaker	8
Polymer	12:2	45	225	clamped planchets	sim. to 129-10 but weaker	7
Polymer	12:2	45	225	loosely cl. plan.[d]	weak, non-uniform foam	6
Polymer	12:4.8	45	225	loosely cl. plan.[d]	v. weak, non-uniform foam	5
Polymer	12:4.8	45	225	loosely cl. plan.[d]	v. weak, non-uniform foam	4
Oligomer[e]	12:3.8	120	225	clamped planchets	v. weak, non-uniform foam	3
Oligomer[e]	12:5.4	120	225	clamped planchets	v. weak, non-uniform foam[f]	2
Oligomer[e]	12:7.1	120	225	clamped planchets	v. weak foam[f]	1

a. Silphenylene amines were oligomers or polymers of 1,4-bis(methylaminodimethylsilyl)benzene

b. Pentaerythritol, $C(CH_2OH)_4$

c. Modulus, 1425 psi; tenacity, 420 psi; elongation at break, 60%

d. This experiment with loosely clamped planchets showed that tight clamping retained the polymer while permitting escape of methylamine

e. The oligomer is considered to have two repeating units: equivalent weight, 118.5

f. Microscopic examination revealed small crystals, probably pentaerythritol

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The planchet was covered with another slightly larger planchet, and the two were clamped together and placed in an oven at 225°C. Both planchets had previously been coated with Teflon by spraying with Fluoroglide (Bel-Art Products, Pequannock, New Jersey) and heating at 400°C for 5 minutes. The progress of curing was determined about every 5 minutes by cooling the container and examining the contents. In 45 minutes of heating, the product became a foamed, soft, resilient, infusible disc. In 16 hours at room temperature, the disc hardened to a much tougher, flexible, resilient disc. It was designated 3640-129-10.

Portions of Polymer 3640-127-3 with a molecular weight of 68,000 were crosslinked with pentaerythritol by the same method. No essentially different materials were obtained; but, in general, the new products were somewhat less foamed, tougher, and less compressible after the crystallization at room temperature occurred. Thermal stability was shown when one foamed disc became essentially non-compressible in 3 hours at 350°C in air, but it was yellow, clear, hard, and tough. In 96 hours at 350°C in air, there was no further apparent change.

5. Preparation of "sandwich panel" (foamed elastomer between aluminum plates)

The polymeric silphenylene amine, 3640-127-2, was mixed with the pentaerythritol (12:2 ratio) by the second procedure described above. A small mold measuring about 1.8 x 1.8 x 0.25 inch was made with two aluminum sheets held apart by L-shaped, 0.25-inch stainless steel strips that served as the sides of the mold. The prepolymer mixture, 2.4 g, was placed in the mold, which was clamped together and placed in an oven at 250°C for 1 hour. When cool, the stainless steel strips were removed without sticking, but the aluminum remained bonded to the resilient foam which had filled the mold. The sample was designated 3640-125-1 and delivered to Marshall Space Flight Center for examination.

6. Stability to heat, water, and benzene

The solid, resilient polymer, 3640-129-9 (Table IX), was heated in an oven at 400°C for 1 hour. It had a crust on the surface, but it was still resilient underneath. It had undergone essentially no change from the original medium brown color. When soaked overnight in benzene, the polymer swelled but did not dissolve. When boiled in water for 1 hour, the polymer remained essentially unchanged, except for the increased resiliency that normally results from heating to 100°C with or without water.

7. Relationship of molecular weight to viscosity

The molecular weights and viscosities of the linear tetramethyl-p-silphenylene methylamine polymers are given in Table X and Figure 5. These data led to values of $K = 13.0 \times 10^{-6}$ and $\alpha = 0.96$ in the Mark-Houwink equation[8] that expresses the relationship between the intrinsic viscosity and the weight-average molecular weight.

Table X. Viscosities and Molecular Weights of Poly(tetramethyl-p-silphenylene methylamine)

Polymer	Viscosity		Molecular weight[b]
	Inherent[a]	Intrinsic	
3640-15-2	0.08	0.070	9,700
3640-33-1	0.23	0.216	26,000
3640-79-2	0.20	0.193	18,000
3640-79-6	0.27	0.297	38,000
3640-131-1	0.49	0.501	68,000

a. Determined at 30°C at a concentration of 1.00 g per deciliter in tetrahydrofuran

b. Weight average, by light scattering

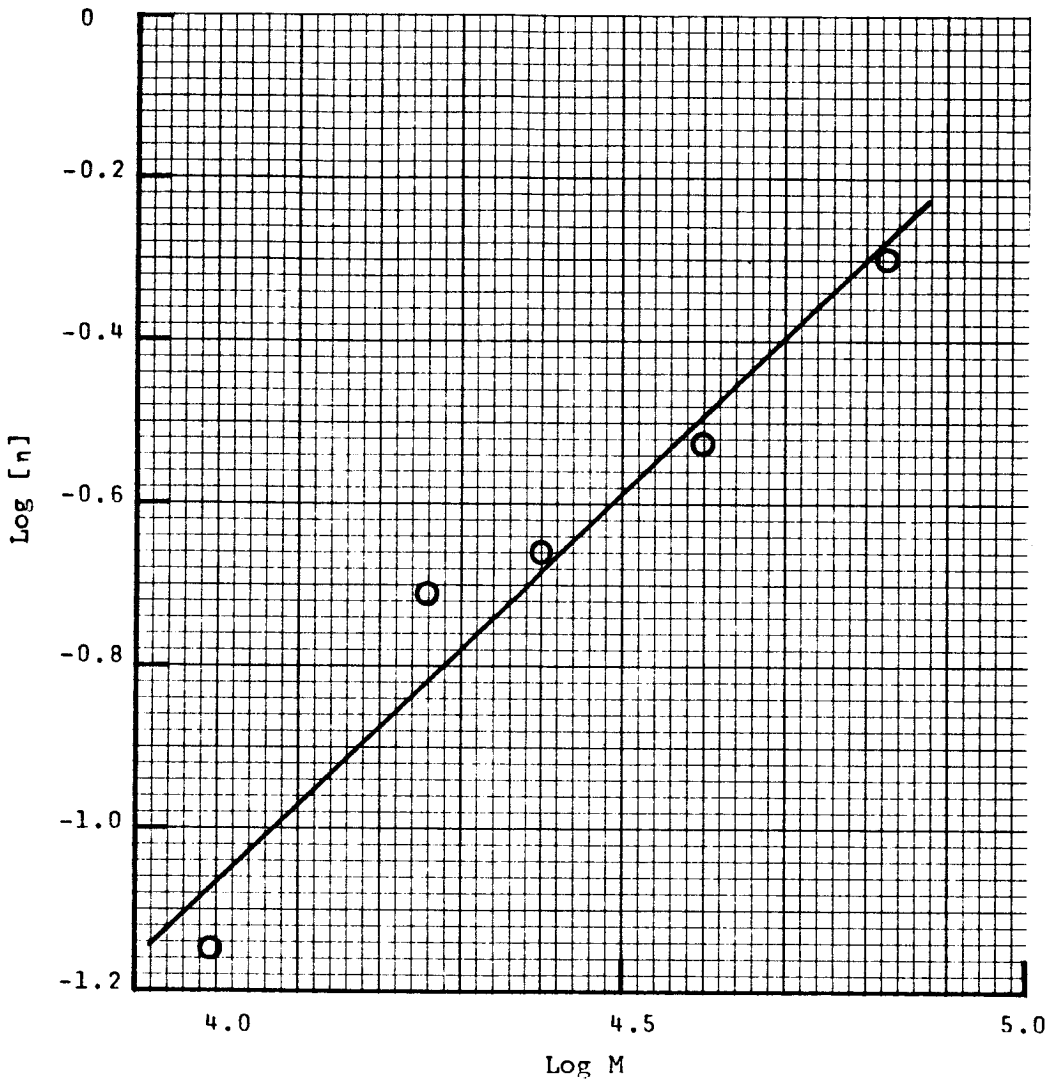

Figure 5. Relation of Intrinsic Viscosity to Molecular Weight of Poly(tetramethyl-p-silphenylene methylamine)

V. COATING AGENTS FOR TITANIUM

A. Discussion

It is characteristic of silylamines and silazanes that they have excellent properties as coating agents. Almost every silicon-nitrogen compound made in this research program has shown some capabilities as a coating agent if it had a low enough vapor pressure to remain in place at the high temperature required for curing. The compounds have, however, had the disadvantages of requiring that they be cured in a horizontal position and at higher temperatures than the available commercial agents. Moreover, they performed only slightly better than the commercial agents. Earlier reports have described methylphenyl silazane[21] and diphenyl silazane[22] coating agents, which were the two most promising of all those tried. The silazane coatings adhered well to aluminum and stainless steel, fairly well to mild steel, and poorly to copper, but they had not been tried on titanium. In response to requests for information, we recently investigated these coatings on titanium.

The diphenyl silazane coating, with or without aluminum pigment, adheres well to aluminum. Without aluminum pigment, it adheres in about the same way to titanium, but with aluminum pigment it adheres poorly to titanium.

The poor results with the pigmented diphenyl silazane on titanium prompted us to try the silphenylene amine polymer, Polymer 3640-127-3, which is described in Section IV. Without aluminum pigment, it adhered to titanium in a manner comparable to the silazanes. With aluminum pigment, it was definitely superior in adhesion at high temperatures, and it did not flow when cured, even in a vertical position. These coatings require curing for about 18 hours at 375°C or above. Completeness of curing is indefinite, because the coatings become progressively more resistant to abrasion over a long period. A pigmented coating, 0.3-mil thick, remained intact for 124 hours at 540°C on unstressed titanium even though it was quenched in water eight times during this period. The uncoated areas of the titanium turned dark blue. The same performance has been observed for several different preparations of the same coating formulation, but variations in the formulation have not been investigated.

The performance of the methylphenyl silazane coating agent[21] pigmented with aluminum was about the same as that of the polymeric silphenylene amine with two important exceptions: The methylphenyl silazane coating agent was fluid enough to flow during curing, and it was finally darker and less shiny. The silazane coating was still intact at the end of 100 hours at 540°C (1000°F) even though it had been quenched in water four times during that period.

The performance of the aluminum-pigmented silphenylene amine and methylphenyl coatings on titanium recalls to mind Butler's[23] statement that probably no organic or semi-organic coating would be satisfactory for use at 1000°F unless it were converted to an adherent inorganic residue during heating. It appears that the silazanes, in general, have the property of being converted to inorganic residues that are adherent. Evidently the aluminum-pigmented silphenylene amine and the methylphenyl agents form unusually stable inorganic residues.

B. Experimental Details

1. Diphenyl silazane coating agent

In previous work, the diphenyl silazane has been prepared in several different ways.[22,24] The diphenyl silazane used in the present experiments was obtained as a by-product of the preparation of hexaphenylcyclotrisilazane. The vehicle consisted of 9 g of by-product, 1 g of ethylenediamine silazane, and 90 g of benzene. A portion of the resulting solution, 10 g, was pigmented by shaking it for 8 hours with glass beads and 0.33 g of aluminum pigment No. 322 (Aluminum Corporation of America) that had been washed with benzene. The pigmented mixture was then doctored onto strips of titanium ("Ti, 8 Al, 1 Mo, 1 V") and cured at 250°C for 16 hours or 350°C for 4-6 hours. The coatings were dull gray, and they could barely be scratched with a fingernail. After heating one specimen 1 hour at 540°C (1000°F) the coating was intact, but it flaked off when quenched in water.

2. Polymeric silphenylene amine coating agent

The vehicle consisted of 1 g of polymeric silphenylene amine, 3640-127-3 (Section IV), and 9 g of benzene. The solution was mixed with 0.33 g of benzene-washed aluminum pigment No. 322 by shaking for 16 hours with glass beads. The pigmented mixture was doctored onto a titanium strip ("Ti, 8 Al, 1 Mo, 1 V") and heated at 375°C for 16 hours. When cool, the coating was bright and silvery, and it could be scratched with a fingernail. After an additional 4 hours at 400°C it was still bright and could barely be scratched. After 1 hour at 540°C (1000°F) the coating

was bright, silvery, and resistant to scratching with a fingernail. Thereafter, essentially no visible change occurred during 124 hours at 540°C with 8 quenches in water, except that the uncoated titanium turned dark blue. The coatings were not removed and were only slightly grayed by being boiled 4 hours each in aqueous solutions of sodium chloride, Tide, and Alconox. Coatings on another type of titanium that is less widely used ("Ti, 6 Al, 2 Sn, 4 Zn, 2 Mo") appeared to be slightly less satisfactory.

3. Methylphenyl silazane coating agent

Aluminum pigment was incorporated into the methylphenyl silazane[25] coating agent in the manner described above for the diphenyl silazane except that the mixture was shaken for only 1 hour. Curing required 18 hours at 350°C before the coating became solid at 350°C. It is doubtful that it could have been cured in any position except horizontal. The final coating was intermediate in color and brightness between the diphenyl silazane and the silphenylene amine coatings. The coating was still intact after 100 hours at 540°C (1000°F). Four times during the heating period the panel was removed from the oven and quenched in cold water without ill effects.

VI. SILYLAMINES AS CURING AGENTS FOR EPOXY RESINS

A. Discussion

The initial studies of silylamines as curing agents for epoxy resins[26] indicated that cured epoxy resins prepared from Epon 828 and bis(methylamino)diphenylsilane (BMADPS) had flexural strengths comparable to those of commercial resins, and they lost strength at 325°C more slowly than any commercial resin that we were able to obtain. The initial work was exploratory; the preferred curing conditions were determined only approximately; and no quantitative data were obtained on the preferred ratio of curing agent to resin. The investigation of silylamines as curing agents was continued under the present contract.

Initially the stoichiometric amount of BMADPS required for curing Epon 828 was calculated from the amine content of BMADPS and the published epoxide equivalent of Epon 828. The ratio was 1.21 g of BMADPS to 1.88 g of Epon 828 or 64 parts of BMADPS per hundred parts of resin. To determine whether the ratio was critical, Epon 828 was cured with 25% more and 25% less than the calculated amount of BMADPS. The flexural strengths of these samples were compared with the flexural strength of a sample prepared previously with a stoichiometric amount of BMADPS.[26] The values for the flexural strengths (Table XI) were 15,800 psi for the sample prepared with a stoichiometric amount, 15,900 psi for the one with 25% less, and 12,200 psi for the one with 25% more. Based on these data, it appeared that it was preferable to use less than an equivalent amount of curing agent rather than more to obtain maximum flexural strength. However, after heating for 1 hour at 325°C, the flexural strength values were 11,100 psi, 0 psi, and 4100 psi for the samples with the stoichiometric amount of agent, with 25% less, and with 25% more, respectively. Since BMADPS is not likely to be used unless high thermal stability is required, the calculated stoichiometric amount of BMADPS appears to be optimum.

A temperature of 120°C appeared to be satisfactory for curing the resin with a stoichiometric amount or 25% less of BMADPS, but the sample with 25% excess BMADPS cracked badly during curing at this temperature.

Table XI. Flexural Strengths of Epon 828 Cured with Different Amounts of Bis(methylamino)diphenylsilane

25% Excess				Stoichiometric[a]		25% Deficiency			
Curing conditions		Flex. str., psi		Flex. str., psi		Curing conditions		Flex. str., psi	
Time, hr	Temp, °C	Initial	After 1 hr, 325°C	Cured, initial	After 1 hr, 325°C	Time, hr	Temp, °C	Initial	After 1 hr, 325°C
20	50	5,500	2,500			4	120	15,900	0
23	50	6,100	3,200			7	120	9,800	0
26	50	8,200	4,100			10	120	8,100	0
29	50	5,700	3,700			13	120	9,300	0
32	50	4,500	2,800			24	120	7,700	0
40	50	4,200	3,100						–
	Av	5,700	3,250				Av	10,150	0
							Max	15,900	0
4	80	4,600	0						
7	80	10,500	2,800						
10	80	12,100	2,400						
13	80	12,200	2,500						
16	80	7,800	2,900						
24	80	4,600	3,100						
	Av	8,650	2,300						
Overall av		7,200	2,800	10,500	6,200				
Overall max		12,200	4,100	15,800	11,200				

a. Data reported previously, reference 26.

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The high thermal stability of Epon 828 cured with BMADPS suggested that it might be useful as an ablative heat barrier. Consequently, a 4x6x0.25-in. sample was cast in a mold on a steel plate and cured at 80°C for 14 hours. The sample bowed on cooling, then it separated cleanly from the plate and finally became flat. When exposed to a high heat flux at Marshall Space Flight Center after being cemented to a plate, its performance indicated that the resin would be valueless unless its transparency were reduced. Consequently, two additional samples containing "Tipersul" (fibrous potassium titanate) were prepared. One contained 6.2% and the other 9.1% of Tipersul. They were cast on sheet steel to which "expanded" sheet-metal mesh had been welded. A small specimen of the resin that contained 6.2% Tipersul had a flexural strength of 13,400 psi. These samples smoked and flamed badly, and so the suggestion was made that glass fiber be incorporated into the resin with Tipersul.

To evaluate the effect of glass fiber, a series of panels was prepared: one contained only resin; two contained resin with Tipersul; and the fourth contained resin, Tipersul, and Refrasil glass fiber. The panels contained gas bubbles, and so a fifth panel was prepared with resin, Tipersul, and Refrasil by a method that reduced the amount of bubbles. In addition, a sixth panel was prepared with resin, Tipersul, Refrasil, and hexaphenylcyclotrisilazane. The last was added because it undergoes an endothermic reaction at high temperatures to form a polymer with high thermal stability.

Evaluation of the samples at George C. Marshall Space Flight Center revealed that the fifth panel performed best; but a decrease in density and some improvement in thermal efficiency and adhesion to the substrate are needed.

B. Experimental Details

1. Strength of epoxy resins cured with different amounts of silylamine

Data were reported previously on the flexural strengths of silylamine-cured epoxy resins made with the calculated stoichiometric amount of BMADPS.[26] Comparable data for resins cured with more and less than the stoichiometric amount of BMADPS are in Table XI. The stoichiometric amount was calculated from the published[27] value of 188 for the epoxide equivalent of Epon 828. The equivalent is the number of grams of resin that contains 1 gram equivalent of epoxide. The equivalent weight of BMADPS, in terms of NH groups, is 121.2. Thus the stoichiometric ratio of BMADPS to Epon 828 (by weight) is 121.2:188 or 64 parts of BMADPS per hundred parts of resin.

a. 25% excess silylamine

Epon 828 (Shell Chemical Company), 41.36 g, was stirred with BMADPS, 33.28 g, for 30 minutes. The liquid was degassed by reducing the pressure until foaming ceased. Then it was poured into a steel mold that had been spray-coated with Fluoroglide, a Teflon mold-release agent manufactured by Chemplast, Incorporated. After the sample had stood at room temperature for 1 hour, it was cured at 80°C for 4 hours. The cured sheet was sawed into strips for further curing experiments and flexural-strength measurements. Curing conditions and flexural strengths are shown in Table XI. A sample made in the same way was cured initially for 20 hours at 50°C before it was sawed into strips for further curing and evaluation as indicated in Table XI. An attempt was made to cure a third panel at 120°C, but it cracked in the mold, evidently because of excessive shrinkage.

The data in Table XI show that the maximum flexural strength obtained in the series with 25% excess silylamine and cured at 80°C was about 12,200 psi, which was reached in 10-13 hours. In the series cured at 50°C, the maximum flexural strength, 8200 psi, was reached in 26 hours. Thermal stress (exposure to 325°C for 1 hour) was slightly more damaging to the series cured at 80°C. The average strength of the thermally stressed samples was 2800 psi, and the maximum observed was 4100 psi. These figures may be compared with 6,200 psi, the average strength, and 11,200 psi, the maximum strength of thermally stressed samples made from Epon 828 and BMADPS mixed in the stoichiometric weight ratio.

b. 25% deficiency of silylamine

Epon 828, 22.56 g, was stirred with BMADPS, 10.89 g, for 30 minutes. Thereafter, the treatment was similar to that described above for 25% excess silylamine. Curing conditions and flexural strengths are in Table XI. All samples decomposed when heated at 325°C for 1 hour.

2. Preparation of epoxy resins for evaluation as heat barriers

Six samples of Epon 828 cured with BMADPS were prepared for evaluation as ablative heat barriers.

The first sample was prepared by stirring 62.04 g of Epon 828 with 39.93 g of BMADPS for 30 minutes. The liquid was deaerated by exposing it to reduced pressure, and then it was poured into a 4x6x0.25-inch mold, the bottom of which was a cold-rolled steel sheet. The resin was cured at 80°C for 14 hours. After the mold was cooled and disassembled, the resin-steel combination was bowed slightly. The resin separated slowly from the steel sheet over a period of 1 hour. The sample, designated 3715-103, was sent to Marshall Space Flight Center. It was reported to have been cemented to a steel plate for heat-flux exposure and to have broken away 10 seconds after exposure began, terminating the test. The sample also gave evidence of transparency to radiant heat, and so two other samples were prepared with Tipersul, fibrous potassium titanate (E. I. du Pont de Nemours and Company, Inc.), to provide opacity.

Epon 828, 58.28 g, and BMADPS, 37.51 g, were stirred with Tipersul, 6.32 g (6.2% of the total), for about 10 minutes. Then the mixture was deaerated by stirring under reduced pressure for 15 minutes. A sample was cast in an open-face, 4x6x0.25-inch mold, the bottom of which was a steel sheet with expanded metal mesh welded to it. The sample, designated 3715-115-1, was cured 3 hours at 120°C in a separate mold and found to have a flexural strength of 13,400 psi (average of 14,600 and 12,200 psi). A third sample was made in the same way as 3715-115-1 but with 9.1% of Tipersul. It was necessary to use a high-speed stirrer to incorporate the larger amount of Tipersul. The third sample was designated 3715-117-1.

A sample containing glass fibers and Tipersul was made by mixing 58.28 g of Epon 828 and 37.51 g of BMADPS with a motor-driven blade stirrer, and then 6.32 g of Tipersul was added with continued stirring. After the mixture had become fluid and appeared to be thoroughly mixed, 6.43 g of Refrasil F-100-1/2, glass fiber, was added slowly. Stirring was difficult, but the glass fiber became broken enough to permit mixing, and finally a thick but fluid mass was obtained. The mixture was poured into a mold that contained a steel panel with expanded steel mesh welded to the surface. Bubbles of gas became apparent, but they could not be removed by reducing the pressure or by gentle warming. The resin was cured for 3.5 hours at 120°C. The sample weighed 101 g, about 3 g less than the starting materials. The sample was designated 3715-127-1.

A sample containing Tipersul and Refrasil was prepared by the method used for the preceding sample and with the same quantities of materials; but they were mixed more quickly, and deaeration of the resin was more successful because of lower viscosity in the mixture. The sample was designated 3715-129-1.

A sample was made with hexaphenylcyclotrisilazane as follows: Epon 828, 60.10 g, and BMADPS, 38.79 g, were mixed by stirring with a motor-driven blade stirrer. Refrasil (F-100-1/2), 6.52 g; Tipersul, 6.52 g; and hexaphenylcyclotrisilazane, 6.70 g, were then added and mixed in the order given. The mixture was deaerated by reducing the pressure before and after it was poured into the mold. Then it was cured 3.5 hours at 125°C. The weight of the sample was 106.0 g, about 12 g less than the starting materials. The panel was designated 3715-131-1.

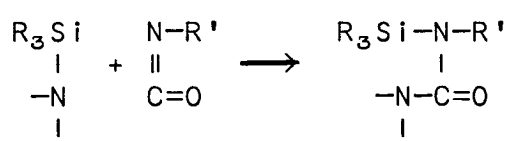
The six samples described above were sent to George C. Marshall Space Flight Center for evaluation. The comments received were that Sample 3715-129-1 was the best of the series, and its performance was encouraging, but additional work should be done to lower the density, to improve autoadhesion to the substrate, and to improve the thermal efficiency. Additional work along these lines has been proposed.

VII. POLYMERIZATION OF ISOCYANATES WITH SILAZANES

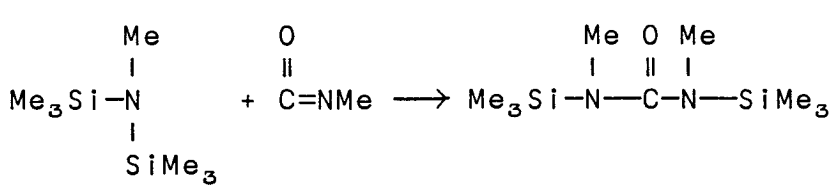
A. Discussion

Silazanes promote a polymerization reaction of diisocyanates. The combination that was studied in most detail was hexamethylene diisocyanate and heptamethyldisilazane, which forms a tough, transparent, slightly flexible solid that is not affected by short periods of boiling in acid or alkali. A small amount of work was done with DDI Diisocyanate, which has a complex aliphatic structure separating the isocyanate groups. The polymer made from DDI Diisocyanate was fairly tough, transparent, highly flexible, and elastic. The polymers of this type that have been studied so far are not stable for extended periods above 150°C. The polymers made from hexamethylene diisocyanate had glass transition temperatures of 65°C or above and the polymers made from DDI Diisocyanate had a glass transition temperature of -10°C. Consequently, they do not appear promising for use at either high or low temperatures. However, they are interesting chemically as a new type of polymer.

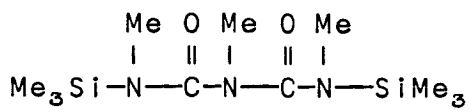
The chemistry of the polymerization is uncertain. Several workers, including Klebe[28] and Fink[29] have studied reactions of isocyanates with silylamines and have shown that the isocyanate adds to the Si-N bond, which then breaks:



According to Klebe,[28] heptamethyldisilazane reacts with methyl isocyanate in this manner:



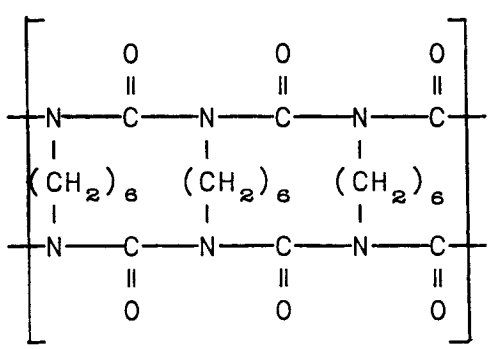
The product is capable of reacting with another isocyanate molecule to form:[28]



It appears that additional molecules of methyl isocyanate would react to form trimethylsilyl-terminated N-methyl nylon-1, but Klebe did not state whether they would.

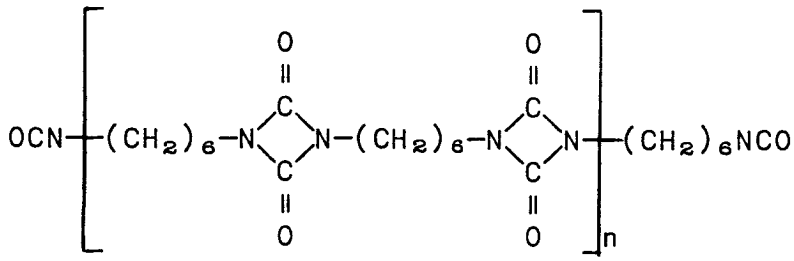
The silazane is evidently a catalyst or an initiator and not a comonomer, because the reaction products were similar when the silazane was present in 5% or 16.7% of the stoichiometric amount. There is a small amount of evidence that the curing temperature alters the properties of the polymers formed by this reaction, but this point has not been pursued thoroughly.

If nylon-1 were formed, it would be highly crosslinked:



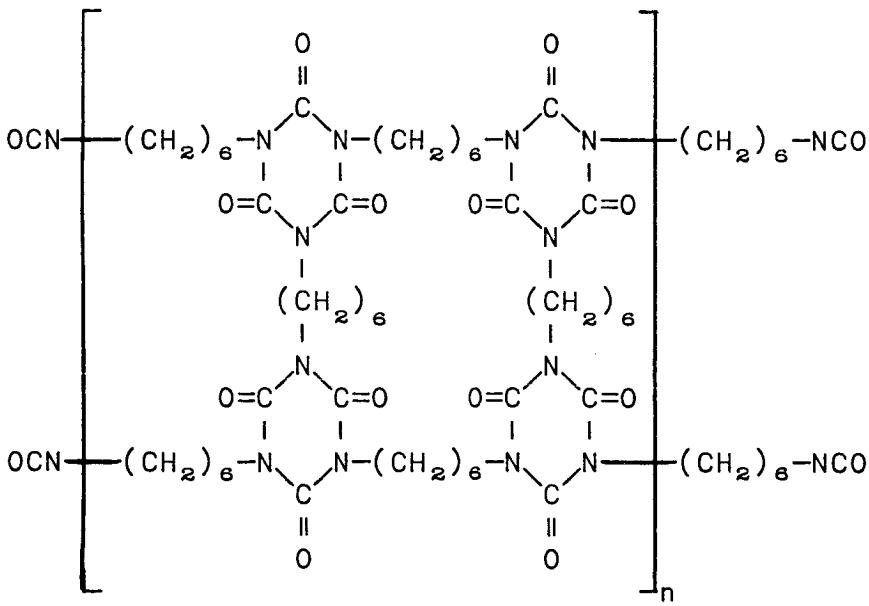
The properties of such a three-dimensional network would probably be similar to those of bakelite, but our product is distinctly different.

Another possibility is that polymerization proceeds through dimerization of the diisocyanate to produce a polymer that contains four-membered rings:



Although aliphatic isocyanates do not ordinarily dimerize, trimethylene diisocyanate was reported to form a polymer resulting from dimerization of isocyanate groups when the monomer was allowed to stand for a week.[30] (No properties were given for the polymer in Chemical Abstracts.)

A third possible route for polymerization of the diisocyanates is by trimerization of the isocyanate groups to form a crosslinked polymer that contains six-membered triisocyanurate rings.



The trimerization of aliphatic diisocyanates proceeds readily in the presence of a number of catalysts, including organo-metallic compounds, amines, acids, and metallic salts. If the polymerization followed this route, the polymer would be a three-dimensional network and would be quite brittle.

Of the three possible structures, nylon-1, dimer, or trimer, the dimer appears to fit the properties of the polymer best; but it is likely that crosslinking by the formation of the trimer also occurs.

The infrared spectrum of a polymer prepared by heating heptamethyldisilazane and hexamethylene diisocyanate in a 1:6 mole ratio at 122°C for 18 hours contained a strong band at 6.0 microns that is attributed to the amide group and only a weak absorption band at 4.4 microns that is attributed to the isocyanate group. With this limited information, however, it is not possible to determine whether four- or six-membered rings are present in the polymer.

The polymer 3992-63-2B, prepared from heptamethyldisilazane and hexamethylene diisocyanate in a 1:6 molar ratio has been studied in the greatest detail. It was a transparent, pale yellow, tough, slightly flexible solid with a tensile strength (nominal) of 6300 psi at 23°C. Its tensile strength at break (nominal) was 4800 psi, elongation at break was 15%, and modulus of elasticity was 150,000 psi.[17] For comparison, the tensile strength is less than that of unoriented nylon 66 (10,000 psi) and is comparable to that of nylon 11. Shear-modulus values were determined at temperatures between -20°C and 150°C by the Clash-Berg torsional method, and the shear modulus-temperature curve is shown in Figure 6.

According to this method, the flex temperature, T_f, was about 49°C, and the glass-transition temperature, T_g, was about 64°C in the samples studied. The flex temperature is defined as the temperature at which the shear modulus is 45,000 psi,[31] and the glass-transition temperature is defined as the temperature at which the shear modulus is 4,260 psi.[32] The ASTM heat-distortion temperature was estimated to be 40°C because the temperature at which the shear modulus is 10^5 psi is about the same as the ASTM heat-distortion temperature determined at a stress of 264 psi.[33] The data on various polymers are summarized in Table XII.

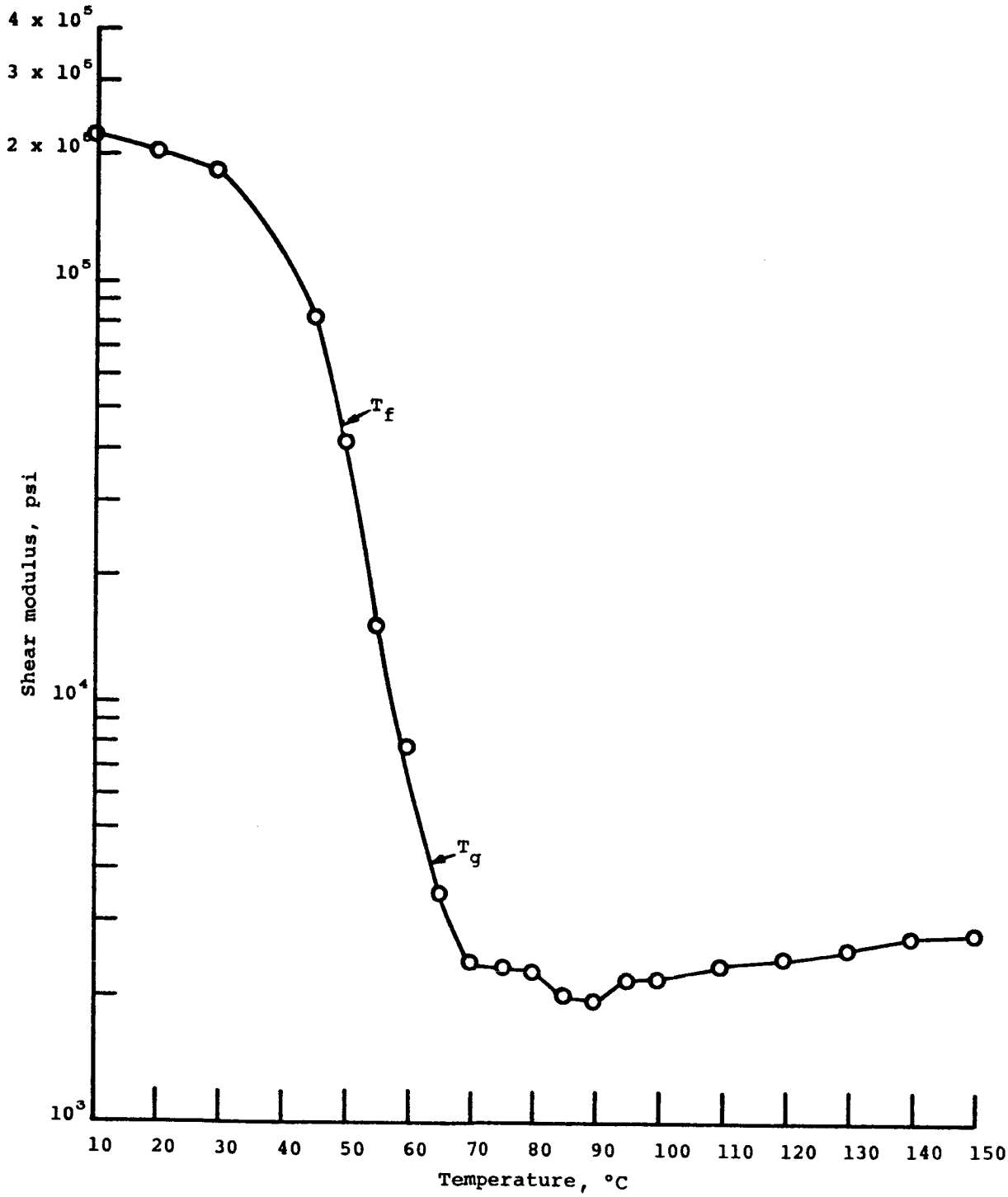


Figure 6. Shear Modulus - Temperature Curve for Polymer 3992-63-2B (Polymer 3992-63-2B was prepared by the reaction of heptamethyldisilazane with hexamethylene diisocyanate in a 1:6 mole ratio)

Table XII. Physical Properties of Isocyanate Polymers Prepared with Heptamethyldisilazane

Polymer 3992-	Diisocyanate	Molar ratio, silaz:diiso[a]	Flex temp., °C[b]	Distortion temp., °C[c]	Transition Temp., °C[d]
63-2B	hexameth[e]	1:6	49	40	64
61-5	hexameth[e]	1:12	56	49	108
61-6	hexameth[e]	1:20	53	49	75
67	DDI[f]	1:6	-25	-30	-11
89-1	hexameth DDI(1:1)	1:6	-16	-28	1

a. Molar ratio, heptamethyldisilazane to diisocyanate

b. Flex temperature, T_f, from shear modulus-temperature curve, Reference 31

c. ASTM heat distortion temperature, from shear-modulus-temperature curve, Reference 33

d. Glass transition temperature, from shear-modulus temperature curve, Reference 32

e. Hexamethylene diisocyanate

f. DDI Diisocyanate, General Mills, Inc.

At temperatures above 90°C, the shear modulus increased slightly (from 2000 psi to 2800 psi) indicating that the polymer was either crosslinked or that the polymer chains were very stiff due to cyclic moieties in the polymer.

Ethyl alcohol apparently plasticizes the polymer to some extent, because the flex temperatures and inflection temperatures of specimens that had been immersed in ethyl alcohol, as the cooling medium, were lower than those of specimens that were not exposed to the alcohol. When Skellysolve B was used as the cooling liquid for measuring the shear modulus below room temperature, no effect on properties was observed.

Polymers that were made by heating heptamethyldisilazane and hexamethylenediisocyanate in 1:12 and 1:20 molar ratios had physical properties that were slightly different from those of the polymer prepared from a mixture with the 1:6 molar ratio. The flex temperature of the polymer that was prepared from the mixture with the 1:12 molar ratio (Polymer 3992-61-5, Figure 7) was 56°C, and the heat-distortion temperature was 49°C. A glass-transition temperature of 108°C was observed for the same polymer, but this is abnormally high. The shape of the curve of shear modulus versus temperature between 70° and 120°C was unexpected. It indicates a higher degree of crosslinking than in Polymer 3992-63-2B.

Values of 53°, 75°, and 49°C were observed for the flex, glass-transition, and ASTM heat-distortion temperatures, respectively, for the polymer that was prepared from heptamethyldisilazane and hexamethylene diisocyanate in a 1:20 mole ratio (Polymer 3992-61-6, Figure 8).

It is likely that the differences between the physical properties of the polymers prepared from the disilazane and the diisocyanate in the various mole ratios were due to different degrees of crosslinking.

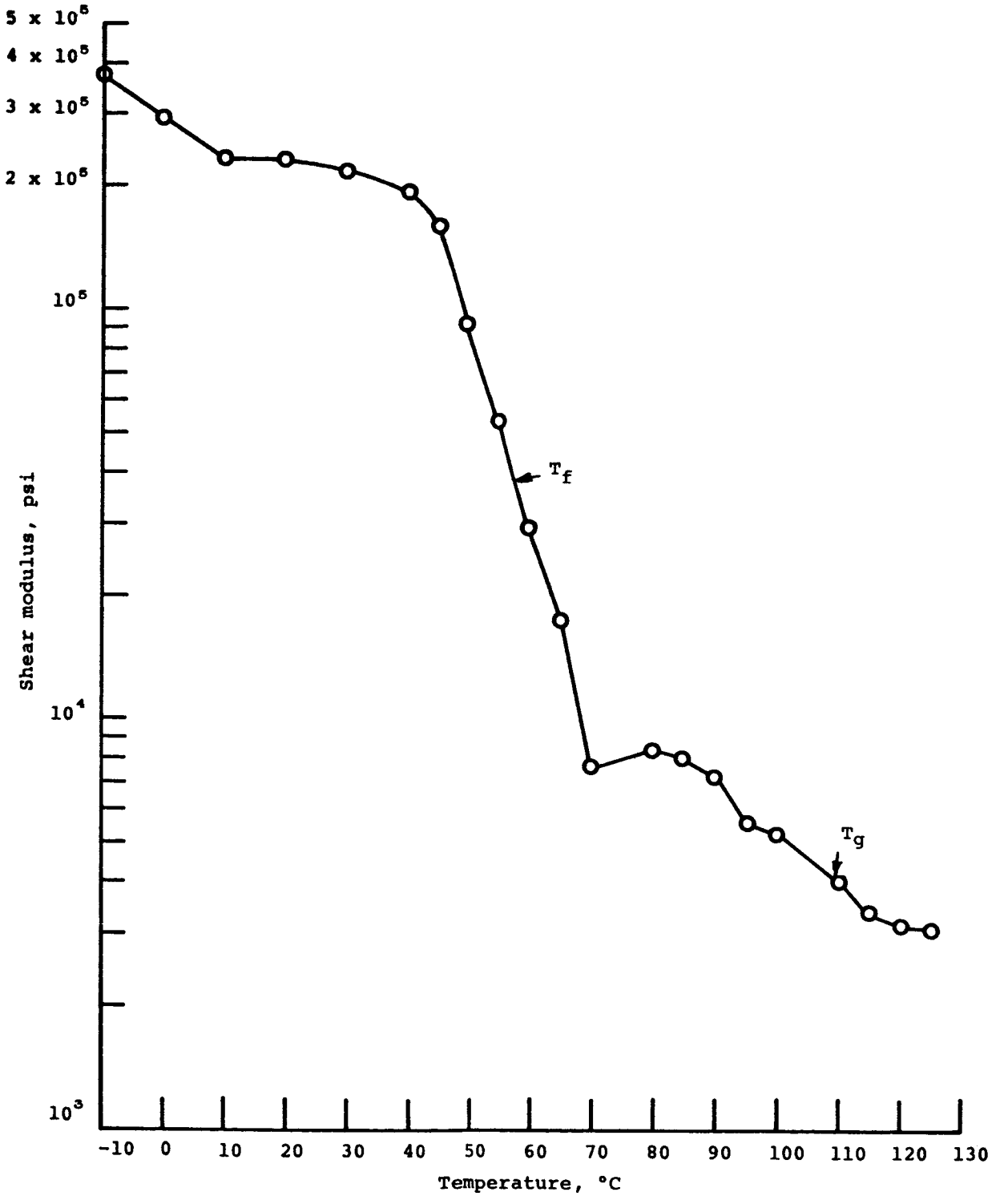


Figure 7. Shear Modulus - Temperature Curve for Polymer 3992-61-5 (Polymer 3992-61-5 was prepared by the reaction of heptamethyldisilazane with hexamethylene diisocyanate in a 1:12 mole ratio)

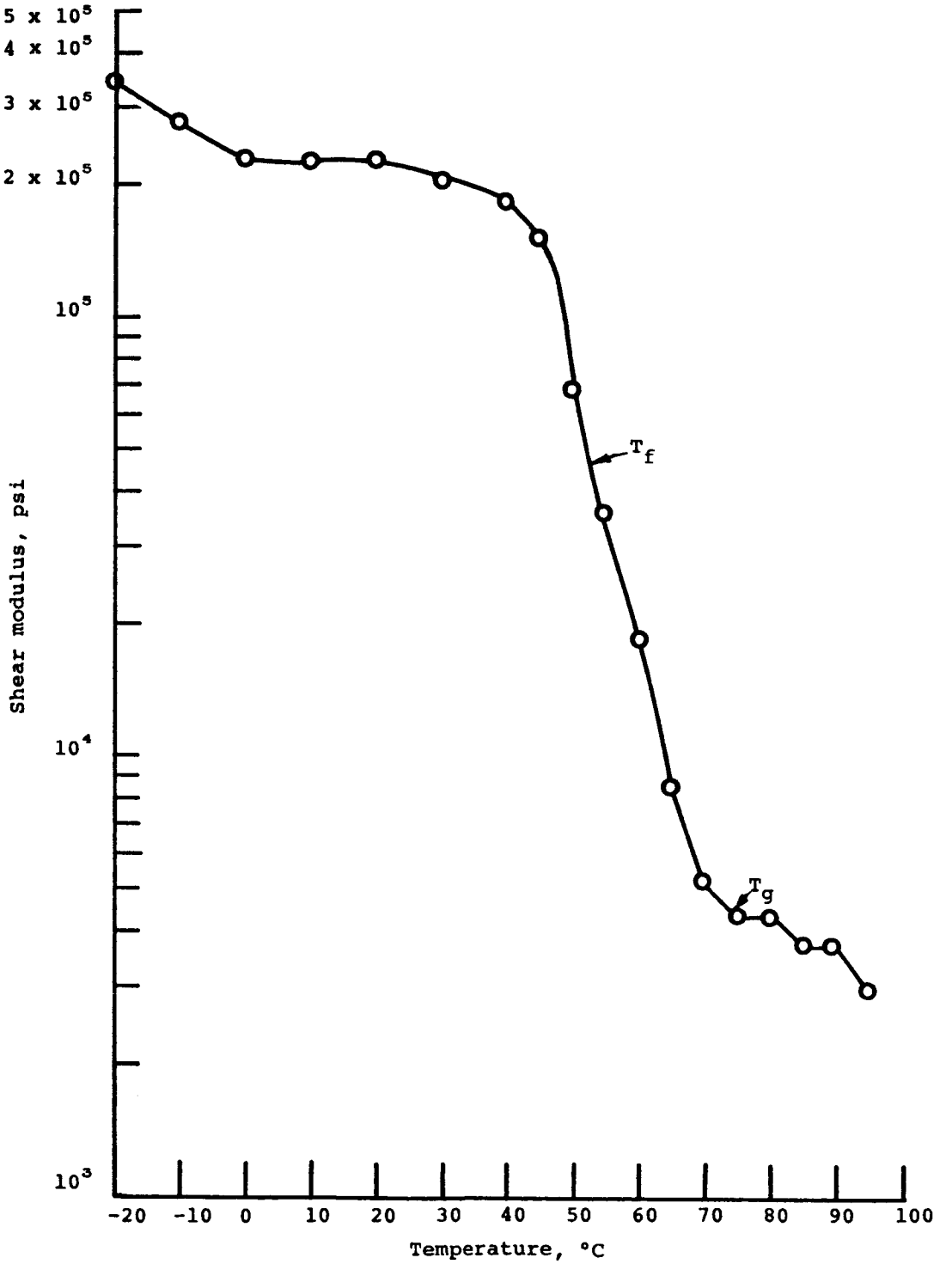


Figure 8. Shear Modulus - Temperature Curve for Polymer 3992-61-6 (Polymer 3992-61-6 was prepared by the reaction of heptamethyldisilazane with hexamethylene diisocyanate in a 1:20 mole ratio)

A polymer was also made with DDI Diisocyanate and heptamethyldisilazane. Its shear modulus-temperature curve, Figure 9, indicated that the flex, heat distortion, and glass transition temperatures were -25°C, -30°C, and -11°C, respectively. These temperatures were roughly 80°C lower than the corresponding temperatures of the hexamethylene polymer.

An equimolar mixture of hexamethylene diisocyanate and DDI Diisocyanate was polymerized with heptamethyldisilazane in a 1:6 molar ratio of silazane to diisocyanate, and the shear modulus data are in Figure 10. The flex, heat-distortion, and glass-transition temperatures were -16°C, -28°C, and -1°C, respectively.

Several exploratory reactions were carried out, but they were not studied thoroughly since the polymerizations just described seemed more promising. Nonamethylcyclotrisilazane reacted with tolylene diisocyanate in 1:3 and 1:2 ratios to form viscous liquids that solidified and then became brittle when heated. Hexamethylcyclotrisilazane reacted with tolylene diisocyanate and hexamethylene diisocyanate to form solids with poor strength. These reactions are summarized in Table XIII. Doubtless more favorable curing schedules could be found, but time was not available.

Preliminary reactions of heptamethyldisilazane and hexamethylene diisocyanate in molar ratios from 2:1 to 1:6 are also summarized in Table XIII. The product obtained with a 2:1 ratio of reactants did not become solid in 7 days at 70°C.

Heptamethyldisilazane and hexamethylene diisocyanate reacted in a 1:1 mole ratio in 18 hours at 70°C to form a tough, flexible, clear, colorless polymer that became quite soft when heated to 120°C (Reaction 4036-155-1).

A polymer, 4036-155-4, made from a mixture with a 1:2 mole ratio was also flexible. It became cloudy and less flexible while standing for a week in air, but it was still tough.

In an effort to clarify the question of polymer structure, methyl isocyanate was sealed in a glass tube in a 1:6 molar ratio with heptamethyldisilazane. After 4 days at 60°C the tube contained an appreciable quantity of crystals. In 10 days at 120°C no further visible change occurred, so the tube was opened, and the crystalline product was isolated. It proved to be the trimethyl ester of isocyanuric acid, m.p. 177-177.5°C.

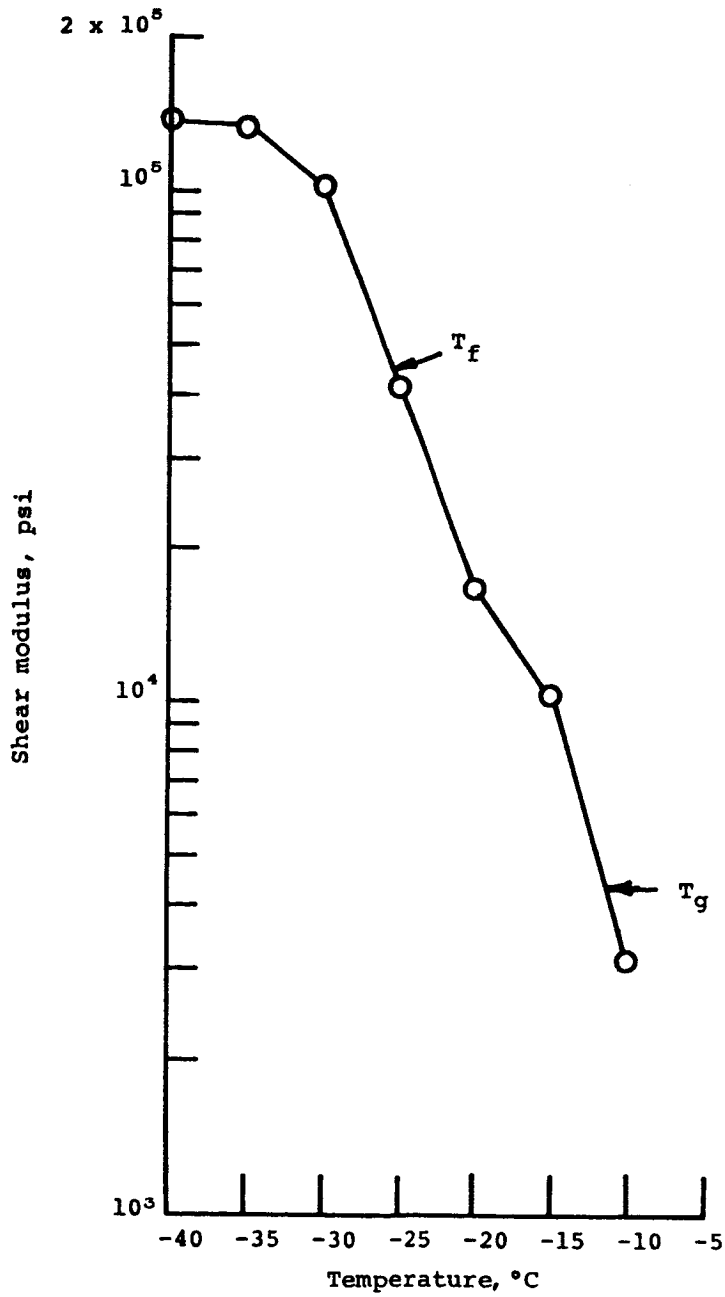


Figure 9. Shear Modulus-Temperature Curve for Polymer 3992-67 (Polymer 3992-67 was prepared by the reaction of heptamethyldisilazane with DDI Diisocyanate in a 1:6 mole ratio)

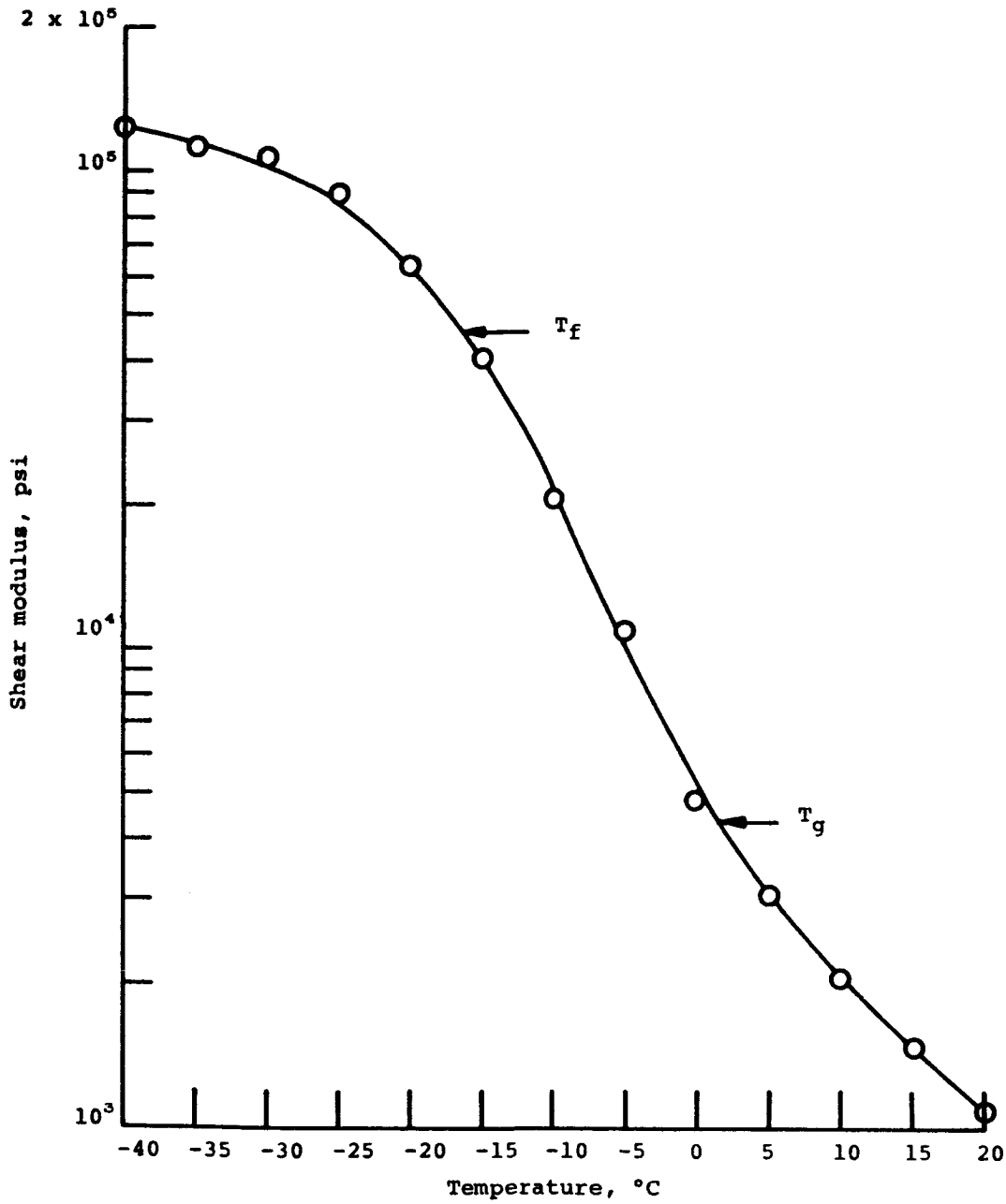


Figure 10. Shear Modulus-Temperature Curve for Polymer 3992-89-1 (Polymer 3992-89-1 was prepared by the reaction of heptamethyldisilazane with hexamethylenediisocyanate DDI Isocyanate in a 50:50 mole ratio this being in a 1:6 mole ratio with the silazane)

Table XIII. Polymerization of Silazanes with Isocyanates

Reaction 4036-	Silazane		Isocyanate		Curing conditions		Character of polymer
	Name	Moles	Name	Moles	Time, hr	Temp., °C	
143-1	nona[a]	1	tolyl[b]	3	18	27	visc. liq., cracked when cooled after 15 min at 120°C
143-2	nona[a]	1	tolyl[b]	2	18	27	isc. liq., soft sticky solid after 2 hr at 43°C
151-1	hexameth[c]	1	tolyl-2,4-[d]	2[e]	1	70	hard, clear solid; friable after 17 hr at 120°C
155-3	hexameth[c]	1	hex di[f]	2	1	70	flexible, clear solid, became cloudy in 30 min in air
155-1	heptameth[g]	1	hex di[f]	1	18	70	tough, flexible, clear solid, softened at 120°C
155-2	heptameth[g]	2	hex di[f]	1	168	70	viscous liquid
155-4	heptameth[g]	1	hex di[f]	2	18	70	tough, flexible, clear solid, softened at 120°C
155-5	heptameth[g]	1	hex di[f]	2	5	120	very flexible, tough, clear solid, brittle after standing overnight
157-1	heptameth[g]	1	hex di[f]	3	18	70	flexible, tough, clear solid; evidence of slight degradation in 2 hr at 120°C
157-2	heptameth[g]	1	hex di[f]	6	72	70	clear, hard, sl. flexible solid; degenerated at 200°C
157-3	heptameth[g]	1	hex di[f]	6	23	120	clear, hard, sl. flexible solid
157-4	heptameth[g]	1	hex di[f]	6	23	120	clear, hard, sl. flexible solid
159-1	heptameth[g]	1	tolyl-2,4-[d]	6	72	120	cracked when removed from oven
159-2	heptameth[g]	1	hex di[f]	6	18	120	clear, hard, sl. flexible solid
159-3	heptameth[g]	1	hex di[f]	6	18	120	clear, hard, sl. flexible solid
159-4	heptameth[g]	1	hex di[f]	6	18	120	clear, hard, sl. flexible solid
159-5	heptameth[g]	1	hex di[f]	6	18	120	clear, hard, sl. flexible solid

[a] Nonamethylcyclotrisilazane

[b] Tolylene diisocyanate, mixed isomers

[c] Hexamethylcyclotrisilazane

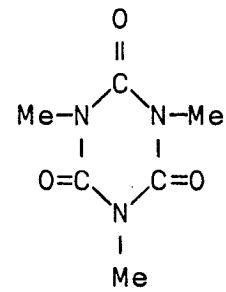
[d] Tolylene 2,4-diisocyanate

[e] Mixed in THF - solvent removed by evaporation with nitrogen

[f] Hexamethylene diisocyanate

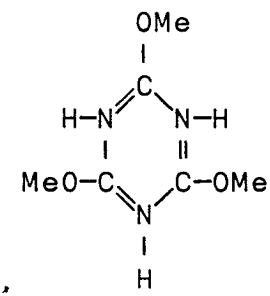
[g] Heptamethyldisilazane

Trimethylisocyanurate



The yield of trimethylisocyanurate from methylisocyanate was 90% of theory, and the carbon-hydrogen-nitrogen analysis was correct. If the methyl groups had been attached to the oxygen atoms, the compound would have been the trimethyl ester of cyanuric acid, and the melting point would have been 135°C.[34,35]

Trimethyl cyanurate



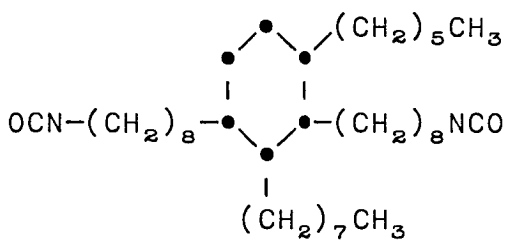
None of Klebe's products melted at similar temperatures.[28] The outcome of the methyl isocyanate reaction does not prove the structure of the polymer, but it gives a strong indication that six-membered rings are present. In addition the carbonyl absorption in the infrared spectrum favors the isocyanurate structure over the cyanurate.

B. Experimental Details

1. Monomers

Hexamethylcyclotrisilazane[36] and nonamethylcyclotrisilazane[37] were prepared by methods described previously. Heptamethyldisilazane was prepared from methylamine and trimethylchlorosilane according to the method described by Osthoff and Kantor.[38] Tolylene 2,4-diisocyanate was obtained from Distillation Products Industries and redistilled before use. Hexamethylene diisocyanate was obtained from Aldrich Chemical Co., Inc. Tolylene diisocyanate, mixed isomers, was obtained from E. I. du Pont de Nemours and Company, Inc.

DDI Diisocyanate was obtained from General Mills, and it was described as derived from a "dimeric fatty acid." The formula is given as O=C=N-[D]-N=C=O where D is a 36-carbon hydrocarbon radical. The formula is probably similar to this:



2. Polymerization

Polymerizations were carried out simply by mixing weighed quantities of the reactants and heating for the periods and at the temperatures shown in Table XIII. Samples having a higher ratio of silazane to isocyanate than 1:6 were heated under nitrogen. The samples that were prepared for physical measurements were polymerized in a mold that was made from two ferrotype plates held apart by rubber gaskets, and the whole was held together by clamps. The monomer-initiator mixture was introduced through a small opening in the gasket, and the mold was heated while in a vertical position. The curing time was 18 hours at 120°C.

3. Measurement of physical properties

Tensile properties were determined at 23°C on microtensile specimens according to ASTM Test Methods D1708-59T and D638-61T.

Shear modulus was determined at various temperatures according to ASTM Test Method D1043-61T on a Clash-Berg torsional modulus apparatus.

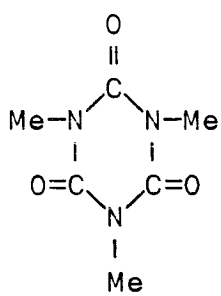
4. Trimerization of methyl isocyanate

Methyl isocyanate and heptamethyldisilazane were mixed in a 6:1 molar ratio and sealed in a glass tube that had been flushed with nitrogen. No reaction was apparent in 4 hours, but after 4 days at 60°C the tube contained a mixture of liquid and crystalline material. The tube was then placed in an oven at 120°C for 10 days, but no further visible change occurred. The crystals were rinsed with dry Skellysolve "B" to yield material with a melting point of 167-174°C. The amount was slightly more than the theoretical yield of trimethyl isocyanurate. Recrystallization from ethanol raised the melting point to 177-177.5°C and reduced the yield to 90% of theory.

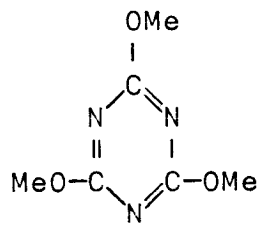
Anal. Calculated for $C_6H_9N_3O_3$: C 42.12, H 5.30, N 24.55.

Found: C 41.90, H 5.26, N 24.44.

Hoffman reported the melting point of trimethyl isocyanurate to be 176°C,[34] and the melting point of trimethyl cyanurate to be 132°C.[35]



trimethyl isocyanurate



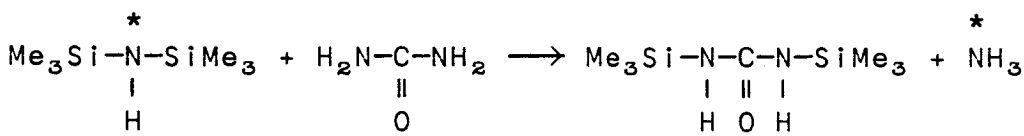
trimethyl cyanurate

VIII. COPOLYMERIZATION OF AMIDES AND SILYLAMINES

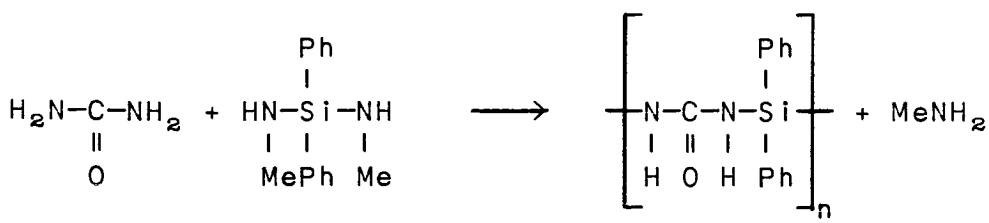
A. Discussion

The reaction of amides with silylamines was studied as a possible route to useful new polymers, but the nature of the properties of the products obtained did not encourage extensive investigation. Reactions occurred, but they evidently did not go to completion and were accompanied by side reactions, so satisfactory polymers were not obtained.

Wannagat and his coworkers[39] showed, with isotopic nitrogen, that urea reacted with hexamethyldisilazane to release the nitrogen of the silazane as ammonia and form N,N'-bis(trimethylsilyl)urea.



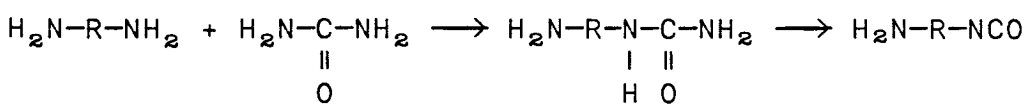
In this reaction, the silicon is monofunctional, and polymerization is not expected. As an extension of this work, we decided to try the reaction of urea with bis(methylamino)diphenylsilane (BMADPS), which is difunctional with respect to silicon and could form a polymer.



The reaction is also capable of forming four- or eight-membered rings.

Reaction of urea with BMADPS, 1:1 mole ratio, started when a homogeneous mixture of the two was heated to 87°C. However, the reaction did not evolve the amount of methylamine expected

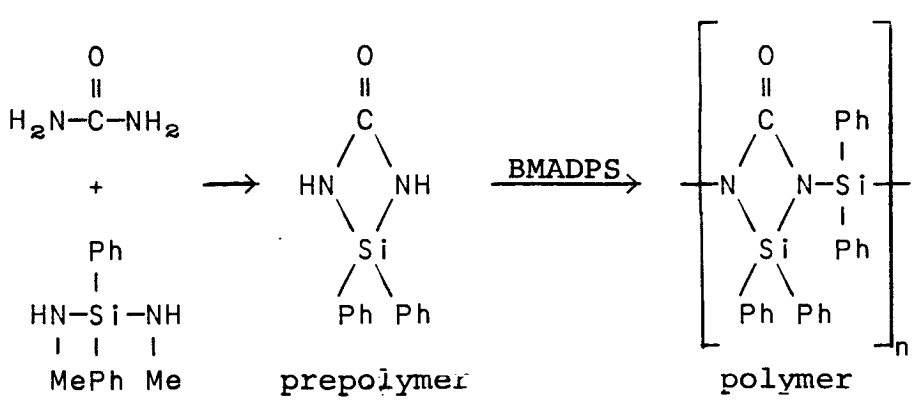
even on heating for 4 hours at 195-205°C. The product solidified to a clear resin on being cooled to about 60°C. The resin became cloudy slowly on exposure to the laboratory air. A sample heated overnight on an aluminum panel at 400°C in air appeared to be relatively unchanged; and the resinous film, which was 10-mils thick, did not change on further standing in laboratory air at room temperature. The lack of embrittlement or solidification at 400°C in such a thick film was unusual, but the film was probably too soft for a coating agent. All of the products were soluble in benzene and carbon tetrachloride. Infrared spectra in carbon tetrachloride showed strong absorption at 2200 $cm.^{-1}$ This absorption is not readily explained unless allene (=C=), carbodiimide (C=N=C), or isocyanate (-N=C=O) is present. The latter is reasonable in view of Inaba's statement[40] that the formation of polyureas by interaction of diamines with urea occurs through a mechanism involving isocyanate.



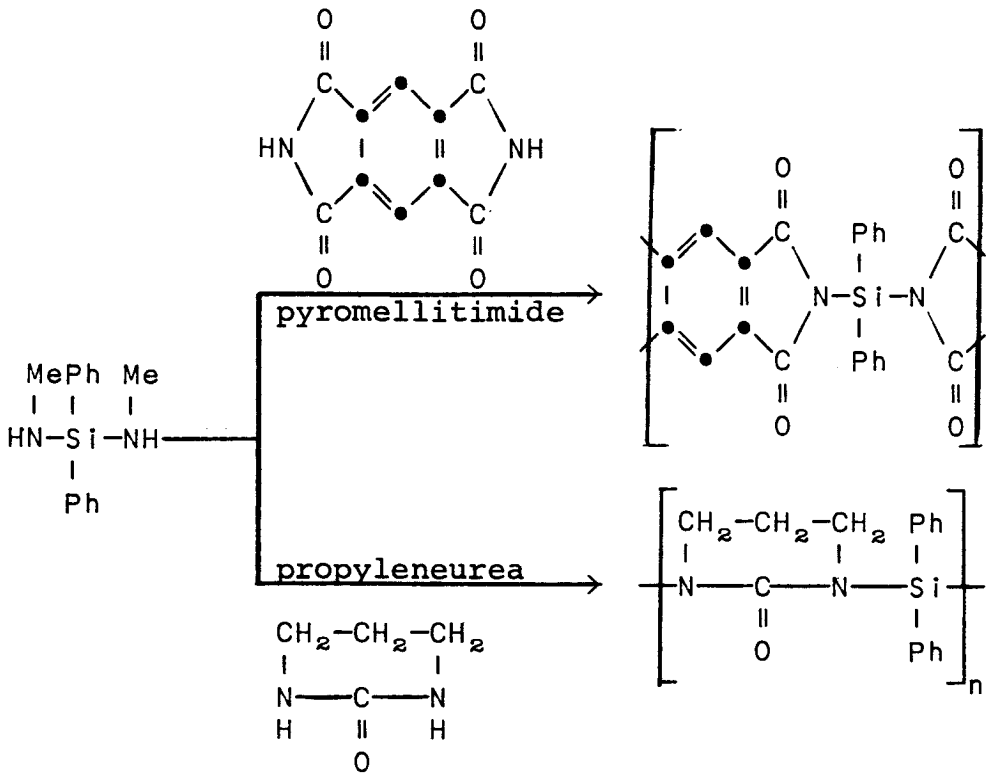
Results with urea and BMADPS in a 1:2 mole ratio were similar.

An attempted polymerization of BMADPS with adipamide in a 1:1 mole ratio resulted in the loss of the theoretical amount of gas and the formation of a friable solid, which was insoluble in hot benzene, carbon tetrachloride, toluene, and tetrahydrofuran (THF).

Another reaction of urea and BMADPS, 1:1 mole ratio in THF, resulted in the formation of a white solid. This reaction was intended to provide a cyclic intermediate that might then react further to form a polymer, but the desired prepolymer either did not form or was not successfully isolated.



Reactions of BMADPS with pyromellitimide and with propylene urea were attempted also.



The reaction of pyromellitimide with BMADPS without solvent produced an infusible solid with much greater thermal stability than the original pyromellitimide, as indicated by its behavior on a hot spatula. When the reaction was run in pyridine, a gel-like product was obtained, but the gel contained a small amount of material that resembled the pyromellitimide. A wax-like material, which was about 40% of the expected product, was isolated by evaporation of a benzene extract of the product. It melted readily when heated on a spatula and then solidified to a film that resembled others made from silazanes.

The reaction of propylene urea and BMADPS produced a brittle resin that was almost completely soluble in benzene and then crystallized on evaporation to form material that melted from 106-150°C. Efforts to isolate a pure product were not successful.

The reaction of a monofunctional amide, N-methylacetamide, with BMADPS was tried to simplify the isolation problems and provide a prototype. The reactants were heated over a period of 17.5 hours at temperatures up to 181°C. About half of the expected methylamine was evolved and almost all of the N-methylacetamide was recovered. The undistillable portion of the product had an average molecular weight of 528, so it was apparently a mixture of low-molecular-weight polymers of N-methyl diphenylsilazanes.

B. Experimental Details

1. Reaction of urea and BMADPS

a. Equimolar amounts

Urea, 1.50 g (0.025 mole), that had been dried overnight in a desiccator was mixed with 6.06 g (0.025 mole) of BMADPS in a 50-ml, 3-neck flask fitted with a magnetic stirrer, thermometer, and reflux condenser. Heating and stirring were started, but no visible change occurred until the temperature reached 87°C. Then foaming started with evolution of gas that had a strong odor of methylamine. About half of the urea dissolved. When foaming subsided, heating was resumed, and foaming occurred again when the temperature reached 122°C. The melt was then clear and colorless. Thereafter, the melt was stirred for an hour at 100°C. The total weight of the apparatus and contents indicated that 1.08 g had been lost as gas. The theoretical weight of methylamine that would have been lost to satisfy the equation given previously was 1.55 g. Heating was continued at 100°C and 0.03 mm pressure for 2 hours. On being cooled to room temperature, the product became a viscous liquid that could barely be poured. Continued heating under reduced pressure at 100°C for 1 hour and at 155°C for 1 hour caused no further visible change except that the product was a solid resin when cool. The total weight loss was only 1.10 g. The resin was readily soluble in benzene and slowly soluble in carbon tetrachloride. Fibers could be drawn readily from the melt, but they were soft and weak. The melt was then held under reduced pressure at 155°C for 4 hours and at 195-205°C for 4 hours, but no visible change occurred. The resin, which was a fairly tough solid at room temperature, was fluid at 60°C. It was soluble in benzene. Films formed by fusion on aluminum panels adhered well, but they became slightly cloudy after standing for several hours in

air. By contrast, a film heated 2 hours at 350°C in air remained clear. When a film was heated on aluminum, 70% remained after 2 hours at 400°C. The same film became slightly cloudy during 30 minutes in boiling water. On further heating, 16% remained after 24 hours at 400°C. The remaining film was still soluble in benzene. Pmr spectra indicated that less than the theoretical amount of N-H was present. Infrared spectra showed strong absorption at 2200 cm^{-1}, which suggested the presence of an unknown group that might be:

=C=,	$-\overset{\vert}{C}=N=\overset{\vert}{C}-$,	or	-N=C=O
allene	carbodiimide		isocyanate

The isocyanate seems more probable.

b. Reaction of urea and BMADPS (1:2 ratio)

On the assumption that urea might react as a tetrafunctional compound, a reaction was carried out with a 1:2 molar ratio of urea and BMADPS. The initial heating period was 3 hours at 80°C, and later the mixture was heated for various periods at temperatures up to 200°C. In appearance, the product was much like the one described in the preceding paragraph. However, the loss of weight, calculated as methylamine, was about 90% of the theoretical amount for the reaction in which one methylamine would be released for each hydrogen of urea. The urea may have had a functionality greater than two; its functionality could be four if steric hindrance did not interfere.

c. Reaction of urea and BMADPS in THF (1:1 ratio)

In a 200-ml, 3-neck flask fitted with a thermometer, condenser, and stirrer were placed 10.90 g (0.045 mole) of BMADPS, 2.70 g (0.045 mole) of urea, and 50 ml of THF. After being mixed, the materials were allowed to stand for 3 days in an atmosphere of nitrogen, but no evidence of reaction or dissolution of the urea was noticeable. Heating and stirring were started, and gas evolution was observed when the temperature reached 60°C. After an hour, the mixture was cloudy, and, after 6 hours total, a white solid, moist with THF, appeared to be the principal component in the flask. After distillation of THF under the reduced pressure of a water aspirator, the weight of the residue indicated that less than half of the expected loss of methylamine had occurred. The residue was washed repeatedly with THF until an amount equal to about 50% of the theoretical yield remained. It melted at 131-133°C.

Anal. Calculated for: $-NH-CO-NH-SiPh_2-$, $C_{13}H_{12}N_2OSi$:

C 64.75, H 5.35, N 11.62.

Found: C 37.98, H 6.42, N 31.77.

The high nitrogen content of the residue is especially difficult to correlate with any expected product.

2. Reaction of adipamide and BMADPS (1:1 ratio)

In a 50-ml, 3-neck flask equipped with a thermometer, stirrer, and condenser were placed 11.18 g (0.0461 mole) of BMADPS and 6.65 g (0.0461 mole) of dry adipamide. When stirred, the mixture became a slurry. Stirring for an hour at 90°C produced no gas evolution and no change in appearance. Further heating produced slow gas evolution at 115°C, but it remained very slow even while the reaction temperature was increased to 190°C over 2 hours. There was little or no change in appearance. During the next 3 hours at 190-240°C the color darkened, and the amount of liquid decreased gradually. The gas was analyzed periodically by chromatography and found to be essentially all methylamine. The product was a friable, gray solid. The total weight loss was 2.72 g which is equivalent to about 2 moles of methylamine for each mole of BMADPS. The gray solid was infusible on a spatula over a flame, although it smoked when quite hot. It was not visibly affected by exposure to boiling water, acetone, benzene, toluene, tetrahydrofuran, or carbon tetrachloride for a few minutes.

3. Reaction of BMADPS with pyromellitimide

Pyromellitimide, 6.317 g (0.0292 mole), and BMADPS, 7.083 g (0.0292 mole), were stirred together in a 25-ml, round-bottom, 3-neck flask fitted with a thermometer, condenser, and magnetic stirrer. The flask was heated in an oil bath, and the first gas evolution was noted at 61°C. At this time, the mixture was a semi-liquid mass that did not flow. When the temperature reached 89°C, the mixture became a lumpy mass that appeared to be dry. Gas evolution continued as the temperature was raised to 165°C over a total time of 3 hours. The temperature was increased further and gas evolution began again when the temperature reached 184°C. Thereafter, the temperature was held at about

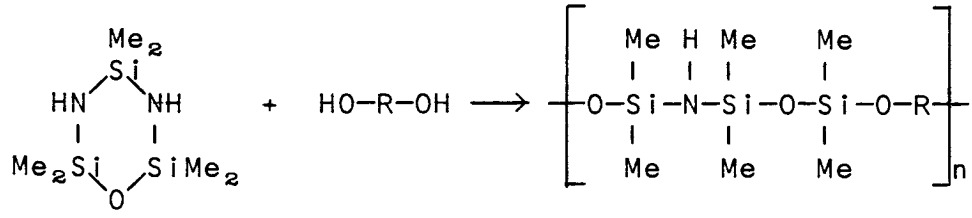
200°C for 3 hours during which time gas evolution gradually decreased and stopped. After the reaction mixture was cooled, the weight loss was found to be 77% of the amount expected for complete elimination of methylamine. A small quantity of crystals in the neck of the flask had a melting point of 263-275°C. Pyromellitic acid melts at 264°C. The product was a friable, gray powder that was only partly soluble in THF and dimethylsulfoxide (DMSO). The DMSO-insoluble portion underwent very little change when it was heated on a spatula until the spatula became red hot. By comparison, the pyromellitimide vaporized considerably below this temperature.

A second reaction was run in pyridine with equimolar amounts of pyromellitimide and BMADPS. The reaction began at room temperature while the mixture was being stirred to dissolve the imide. Thereafter, the mixture was refluxed for 4 hours. A sample of gas collected during this period contained both methylamine and ammonia, as detected by infrared spectra. After being cooled, the reaction mixture was a brown gel that contained small cream-colored particles. The product was stirred with benzene and centrifuged to yield a solid layer, a gel-like layer, and a liquid layer. The major portion was the benzene-soluble fraction, which, after evaporation, yielded a yellow semi-crystalline mass (about 40% of the theoretical yield of the expected polymer). It melted when heated gently on a spatula, then it foamed and solidified on being heated to a higher temperature. The solid formed resembled coatings made from silazanes except that it had poor adhesion.

IX. REACTIONS OF CYCLIC SILOXAZANES WITH ORGANIC DIOLS

A. Discussion

A variant of the diol-diaminosilane reaction was tried with a cyclic siloxazane that was reported by Andrianov.[41] The reaction was:



2,2,4,4,6,6-hexamethyl-1-oxa-3,5-diazacyclohexasilane

The siloxazane formed polymers in reactions with three diols, ethylene glycol, hydroquinone, and p,p'-biphenol. The reaction with hydroquinone produced a polymer with a molecular weight of about 900,000, as determined by light scattering. The polymer was a tacky, elastic solid at room temperature, and it was detectably soft at -78°C. A solution of it in benzene was tried as a coating agent. It did not flow during curing, and it remained soft for 3.5 hours at 400°C in air. Furthermore, the coating felt fairly soft when all of the panel but the point of inspection was surrounded by dry ice. The poor abrasion resistance is undesirable in a coating, but the softness at -78°C is interesting.

The fact that the siloxazane-hydroquinone reaction product is a high polymer with Si-N bonds makes it unusual and offers unique possibilities for structural modifications, but a small amount of effort to crosslink the polymer with pentaerythritol was not successful.

Moisture sensitivity was greatest in the polymer made from ethylene glycol, and it was least in the one made from p,p'-biphenol. The ethylene glycol polymer was sensitive even to

atmospheric moisture, while the biphenol polymer merely became slightly softer when boiled for 30 minutes in water. Each of the three polymeric products was elastic, but only the one made from hydroquinone retained detectable compressibility at -78°C. None had thermal stability equal to the silphenylene polymers (Sections III and IV), and none appeared to be potentially useful as coating agents since they did not readily form abrasion-resistant films when heated on metal surfaces.

B. Experimental Details

1. Preparation of 2,2,4,4,6,6-hexamethyl-1-oxa-3,5-diazacyclohexasilane

The method of Andrianov[41] was used to prepare 2,2,4,4,6,6-hexamethyl-1-oxa-3,5-diazacyclohexasilane. In the first step, dichlorotetramethyldisiloxane was prepared by the method of Patnode and Wilcock.[42] Water in dioxane was added to dimethyldichlorosilane in ether, and the hydrolysis product was distilled to yield 17% of the theoretical amount of dichlorotetramethyldisiloxane boiling at 135-137°C. An equimolar mixture of the disiloxane and dimethyldichlorosilane dissolved in toluene was treated with liquid ammonia. The toluene-soluble product was distilled to yield the crude cyclotrisildiazoxane, b.p. 96-116°C at 16 mm pressure. The liquid was drained away from the semicrystalline product to yield 30% of the theoretical amount of 2,2,4,4,6,6-hexamethyl-1-oxa-3,5-diazacyclohexasilane that melted over a range of 43-48°C (Andrianov, 46-47°C). Recrystallization was not attempted because of excessive solubility in ether, which was the recommended solvent.

2. Polymerization of cyclotrisildiazoxane with ethylene glycol

Hexamethylcyclotrisildiazoxane, 2.40 g (0.0109 mole), and ethylene glycol, 0.67 g (0.0108 mole), were stirred together at 44°C for 1 hour while ammonia was evolved slowly. The temperature was raised to 160°C over a 4-hour period while the liquid became gradually more viscous. The theoretical change in weight occurred, and a 1% solution of the resulting polymer in benzene had an inherent viscosity of 0.44 deciliters per gram, measured at 30°C. The polymer was a viscous oil at room temperature, gelatinous at 0°C, and a tacky solid at -80°C. It absorbed moisture rapidly from the laboratory air. It contained 4.51% nitrogen (theory, 5.01%).

Attempts to crosslink the polymer with pentaerythritol in tetrahydrofuran resulted in no visible reaction in 40 hours of refluxing. However, when 10% of the stoichiometric amount of pentaerythritol was mulled into the polymer, and the mass was heated for 2.5 hours at 135-140°C at 0.5 mm pressure, a rubbery, elastic, tacky solid was formed. The product contained visible agglomerates of an unidentified material. When exposed to the atmosphere for an hour, the rubbery polymer lost most of its toughness and resiliency. When heated at 400°C, the polymer was converted to a friable mass in 15 minutes.

3. Polymerization of the cyclotrisildiazoxane with p,p'-biphenol

Hexamethylcyclotrisildiazoxane, 2.35 g (0.0106 mole), and p,p'-biphenol, 1.98 g (0.0106 mole), were stirred together in ether, and the ether was removed by distillation without any apparent reaction. The mixture, which was pasty, was heated further; and evolution of gas occurred at 145°C. The temperature was increased to 180°C for 1 hour. The mass did not become fluid, but it was slightly rubbery at 180°C. A 1% solution of the resulting polymer in benzene had an inherent viscosity of 0.32 deciliters per gram measured at 30°C. The polymer was an opaque, slightly elastic solid. It was not visibly affected by atmospheric moisture. When heated for 1 hour at 200°C, elastic threads could be drawn from the polymer at that temperature. The polymer became dark brown when heated overnight at 300°C, but it still retained some of its resilience.

The molecular weight was apparently increased by heating the polymer for 1 hour at 250°C and 0.5 mm pressure, and the inherent viscosity of a 1% solution of the polymer in benzene was increased to 0.39 deciliters per gram at 30°C. The tough, elastic solid product was weakened a little by boiling in water for 30 minutes. When heated for an additional hour at 400°C, the polymer became a tough, dark brown mass; but it still retained some resilience.

4. Polymerization of the cyclotrisildiazoxane with hydroquinone

Hexamethylcyclotrisildiazoxane, 2.40 g (0.0109 mole), and hydroquinone, 1.20 g (0.0109 mole), were stirred together at 88°C for 2 hours while ammonia was evolved. The mixture finally became too viscous for stirring. The theoretical change in weight occurred, and a 1% solution of the resulting polymer

in benzene had an inherent viscosity of 0.80 deciliters per gram measured at 30°C. The polymer was a rubbery, elastic, tacky solid. It absorbed moisture slowly from the laboratory air, and lost most of its toughness and resilience on standing overnight in the laboratory. The polymer contained 3.03% nitrogen (theory, 4.71%).

The molecular weight of the polymer apparently was increased by heating for 2.5 hours at 250°C at 0.5 mm pressure. A tough, rubbery, elastic, slightly tacky polymer was obtained. It swelled in benzene and tetrahydrofuran; but it was not soluble, even when heated in either solvent. When heated at 400°C, the polymer retained some resilience after 45 minutes; but it lost most of its resilience and became friable in 1 hour. It absorbed moisture slowly from the atmosphere and lost most of its toughness and resilience overnight.

A second reaction was started in the same way as the one just described. The product, after reaction at 89°C for 2 hours, was slightly tacky, colorless, and elastic; it had an inherent viscosity of 0.91 and a molecular weight, by light scattering, of 930,000.

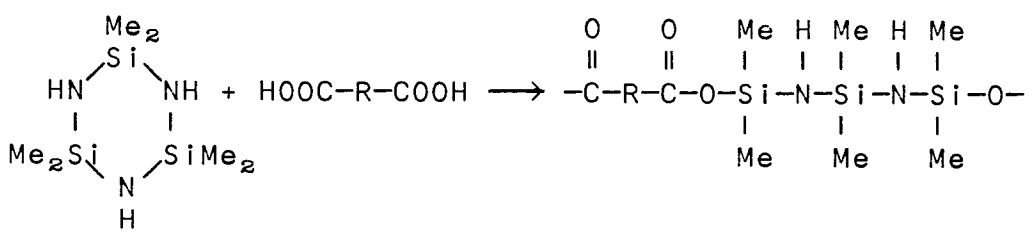
When a small sample of the polymer was heated on an aluminum panel, it softened but did not spread over the surface. When a 10% solution of the polymer in benzene was placed on an aluminum panel, it spread evenly over the surface, and a thin film of the polymer remained after benzene evaporated. The film darkened slowly in 3.5 hours at 400°C, but it did not flow during curing even when in a vertical position. After 3.5 hours at 400°C, the film was gelatinous and soft even when surrounded by dry ice. After an additional 1.5 hours at 400°C, the film peeled away from the panel in small fragments.

Another portion of the polymer was placed on an aluminum panel and heated in air over a period of 3.5 hours at gradually increasing temperatures to 375°C. The polymer then contained a few bubbles and was still compressible. After cooling between slabs of dry ice, it was still soft. Time did not permit further investigation.

X. REACTION OF CYCLIC SILAZANES WITH DIBASIC ACIDS

A. Discussion

The reactions of cyclic silazanes with organic dibasic acids was investigated as a route to polymers. The reaction is related to successful polymerizations that occur when cyclic silazanes are treated with diols as reported by Curry and Byrd[6] and also when cyclic siloxazanes are treated with diols (Section IX). The outstanding difference is that the dibasic acids yield esters of silicon in a silazane structure that had not been studied previously.



Russian investigators[43] made a polymer by treating hexamethylcyclotrisilazane with malonic acid, but they gave no data on molecular weight or stability. An attempt to reproduce their findings resulted in a slow reaction at 50°C to form a red, viscous liquid. A thin film of the liquid in air changed from clear to grainy and milky in 15 minutes. At 160°C under nitrogen, it became black in 40 minutes. Attempts to form the polymer at a higher temperature evidently failed because of thermal decomposition of the malonic acid. In our study, the reaction has been conducted under a variety of conditions - with two silazanes (hexamethylcyclotrisilazane and hexaphenylcyclotrisilazane) and with three acids (malonic, adipic, and terephthalic).

The closest approach to an interesting polymer of this general type was made with hexamethylcyclotrisilazane and terephthalic acid. At one stage, the product was a resin that could be drawn out into long elastic fibers, but the fibers reacted with laboratory air and became friable within a minute. The

resin was liquid at 200°C, and heating at 250°C to induce further polymerization caused decomposition instead. Attempts to determine the molecular weight by light scattering were unsuccessful, apparently because the benzene solution of the polymer was too sensitive to moisture.

Hexaphenylcyclotrisilazane and terephthalic acid formed a brown, brittle solid that was liquid at 180°C.

Adipic acid and hexamethylcyclotrisilazane yielded a product that was a viscous liquid with a molecular weight of only 460.

A reaction of hexaphenylcyclotrisilazane with adipic acid in tetrahydrofuran (THF) appeared promising at first, but the molecular weight of the product proved to be only about 675.

The reactions with hexamethylcyclotrisilazane were rapid compared to those with hexaphenylcyclotrisilazane. The latter were doubtless incomplete in some cases. In general, the reaction does not appear promising as a source of polymers. The only product that may have had a suitably high molecular weight was that made from hexamethylcyclotrisilazane and terephthalic acid, and it was sensitive to both heat and moisture.

B. Experimental Details

1. Reaction of hexamethylcyclotrisilazane with malonic acid

Hexamethylcyclotrisilazane, 4.38 g (0.02 mole), was dissolved in 15 ml of distilled pyridine. To this was added 2.08 g (0.02 mole) of malonic acid dissolved in 15 ml of pyridine. The reaction mixture was refluxed 3.5 hours. The solvent was distilled off leaving 3.6 g of a black liquid in the flask. The liquid was centrifuged and a black tarry material settled out. This material had no properties that encouraged further work.

In a second reaction without solvent, the two mixed reactants were heated at gradually increasing temperatures from 50-155°C for 5 hours. In the beginning, the mixture was a viscous red liquid, and most of the ammonia was evolved rapidly. Subsequent heating in an effort to increase the viscosity apparently caused decomposition, because black specks appeared in the melt, but no appreciable change in viscosity occurred.

In a third reaction without solvent, the temperature was kept at 50°C for 13 hours. The product, when cool, was a red-brown viscous liquid that would flow readily at room temperature.

Anal. Calculated for $C_9H_{22}N_2O_4Si_3$: C 35.26, H 7.23.

Found: C 35.51, H 6.91.

A film of the red-brown liquid on glass became milky and grainy in about 15 minutes. After the liquid was heated at 160°C for 40 minutes in nitrogen, black specks appeared.

2. Reaction of hexamethylcyclotrisilazane with terephthalic acid

Hexamethylcyclotrisilazane, 4.39 g (0.02 mole), was dissolved in 50 ml of THF, and 3.32 g (0.02 mole), of terephthalic acid was added gradually with stirring in an atmosphere of nitrogen. The temperature rose about 5°C. The mixture became clear in 2 hours of refluxing as ammonia evolved. In 4 additional hours of refluxing, the only change observed was slow evolution of ammonia. The solvent was distilled off, and the reactants were heated at 160°C for 1.5 hours and at 170°C at 0.04 mm for 1 hour. The product was a viscous liquid when hot and a rubbery solid at room temperature.

Anal. Calculated for $C_{14}H_{24}N_2O_4Si_3$: C 45.62, H 6.56.

Found: C 48.23, H 6.66.

When a portion of the rubbery solid was removed from the flask, long elastic fibers were formed. At first, they were lively and tough, but they became chalky within a few minutes as they were flexed in air. When a small sample was heated at 250°C in nitrogen for 18 hours in an effort to drive the polymerization further, black particles appeared in the melt. An effort to determine the molecular weight of the rubbery polymer was unsuccessful, because the benzene solution was excessively sensitive to moisture. Because of the low melting point and the lack of encouraging thermal and hydrolytic stability no further work was undertaken on this reaction.

3. Reaction of hexaphenylcyclotrisilazane and terephthalic acid

Equimolar quantities of hexaphenylcyclotrisilazane and terephthalic acid were refluxed in benzene for 24 hours while the acid went into solution gradually and ammonia evolved. The solvent was removed, and further heating at 175°C for 1.5 hours and at 190°C for 1 hour at 0.1 mm produced a material that was a viscous liquid while hot and a solid when cool. The solid product was brown and brittle.

Anal. Calculated for $C_{44}H_{36}N_2O_4Si_3$: C 71.32, H 4.90.

Found: C 71.38, H 4.96.

4. Reaction of hexamethylcyclotrisilazane and adipic acid

Equimolar quantities of hexamethylcyclotrisilazane and adipic acid were refluxed in THF for 14 hours. Then the THF was removed, and the residue was heated at 175°C for 2 hours at atmospheric pressure and at 125°C for 2 hours at 0.06 mm. The product was a liquid while hot and a brittle solid when cool. It had a molecular weight of 460 (theory, 346.6).

5. Reaction of hexaphenylcyclotrisilazane with adipic acid

Hexaphenylcyclotrisilazane, 5.9 g (0.01 mole), was dissolved in 15 ml of tetrahydrofuran. To this was added slowly 1.46 g (0.01 mole) of adipic acid dissolved in 15 ml of tetrahydrofuran. The resulting mixture was refluxed 14 hours while ammonia evolved slowly. The solvent was evaporated at reduced pressure, and the reaction was heated at 180°C at 0.06 mm for 1 hour. The product, 6.8 g, was a brittle yellow-white solid.

Anal. Calculated for $C_{42}H_{40}N_2O_4Si_3$: C 69.96, H 5.59, N 3.88, O 8.88, Si 11.69.

Found: C 68.45, H 5.79, N 3.54, O 10.69 (by difference), Si 11.53.

Mol. Wt. Calculated: 721.05.

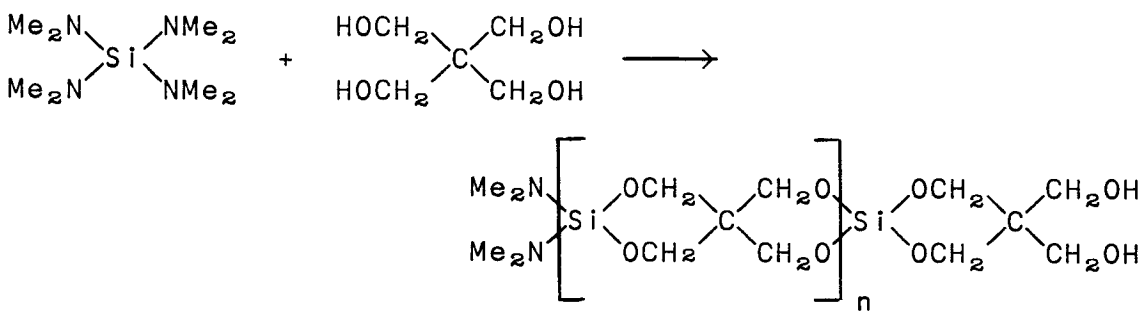
Found (vapor osmometry): 674.

XI. SILASPIRANE POLYMERS

A. Discussion

The reaction of tetrakis(dimethylamino)silane with pentaerythritol offered a possible route to silaspirane polymers through a variant of the diol-diaminosilane reaction. In spite of the strong possibility that crosslinking would prevent success, the silaspirane structure was so desirable that the reaction was investigated.

All attempts to carry out the reaction under various conditions produced only intractable powders that were evidently products of crosslinking and incomplete reactions. The hoped-for reaction was:



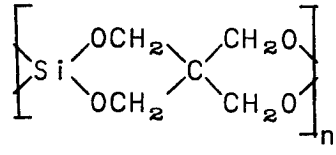
Tetrakis(dimethylamino)silane and pentaerythritol reacted very slowly. The aminosilane dissolves readily in many organic solvents, but pentaerythritol dissolves only in highly polar solvents. When the two were mixed, stirred, and heated, no appreciable amount of reaction occurred until the temperature reached 180°C, and 8 hours at 180°C produced only slight reaction as indicated by only a small change in weight and appearance. Attempted reactions in toluene, triethylamine, and tetrahydrofuran were no more successful. o-Dichlorobenzene, which does not dissolve pentaerythritol, was also tried as the reaction medium, because of its high boiling point. In the experiments in o-dichlorobenzene, the reactants and solvent were placed in a glass vessel with glass beads and shaken violently for 32 hours in the manner that is used to disperse pigments in paint. Then the mixture, containing finely divided

pentaerythritol, was refluxed at 180°C. In one experiment, the starting materials were recovered almost unchanged after 8 hours at 180°C. In another similar experiment, heating at 180°C was continued for 30 hours. The longer period of heating produced a detectable amount of reaction. The product was a tan-colored powder that was insoluble in water, ethyl alcohol, acetone, tetrahydrofuran, xylene, pyridine, anisole, or triethylamine. When heated on a spatula, it appeared to be unusually stable, but later it was found not to be so.

Reactions of tetrakis(dimethylamino)silane and pentaerythritol in dimethylsulfoxide, without and with magnesium fluoride as a catalyst, yielded intractable white powders.

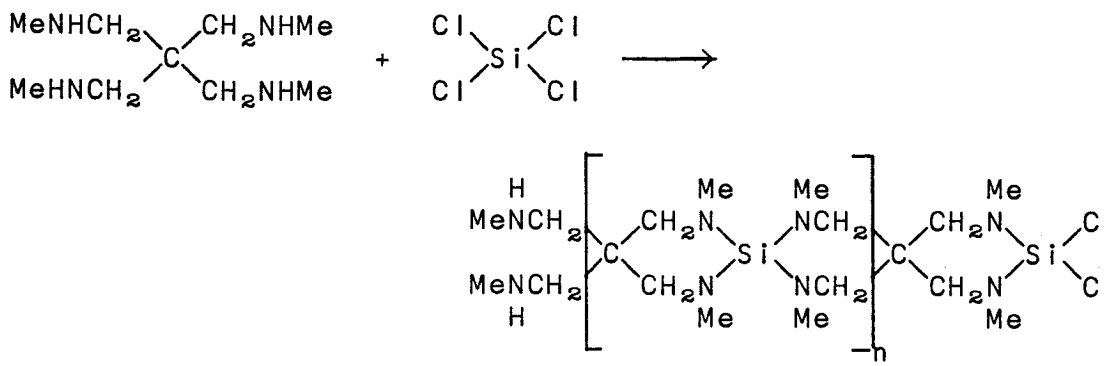
A reaction of tetrakis(dimethylamino)silane and pentaerythritol, in a mixture of benzene and DMSO, in which the reactants were mutually soluble, also produced an insoluble solid product.

When the products from the above reaction in DMSO and DMSO-benzene were ashed, the weight losses showed that they were not silica. The weight losses indicated contents of 22-33% of silicon in the extracted products, whereas the theoretical value is 17.5% for the following formula or crosslinked versions of it:



Thus, it appears that there was a considerable amount of high-silicon-content material in the product. Marvel[44] obtained similar results from the reaction of pentaerythritol with silicon tetrachloride, but he reported that his products did not have outstanding thermal stability. They lost 19-55% of their weight in 12 hours at 300°C. The weight losses on heating our products at 300°C for 12 hours were similar to those that Marvel observed.

Tetrakis(methylaminomethyl)methane was treated with silicon tetrachloride in an effort to obtain a silaspirane silicon-nitrogen polymer. Again, a strong factor favoring ring formation would be required to prevent defeat of the attempt by crosslinking.



The reactants were refluxed in triethylamine for 4 hours, and the triethylamine-soluble portion of the product was found to be a viscous liquid that amounted to more than the theoretical yield. Evidently, the reaction was incomplete.

B. Experimental Details

1. Preparation of monomers

a. Preparation of tetrakis(dimethylamino)silane

Anderson's[45] and Waterman's[46] methods were reviewed as patterns for the following reactions: Anderson's procedure was tried by treating one mole of silicon tetrachloride in ether with a slight excess of amine, but the desired product was obtained in only about 1% yield; the remainder was chlorotris(dimethylamino)-silane, b.p. 68-70°C at 13 mm, m.p. 2-3°C.

Waterman's method with a pressure reactor was tried for converting the monochlorotriamino silane made above into tetrakis-(dimethylamino)silane. The tris compound was heated with an excess of dimethylamine for 8 hours at 100°C and 96 hours at 60°C in a stainless steel bomb. Essentially all of the tris compound was recovered.

In a third attempt, silicon tetrachloride, 84.88 g (0.50 mole), dissolved in 2 liters of toluene was stirred under dry dimethylamine for 4 hours. The reaction mixture was then refluxed for 4 hours, cooled, and filtered. The toluene was removed by distillation, and the colorless liquid product was distilled. The desired tetraamino compound amounted to 17.4 g (17% of theory), b.p. 75-77°C at 13 mm, m.p. 12-15°C, neutral equivalent 52.5 (theory 51.1).

In a fourth attempt, dimethylamine was bubbled into 70 grams of chlorotris(dimethylamino)silane in refluxing toluene. Addition was continued for 12 hours. The product, tetrakis-(dimethylamino)silane, b.p. 77°C at 16 mm, m.p. 13-15°C, amounted to 85 g, (99.4% yield), and had a neutral equivalent of 52.0 (theoretical 51.1).

b. Preparation of tetrakis(methylaminomethyl)methane

Tetrakis(methylaminomethyl)methane was prepared by amination of pentaerythritol tetraiodide. The tetraiodide, 25.0 g (0.043 mole), was heated with 360 ml (252 g, 8.1 moles) of methylamine in 450 ml of dioxane at 100°C for 24 hours. The dioxane was distilled, and the residue was stirred with 10 g of solid sodium hydroxide and extracted with ethanol to leave a white powder. From the extract solution was distilled 3.5 g of pale yellow liquid that boiled at 234-238°C. Van Alphen[47] reported 235-238°C as the boiling point. The yield was 43% of theory.

2. Reactions of tetrakis(dimethylamino)silane with pentaerythritol

a. Initial attempts

In each of the initial reactions, 5.0 g (0.025 mole) of pentaerythritol was mixed with 3.33 g (0.025 mole) of tetrakis-(dimethylamino)silane either with or without a solvent.

Without a solvent, the mixture was heated at 180°C for 8 hours. Only partial reaction appeared to occur, and the product was a gritty, non-uniform mass.

In two additional attempts, the reactants were refluxed in toluene and in THF for 7 hours, but only a small amount of reaction took place in either solvent, as indicated by the fact that only a trace of dimethylamine was formed. After the solvent had been removed and the reactants were heated 8 hours at 180°C, the product from each reaction was a gritty, non-uniform mass.

In a fourth attempt, steps were taken to reduce the particle size of the pentaerythritol. Pentaerythritol and THF were shaken violently with glass beads for 32 hours to disperse the pentaerythritol. Tetrakis(dimethylamino)silane was added to the dispersion, and the mixture was refluxed for 8 hours. The THF was then removed, and the mixture was heated for an additional 8 hours at 180°C. Dimethylamine was emitted steadily. The product was mixed with THF and filtered to yield 3.57 g of powder, and 1.41 g of liquid, m.p. 17-20°C. The powder darkened slowly but did not fuse even when heated to red heat. The total weight lost in the reaction was 3.35 g or 78% of theory for dimethylamine.

In a fifth attempt, o-dichlorobenzene was used as the reaction medium. The pentaerythritol and the tetrakis(dimethylamino)silane were shaken together for 32 hours with glass beads. The resulting slurry was refluxed at 180°C for 8 hours, the solid portion was filtered from the solvent, and the solid was washed with THF and dried. It had a melting point of 263-264°C, slightly higher than that of pentaerythritol.

Duplication of the fifth attempt with heating time increased to 30 hours produced an infusible insoluble powder with essentially no material remaining in the solvent. The powder resembled the product of the fourth attempt. It did not fuse and darkened only slowly at red heat.

b. Reactions in triethylamine

Tetrakis(dimethylamino)silane, 2.50 g (0.125 mole), and pentaerythritol, 1.70 g (0.125 mole), were placed in 30 ml of triethylamine with 10 glass beads (0.125-in. diameter) and shaken violently for 40 hours. The dispersion did not settle on standing. After refluxing for 48 hours in an atmosphere of nitrogen, the dispersion separated rapidly. The insoluble material was filtered off and washed with triethylamine and tetrahydrofuran. It weighed 1.67 g and melted at 262°C, which is the correct melting point for pentaerythritol.

A second reaction was run in the same manner but with 0.01 g of magnesium fluoride added. The result was the same.

c. Reactions in dimethylsulfoxide

The reactants, in the amounts given above for reactions in triethylamine, were shaken with the glass beads in 30 ml of DMSO for 40 hours. The mixtures, one with magnesium fluoride and one without, both contained dispersed liquid phases but no solid phases. The aminosilane was insoluble. Heating and stirring for 32 hours at 60°C produced a slow evolution of amine that was more rapid in the sample with magnesium fluoride. Insoluble solids appeared gradually. At the end of 32 hours, the DMSO was removed at reduced pressure. The residues were pastes, which were washed with hot triethylamine and filtered. The resulting powders weighed 2.12 g (with catalyst) and 1.85 g (without catalyst). A 0.5-g aliquot of each sample was extracted with ethanol in a Soxhlet extractor for 16 hours, and the residues weighed 0.190 g (with catalyst) and 0.134 g (without catalyst). In each case, the extracts, after the ethanol was removed, melted at 262°C. The residues darkened to light tan slowly when heated on spatulas to red heat.

Another reaction was carried out in the manner just described, except that the reaction medium was 30 ml of DMSO and 10 ml of benzene. Shaking with glass beads was unnecessary, because the reactants dissolved in the mixed solvents. Magnesium fluoride, 0.01 g, was added, and the solution was stirred 24 hours at 60°C. Dimethylamine was evolved slowly, and a small amount of precipitate appeared in about 8 hours. The product was isolated as described before. The silicon contents of the products were determined by ashing weighed samples at gradually increasing temperatures up to 550°C. The amount of silicon was then calculated from the weight of the white powdery residue, which was silicon dioxide. The results are given in Table XIV.

The extracted product obtained from the reaction in DMSO and benzene was heated at 300°C in air to determine its rate of weight loss. It lost 50% of its weight in 1.5 hours and then became essentially stable in an additional 24 hours.

Table XIV. Silicon Content of Products from Attempted Silaspirane Reactions

	DMSO		DMSO-benzene
	with MgF_2	without MgF_2	with MgF_2
Yield, % of theory[a]	40	25	40
Silicon content of product, %[b]	32.9	25.4	21.7

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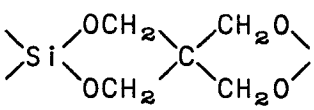
a. Desired product, 

Theoretical silicon content: 17.5% for the desired product, 46.7% for silica.

The actual product was evidently crosslinked and was not the desired product

b. Calculated from the weight of residue after ashing

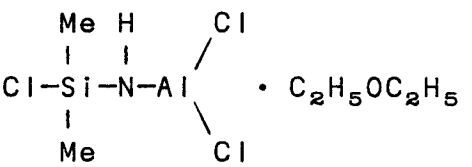
3. Reaction of tetrakis(methylaminomethyl)methane with silicon tetrachloride

Under anhydrous conditions, tetrakis(methylaminomethyl)-methane, 0.647 g (0.0034 mole), was dissolved in 50 ml of triethylamine and dropped into a stirred 300-ml quantity of triethylamine while silicon tetrachloride, 0.583 g (0.0034 mole), was dropped in simultaneously over a period of 3 hours. The temperature rose to 35°C. The resulting mixture was refluxed for 4 hours, allowed to stand overnight, and filtered. The precipitated salt was washed with triethylamine, freed of liquid by evaporation under reduced pressure, and weighed. The amount of salt was 1.3 g, which was 70% of the theoretical amount of triethylamine hydrochloride. The triethylamine-soluble portion, after evaporation of the triethylamine, was a viscous liquid and weighed 1.2 g, which was more than the theoretical amount. The benzene-soluble portion of this viscous liquid was about 90% of the total, but it was also an oil, and its solution viscosity indicated that its molecular weight was insignificant.

XII. SILICON-NITROGEN-ALUMINUM POLYMERS

A. Discussion

The preparation of a silicon-nitrogen-aluminum polymer was attempted with a compound described by Wannagat.[48] The structure given by Wannagat is



He prepared it from hexamethylcyclotrisilazane and aluminum chloride. It was planned to determine whether the compound would react with ammonia to form a polymer.

Wannagat's procedure was followed with partial success, and treatment of the chloro compound with ammonia yielded material that was sensitive to moisture. Then, the aluminum chloride was replaced by phenoxyaluminum chloride in the reaction with hexamethylcyclotrisilazane in an attempt to form a dichloro Si-N-Al compound. Treatment of the product with ammonia yielded a viscous liquid that was sensitive to moisture and not polymeric. Heating the viscous liquid at reduced pressure changed the product to a resin, but it was not polymeric as indicated by solution viscosity. Also, it did not have the desired elemental composition, although the nitrogen content was almost correct. It was evident that the series of reactions attempted did not proceed readily as required for polymerization.

B. Experimental Details

1. The trifunctional halide

In the first attempt to prepare Wannagat's trifunctional Si-N-Al monomer, 6.6357 g (0.0301 mole) of hexamethylcyclotrisilazane was treated with 8.0297 g (0.0301 mole, Al_2Cl_6) of aluminum chloride in 15 ml of benzene according to the published directions.[48] During addition of the first portion of the Al_2Cl_6 under nitrogen, the temperature rose to 50°C. After addition was complete, the mixture was stirred for 48 hours at 76-78°C. An off-white insoluble powder was separated by centrifugation. An attempt was made to distill the portion of the powder that was soluble in ether (about 75%), but such a small amount of distillable product was obtained that the reaction was repeated with a larger amount of aluminum chloride.

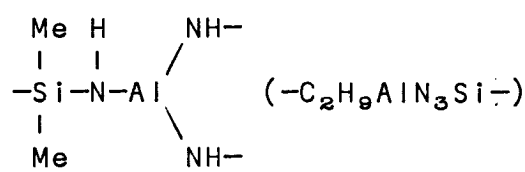
In the second preparation, the molar ratio was changed from that used by Wannagat, because it appeared that each mole of hexamethylcyclotrisilazane should be capable of reacting with 1.5 moles of aluminum chloride (Al_2Cl_6). With this modification of the procedure just described, a distilled liquid product was obtained that amounted to 30.9% of the theoretical yield. This liquid reacted violently with water and had an elemental composition that indicated less than the theoretical amount of ether.

Anal. Calculated for $C_2H_7AlCl_3NSi$: C 11.63, H 3.42, Cl 51.50.

Calculated for $C_6H_{17}AlCl_3NOSi$: C 25.68, H 6.11, Cl 37.90.

Found: C 20.59, H 4.79, Cl 48.1.

The liquid product, 1.57 g, was dissolved in 50 ml of dry ethyl ether and stirred in an atmosphere of ammonia for 1 hour. The white, insoluble product that formed was separated by centrifugation and washed with ethyl ether. After the solvent had been removed, the white powder weighed 1.92 g. It was insoluble in benzene, THF, dimethylforamide, or hexane, and it reacted with water to liberate ammonia. The theoretical amount of product, including the by-product ammonium chloride, was 1.74 g. However, the starting material evidently contained less than the theoretical amount of ether, and so the weight of product, combined with the expected weight of ammonium chloride, was reasonably consistent with the desired structure:



The next step was to carry out Wannagat's reaction with a difunctional aluminum compound and then ammonolyze the product to obtain a linear Si-N-Al polymer.

2. The difunctional halide

The method of G. Baddeley[49] was used to prepare phenoxyaluminum dichloride. Equimolar quantities of aluminum trichloride and phenol were heated at temperatures up to 175°C until the evolution of hydrogen chloride ceased. The phenoxyaluminum dichloride was distilled under reduced pressure. Its boiling point at 12 mm pressure was 196°C; Baddeley[49] reported 210°C at 15 mm pressure. A yield of 68.4% phenoxyaluminum dichloride was obtained. Chemical analysis of the product gave 37.2% Cl; theory is 37.7%.

The reaction of phenoxyaluminum dichloride was carried out as follows: Hexamethylcyclotrisilazane, 20.28 g (0.0924 mole), dissolved in 100 ml of dry benzene was refluxed with phenoxyaluminum dichloride, 52.82 g (0.277 mole), for 8 hours. At first the reactants dissolved almost completely, and then a white precipitate began to form. Reaction appeared to have stopped in 8 hours, so the solid was separated by centrifugation. The benzene-soluble portion was considered to be the product. After removal of the benzene, it was a resinous mass that amounted to 36.0 g or 50% of the theoretical yield.

Anal. Calculated for $C_8H_{12}AlCl_2ONSi$: C 36.38, H 4.58, N 5.30, Cl 26.84.

Found: C 27.85, H 5.44, N 6.95, Cl 28.6.

The resinous mass, 10.8 g, was dissolved in 300 ml of benzene and stirred in an atmosphere of ammonia for 2.5 hours. The temperature rose to 40°C and then returned to room temperature. The white solid that formed was removed by centrifugation and was found to weigh 9.5 g or about twice the amount of ammonium chloride expected. The benzene-soluble portion was a viscous liquid, which weighed 3.34 g or about 40% of the amount expected. The nitrogen content of the viscous liquid was 13.5% (theory, 13.45%). The inherent viscosity of a 1% solution of the liquid in benzene was 0.02 deciliters per gram at 30°C. Hence, it was not polymeric. The liquid product was heated at 0.5 mm pressure. A few bubbles appeared as the temperature rose to 100°C. Subsequent heating for 5 hours at temperatures up to 175°C caused very little additional change, but the mass solidified to a resin when it cooled. The resin liquefied on exposure to the laboratory air for about an hour, and it had the following composition:

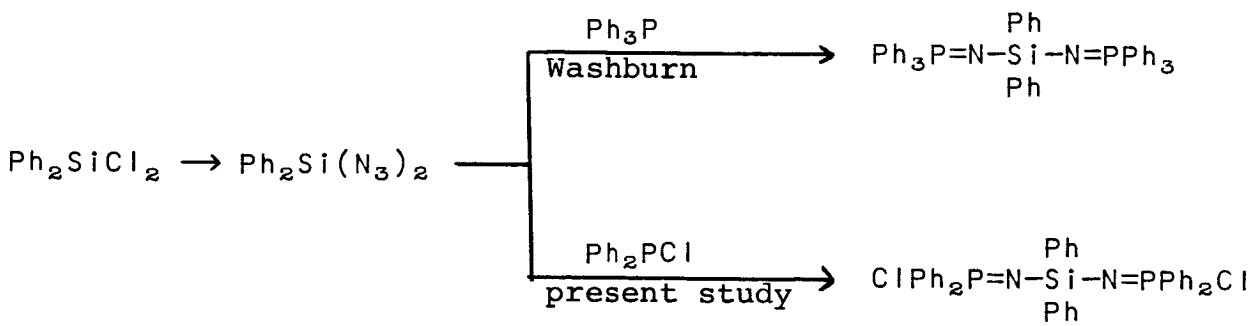
Anal. Calculated for $C_8H_{13}N_2OSiAl$: C 46.14, H 6.29, N 13.45.

Found: C 34.7, H 7.42, N 12.40

XIII. SILICON-NITROGEN-PHOSPHORUS COMPOUNDS

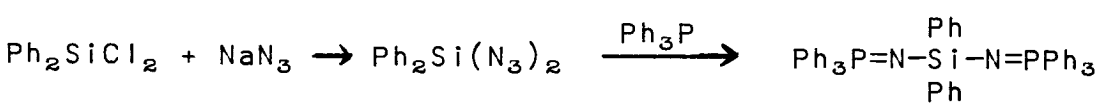
A. Discussion

Silicon-nitrogen-phosphorus compounds have been shown to have desirable stability characteristics, and an attempt is being made to form polymers of Si-N-P compounds by methods similar to those that have been used for preparing Si-N compounds. Washburn and Baldwin[50] prepared diphenylsilyl-bis(imidotriphenylphosphorane) by a method that appeared to be suitable, with modification, for making a reactive dichloride for polymerization with ammonia:



An attempt to prepare the dichloride resulted, however, in the formation of a ring compound containing nitrogen and phosphorus but no silicon.

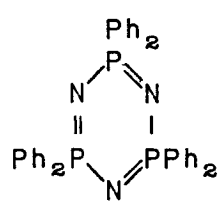
Washburn's polymer prototype was prepared without difficulty by the published method.[50]



The pure Si-N-P compound was not appreciably changed by exposure to boiling water for 30 minutes. On being heated with concentrated hydrochloric acid in a test tube immersed in boiling water, the compound changed from a free-moving powder to an agglomerate in 2 minutes, and its melting point rose to 211-221°C.

The thermal stability of diphenylsilyl-bis(imidotriphenylphosphorane) was estimated by determining the amount of gas produced by heating the phosphorane in a sealed evacuated tube at 450°C for 1.5 hours. The method and results with a number of other Si-N compounds were described previously.[51,52] The phosphorane released 1.7 ml of gas per gram (average of 1.73 and 1.70) and became dark brown in color. Comparable experiments with silazanes indicated that even hexamethylcyclotrisilazane (0.6 ml per g) is more stable. Hexaphenylcyclotrisilazane released 0.4 ml and nonamethylcyclotrisilazane released 0.03 ml of gas per gram. However, the thermal stability of the phosphorane is reasonably good compared to that of benzene or commercial siloxane.[52] Apparently the phosphorane is more stable hydrolytically and slightly less stable thermally than the silazanes that we have made.

When diphenylchlorophosphine was substituted for triphenylphosphine in the above reaction, the amount of nitrogen produced by decomposition of the azide indicated that the reaction was proceeding as desired. Subsequent attempts to isolate the dihalide were complicated by the fact that pyridine, which was used as the solvent, apparently formed a fairly stable complex with the product. Since it was likely that pyridine would not interfere with the reaction of the dihalide and ammonia, part of the pyridine solution of the dihalide was treated with ammonia, and approximately the theoretical amount of ammonium chloride was obtained. The main product was crystalline and it evolved a gas while melting partially at about 115°C. Efforts to isolate and identify intermediates at several stages in the process finally produced three crystalline materials that melted at about 230°C. Two of these were obtained in two different preparations at the stage where the dichlorophosphorane was expected; the third was obtained after treatment of the expected dichlorophosphorane with ammonia. The three materials proved to be 2,2,4,4,6,6-hexahydro-2,2,4,4,6,6-hexaphenyl-1,3,5,2,4,6-triazatriphosphorine, evidently the principal product of the reaction.



The mechanism by which the triazatriphosphorine was formed is uncertain, but it appears that phosphorus and silicon may have exchanged chloride and azide groups. Then the cyclic P-N compound was formed from the azidophosphine.

$$3\ \begin{array}{c} Ph \\ | \\ P-N_3 \\ | \\ Ph \end{array} \longrightarrow (Ph_2PN)_3 + 3N_2$$

Formation of the triazatriphosphorine is strong evidence that the proposed approach to a silicon-nitrogen-phosphorus polymer is not feasible.

B. Experimental Details

1. Diphenylsilyl-bis(imidotriphenylphosphorane)

Diphenylsilyl-bis(imidotriphenylphosphorane) was prepared by the method of Washburn and Baldwin.[50] The synthesis was completed with a yield of crude product of 98% of theory, but after purification the yield was 28% of theory. The crude material was purified by dissolving it in benzene and precipitating with hexane and finally by recrystallization from benzene-isopropanol. The melting point was 191-193°C.

After being exposed to boiling water for 30 minutes, and then being dried, the melting point of the phosphorane was found to be 190-192°C. When exposed to boiling concentrated hydrochloric acid for 2 minutes, the powder agglomerated. After being dried, it melted at 211-221°C.

The thermal stability of the phosphorane was evaluated by the method described previously,[52] in which the amount of gas produced when a sample is heated in an evacuated glass tube for 1.5 hours at 450°C is determined. The phosphorane produced 1.7 ml of gas per gram and became dark brown in color. Under the same conditions,[51,52] hexamethylcyclotrisilazane released 0.6 ml, nonamethylcyclotrisilazane released 0.03 ml, and benzene released 0.9 ml of gas per gram.

2. Attempt to prepare diphenylsilyl-bis(imidodiphenylchlorophosphorane)

The stepwise procedure for the preparation of diphenylsilyl-bis(imidotriphenylphosphorane) described by Washburn and Baldwin[50] was modified in an attempt to prepare diphenylsilyl-bis(imidodiphenylchlorophosphorane). Diphenyldichlorosilane, 11.11 g (0.0439 mole), was stirred for 24 hours at ambient temperature under nitrogen with 5.71 g (0.0878 mole) of sodium azide in 100 ml of pyridine that had been purified by distillation from phthalic anhydride followed by distillation from potassium hydroxide. The infrared spectrum of the reaction solution showed strong azide absorption at 4.68 μ (2137 cm^{-1}). Sodium chloride, 5.06 g (98.6% of theory), was removed by filtering.

A solution of 19.60 g (0.0888 mole) chlorodiphenylphosphine, Aldrich Chemical Company, in 35 ml of purified pyridine was added dropwise to the gently refluxing azide solution. The nitrogen evolved (98% of theory) was measured by the displacement of water. The infrared spectrum of the reaction solution indicated the absence of the azide. The residue remaining after evaporation of the pyridine at reduced pressure was a cream-colored paste which was insoluble in ether and in benzene. Recrystallization from pyridine gave white crystals which melted at 210-220°C. Recrystallization from a pyridine-benzene mixture gave a white crystalline material, m.p. 231-233°C. Analysis indicated the presence of chemically combined pyridine, since the product contained more C, H, and N than the desired compound. Also, the crystals, designated Product A, had a faint odor of pyridine.

Anal. Calculated for $C_{36}H_{30}Cl_2N_2P_2Si$: C 66.36, H 4.64, Cl 10.88, N 4.30, P 9.51, Si 4.31.

Found: C 69.28, H 5.34, Cl 6.03, N 8.00.

To avoid the complications involved in the separation and recrystallization of the diphenylsilyl-bis(imidodiphenylchlorophosphorane), the amination reaction was attempted in the pyridine solution. The procedure described in the preceding section was followed. The reaction of 13.02 g (0.200 mole) of sodium azide and 25.10 g (0.099 mole) of diphenyldichlorosilane yielded 12.09 g of sodium chloride (103% of theory). During the dropwise addition of the solution of chlorodiphenylphosphine (44.13 g, 0.200 mole), 92% of the theoretical nitrogen was evolved. White crystals, Product B, precipitated from the reaction solution on standing. They were filtered off and rinsed with benzene. The melting point was 226-228°C, and the infrared spectrum was almost identical

with that of Product A. The yield was 11% of theory. A portion of the filtrate (44.4%) was stirred several hours with dry ammonia gas at ambient temperature. The precipitate that formed was removed by filtering. It weighed 3.86 g, and, assuming it to be ammonium chloride, it was 88% of the theoretical yield. The pyridine solution was evaporated to dryness, and 17.24 g of a pale yellow powder was obtained. It melted at 115-170°C with evolution of gas. The powder was insoluble in hexane, but it was soluble in benzene. Several recrystallizations from benzene-hexane gave crystals melting at 225-229°C (Product C).

It was apparent that Products A, B, and C were identical. Mixtures of A + B and B + C had the same melting points as the individual products, and their solubility characteristics were identical. The melting points coincided with that of 2,2,4,4,6,6-hexahydro-2,2,4,4,6,6-hexaphenyl-1,3,5,2,4,6-triazatriphosphorine, which was reported by Haber[53] to be 230-232°C. The analysis and molecular weight confirmed the identification.

Anal. Calculated for $C_{36}H_{30}N_3P_3$: C 72.36, H 5.06, N 7.03, P 15.55.

Mol. Wt.: 597.6.

Found: C 72.16, H 5.18, N 6.98, P 15.1.

Mol. Wt. (vapor osmometry in benzene): 640.

XIV. STUDIES OF THE CHARACTERISTICS OF SILICON-NITROGEN BONDS

A. Discussion

The continuing studies of the fundamental characteristics of silicon-nitrogen bonds has included four different subjects in the past year. The studies were made as a result of questions that arose or opportunities that appeared in connection with the search for routes to polymers.

1. Relative rates of hydrolysis

Earlier studies showed that hydrolytic stability depended on both the electronic and steric character of the groups attached to the silicon and nitrogen atoms.[54,55] Recent work was an extension of these studies to obtain additional comparative data on new compounds prepared during the past year. The new compounds studied were bis(dimethylamino)diphenylsilane, tris-(dimethylamino)phenylsilane, tetrakis(dimethylamino)silane, and bis(*p*-methylanilino)diphenylsilane. Attempts were made to prepare bis(*p*-chloroanilino)diphenylsilane for comparison with its unchlorinated equivalent and methylanilino compound, but difficulty was experienced in isolating the product of the reaction between *p*-chloroaniline and diphenyldichlorosilane.

It was found that introduction of methyl groups into the *para* positions of the anilino groups of dianilinodiphenylsilane accelerated hydrolysis slightly as shown by the data in Table XV. The effect apparently resulted from electron release by the methyl group since steric factors were not involved. The differences in the relative rates of hydrolysis of the bis-, tris-, and tetrakis(dimethylamino)silane compounds (Table XV) were too small to show a significant effect of these variations in structure. However, bis(dimethylamino)diphenylsilane was so much more stable than bis(methylamino)diphenylsilane that the stabilizing effect of the additional methyl group on each nitrogen was obvious. It is difficult to understand how the hydrolysis rates in water could be so profoundly affected by the addition of one methyl group to each nitrogen atom. On the other hand, all of the dimethylaminosilanes hydrolyzed completely in less than 1 minute in dilute acid. Dianilinodiphenylsilane has less steric shielding for the N-Si-N group than bis(dimethylamino)-diphenylsilane, but the anilino compound is much more stable. Here the electronic factors are evidently dominant.

Table XV. Relative Rates of Hydrolysis of Silylamines[a]

Silylamine	CCl_4+H_2O		CCl_4+H_2O+HCl	
	Hydrolysis in first 20 min, %	Rate, % per hr	Time for 25% hydrolysis, min	Hydrolysis in first 20 min, %
Dianilinodiphenylsilane[b]	-	-	5	40
Hexaphenylcyclotrisilazane[b]	-	-	5	42
Bis(p-methylanilino)diphenylsilane	-	-	2	56
2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane[b]	3.5	0.2	-	-
Bis(dimethylamino)diphenylsilane	1.0	0.4	<1	100
Tetrakis(dimethylamino)silane	1.2	0.6	<1	100
Tris(dimethylamino)phenylsilane	2	1	<1	100
Nonamethylcyclotrisilazane[b]	0.8	1.2	<1	100
Tris(isopropylamino)isopropylsilane[b]	1	2	-	-
Octamethylcyclotetrasilazane[c]	4	2	<1	100
Hexamethylcyclotrisilazane[b]	23	38	-	-
Bis(methylamino)diphenylsilane[b]	80	600	-	-
Dianilinodimethylsilane[b]	100	3000	-	-

a. Method discussed previously (References 54 and 55). Approximately 5 milliequivalents of silylamine was shaken with 50 ml of carbon tetrachloride and 100 ml of water. Samples of the water were taken periodically for titration. The amount of titratable amine was the amount hydrolyzed.

b. Previously reported, Reference 54

c. Previously reported, Reference 55

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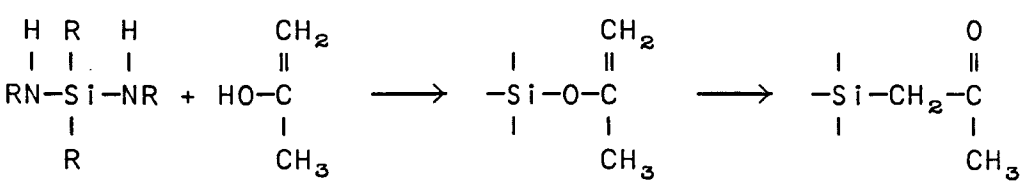
2. Reaction with acetone

The reaction of silylamines with acetone was studied with pmr spectrometry in an attempt to determine the effect of structure on reaction rates. It was hoped that a correlation would be found between the effects of structure on the rate of reaction with acetone and on the effects on hydrolytic stability. The basis of this study was the assumption that the enol form of acetone reacted in the manner of hydroxy compounds to split the Si-N bond. The reaction of silylamines with acetone proved to be so much slower than hydrolysis that an extensive comparison was not made, and the actual course of the reaction was not determined. Although the primary aim of the investigation was not fully accomplished, some interesting facts were revealed, and the method would probably be useful as a means of studying reaction rates of the more reactive silylamines.

The half-life of bis(methylamino)dimethylsilane in acetone-h_6 was found to be 1 hour at 34°C, while in acetone-d_6 its half-life is about 2 hours at 34°C. By contrast, hexamethylcyclotrisilazane undergoes no significant change in acetone-h_6 in 3 days. The greater stability of the cyclic silazanes in the presence of water was reported earlier[54] when it was learned that bis(methylamino)dimethylsilane hydrolyzed more than 100 times as fast as hexamethylcyclotrisilazane. The isotype effect in the acetone reaction indicates that the reaction involves enolization.

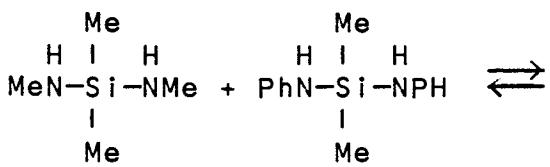


V. VI.

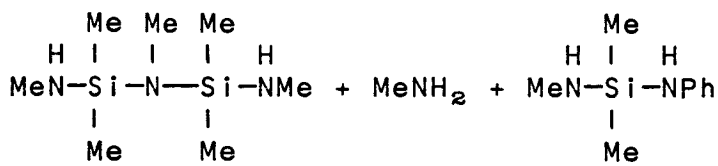
Pmr spectra did not detect the presence of V, and this is construed as strong evidence that V is absent. New peaks observed in the pmr spectra are compatible with the presence of VI.

3. Amine exchange

Silicon-nitrogen compounds undergo amine exchange rapidly even at room temperature. When dianilinodimethylsilane was mixed with bis(methylamino)dimethylsilane, the product of amine exchange, methylaminoanilinodimethylsilane, was detected within 30 minutes by both gas chromatography and proton magnetic resonance spectrometry.

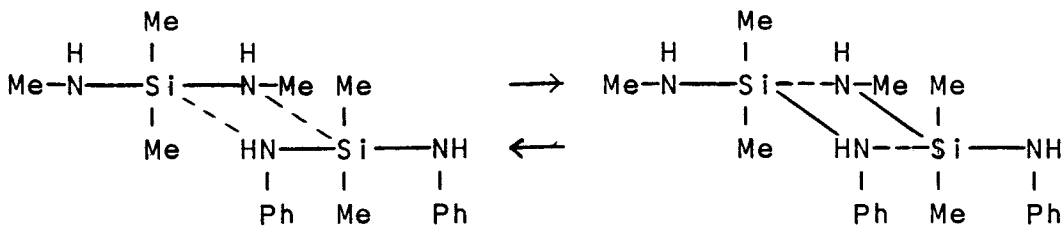


VII. VIII.



IX. X. XI.

Within 24 hours, pmr spectra indicated that approximately two-thirds of the bis(methylamino)dimethylsilane originally present had been converted to the exchange product. The reaction probably proceeds by intermolecular association of nitrogen with the d-orbitals of silicon followed by exchange, as represented by this equation:



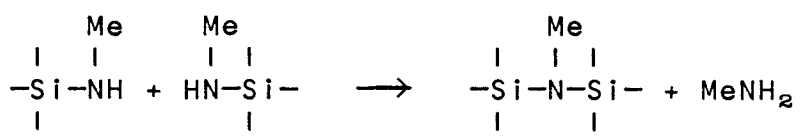
It is generally agreed that the character of Si-N bonds is partly determined by intramolecular involvement of the unshared electrons on the nitrogen with the d-orbitals of the silicon. If intermolecular involvement also occurs, amine exchange is a simple process. The extent of intermolecular involvement doubtless varies with the electrical and steric character of the substituents, and probably a manifestation of the interaction was seen in the unexpectedly high molecular weight reported in Section III for bis(methylamino)methylphenylsilane.

An attempt was made to observe interaction between bis(methylamino)dimethylsilane and dianilinodiphenylsilane, but the two were not mutually soluble. When dianilinodiphenylsilane was added to a benzene solution of bis(methylamino)dimethylsilane, the complexity of the Si-CH_3 absorption increased over a period of 24 hours. A similar increase in complexity would not have occurred without the dianilino compound.

4. <u>A study of special features of pmr spectra</u>

Proton magnetic resonance spectrometry has been utilized effectively for identification and analysis throughout the project. Consequently, when unexpected features of spectra were encountered, special effort was made to determine the reasons because of the possibility that a significant characteristic of the Si-N bond might be involved. For example, it would be of theoretical interest if rotation about the Si-N bond were restricted by the involvement of the unshared electrons of the nitrogen atom with the d-orbitals of the silicon.

The spectra of bis(methylamino)dimethylsilane and dianilinodiphenylsilane showed unexplained doublets for the Si-CH_3 and N-H absorptions, respectively. However, subsequent preparations of the two materials did not show the same doublets consistently. A fresh preparation of bis(methylamino)dimethylsilane had only one Si-CH_3 peak, but as it stood sealed in a glass tube at room temperature, it acquired a second Si-CH_3 peak of gradually increasing intensity. The change could be explained as intermolecular condensation with the formation of methylamine.



It now appears that the difficulties encountered in interpretation of the pmr spectra can be attributed to several factors, such as self-condensation, intermolecular association, intermolecular exchange, and reactivity with solvents.

B. Experimental Details

1. Preparation of compounds

The method of preparing bis(p-methylanilino)diphenylsilane was the same as that used for preparing dianilinodiphenylsilane.[54] The same method was used also in an attempt to prepare bis(p-chloroanilino)diphenylsilane, but no product was obtained. The preparations of bis(methylamino)dimethylsilane and dianilinodimethylsilane were described earlier.[54] Other sections of this report contain descriptions of preparations as follows: bis(dimethylamino)diphenylsilane and tris(dimethylamino)-phenylsilane, Section III; and tetrakis(dimethylamino)silane, Section XI.

2. Comparison of hydrolysis rates

The method of studying hydrolysis rates was described earlier.[54] The method consists of dissolving approximately 5 milliequivalents of the silylamine in 50 ml of carbon tetrachloride and shaking it with 100 ml of distilled water or an acidic solution containing 5 milliequivalents of hydrochloric acid. The amount of amine in the aqueous layer, determined usually by titration, indicates the amount of hydrolysis.

When p-toluidine was formed by hydrolysis, it was determined by ultraviolet spectroscopy. The distribution coefficient of p-toluidine between water and carbon tetrachloride was determined and considered in the subsequent calculations. The amount of hydrolysis with distilled water was less than about 10%, the minimum detectable, in 6 hours. The hydrolysis rate with dilute hydrochloric acid was much faster as shown in Figure 11. The compound was 25% hydrolyzed in 2 minutes and 56% hydrolyzed in 20 minutes. Comparable figures for dianilinodiphenylsilane[54] were 25% in 5 minutes and 40% in 20 minutes, and for hexaphenylcyclotrisilazane,[54] 25% in 5 minutes and 42% in 20 minutes. The data are summarized in Table XV.

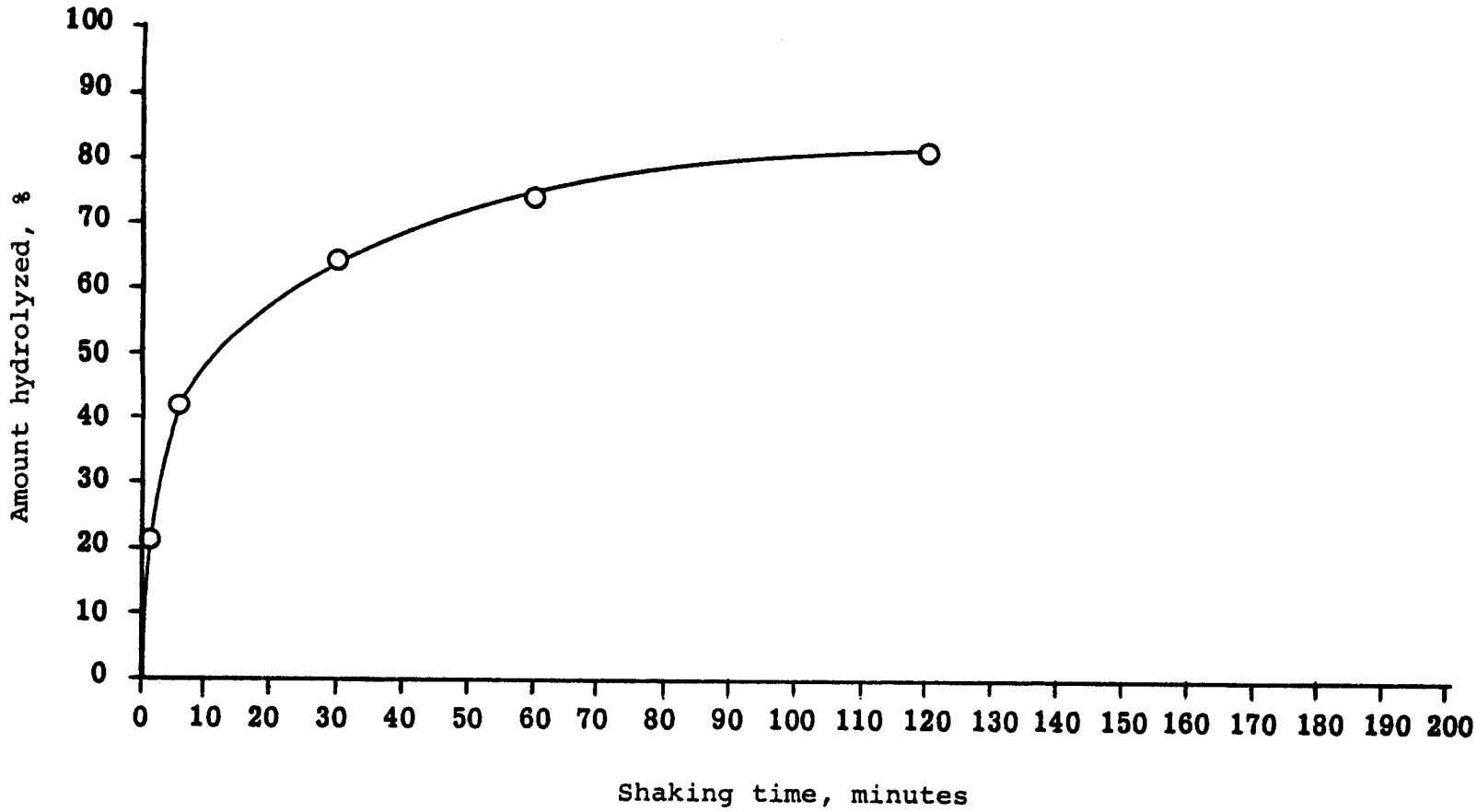


Figure 11. Hydrolysis of Bis(p-methylanilino)diphenylsilane in Carbon Tetrachloride and Dilute Hydrochloric Acid

When tetrakis(dimethylamino)silane was dissolved in carbon tetrachloride and shaken with water (the usual method) about 1.2% of it apparently hydrolyzed in 1 minute, and then the rate fell below 1% per hour. The initial hydrolysis was probably an erroneous indication given by a trace of impurity. In 3.3 hours, only 2.5% had hydrolyzed. When a carbon tetrachloride solution of the tetrakis compound was shaken with dilute hydrochloric acid, the compound was hydrolyzed completely in 1 minute, the time at which the first sample was taken. The data are summarized in Table XV and plotted in Figure 12.

Tris(dimethylamino)phenylsilane (Figure 13 and Table XV) and bis(dimethylamino)diphenylsilane (Figure 14 and Table XV) also exhibited small amounts of rapid initial hydrolysis that are attributed to impurities.

3. Reaction with acetone

Bis(methylamino)dimethylsilane was dissolved in deuterated acetone (acetone-d_6) in approximately a 1:1.5 mole ratio. The Si-CH_3 peak was seen in the pmr spectrum, as expected. Gradually a new Si-CH_3 absorption grew at the expense of the Si-CH_3 absorption of the original compound, which was approximately half gone in 2 hours. A similar experiment with a 1:1.6 mole ratio of silylamine to acetone-h_6 indicated a half-time of about 1 hour for the reaction. In a similar experiment with hexamethylcyclotrisilazane and acetone-h_6 in a mole ratio of 1:3.6, no significant change in the Si-CH_3 peaks was observed in 3 days.

4. Amine exchange

Bis(methylamino)dimethylsilane, 0.5081 g (0.00430 mole), was mixed with 0.4346 g (0.00179 mole) of dianilinodimethylsilane in a pmr sample tube. The tube was cooled in dry ice, evacuated, and sealed. The spectrum, approximately 30 minutes after the reactants were mixed, contained an Si-CH_3 peak that was not characteristic of either pure compound. This peak intensity increased over a period of 24 hours at the expense of the other Si-CH_3 peaks that were characteristic of the original compounds. To be more specific, a new Si-CH_3 peak grew gradually at the expense of the Si-CH_3 peaks of bis(methylamino)dimethylsilane and dianilinodimethylsilane, the N-CH_3 region became more complex, and a new peak appeared in the aniline N-H region. The new Si-CH_3 peak was intermediate in chemical shift between the Si-CH_3

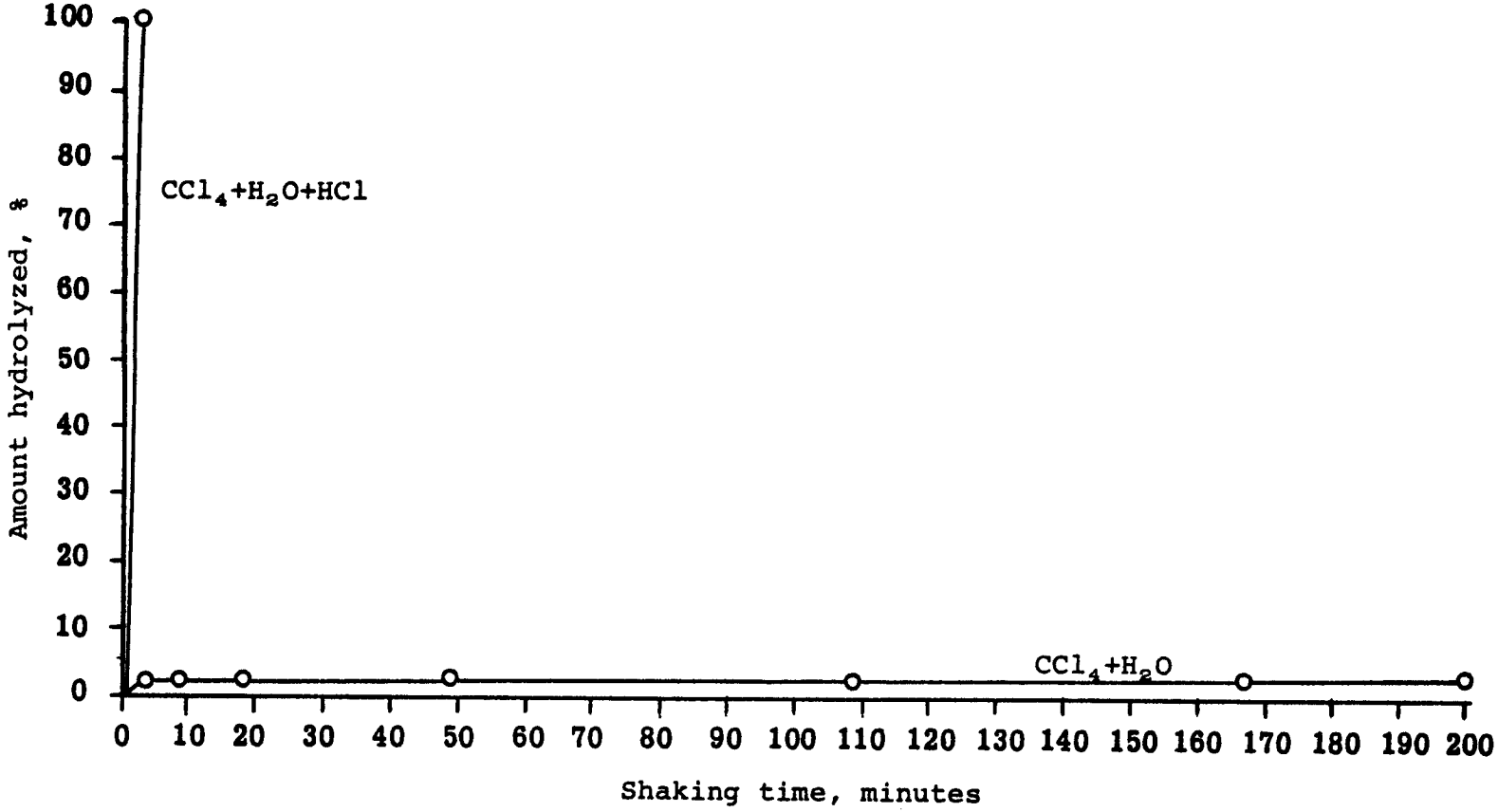


Figure 12. Hydrolysis of Tetrakis(dimethylamino)silane

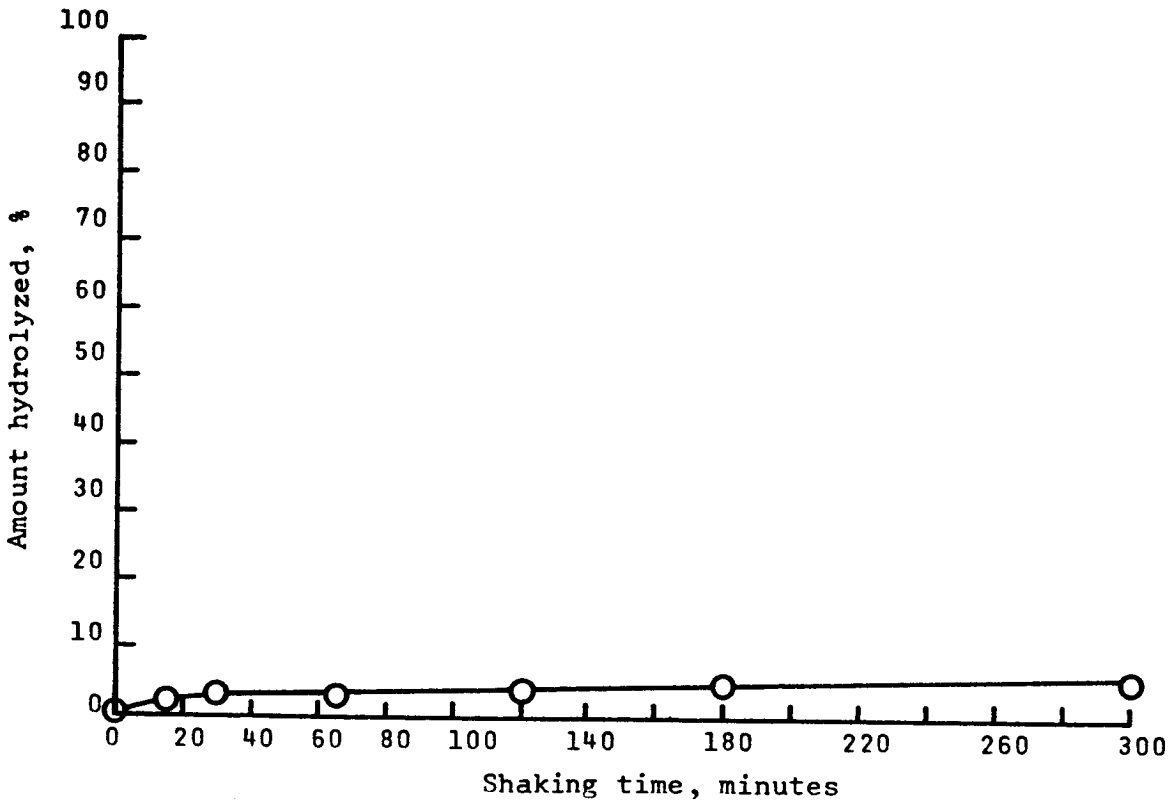


Figure 13. Hydrolysis of Tris(dimethylamino)phenylsilane in Carbon Tetrachloride and Water

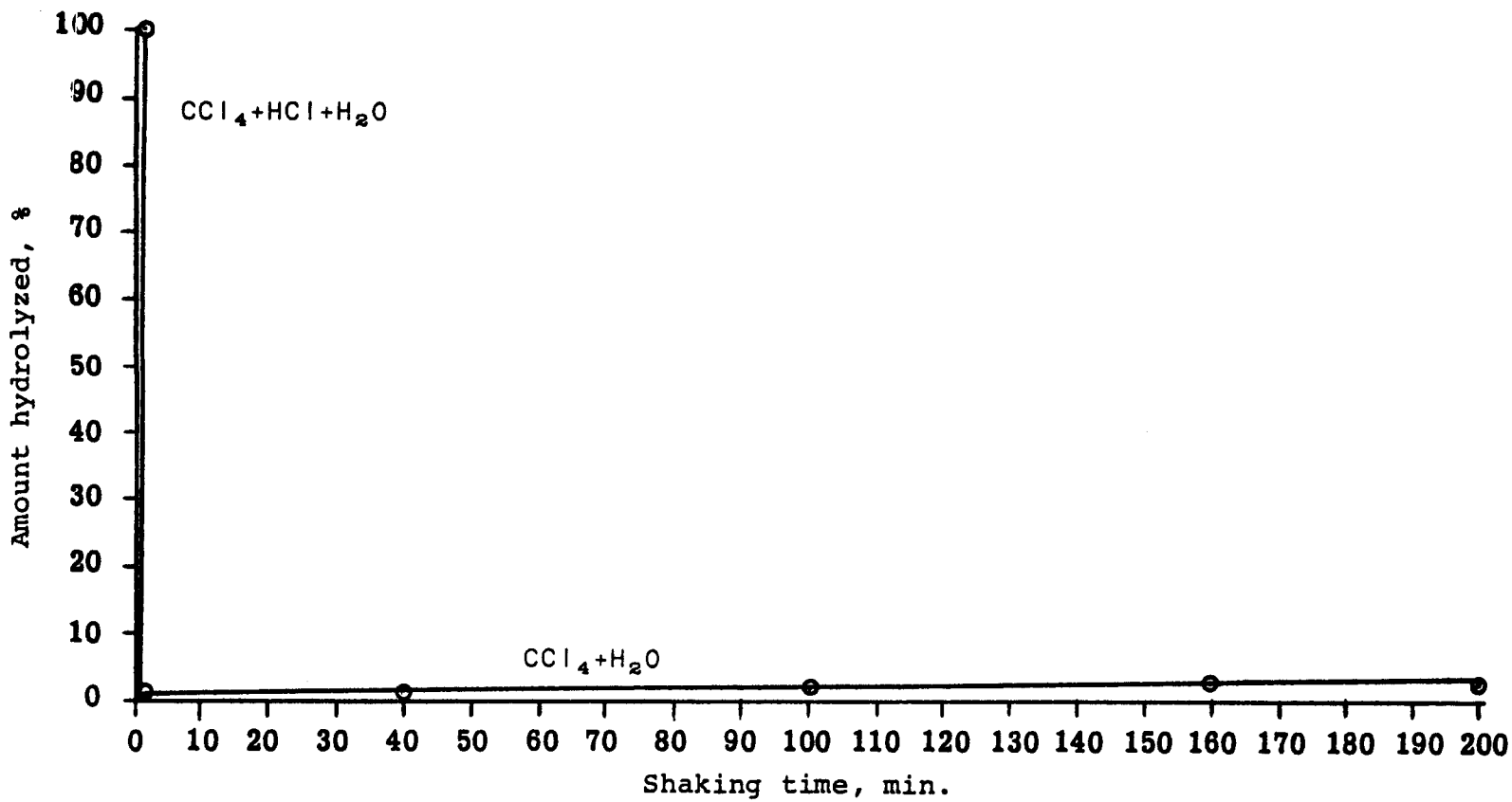


Figure 14. Hydrolysis of Bis(dimethylamino)diphenylsilane

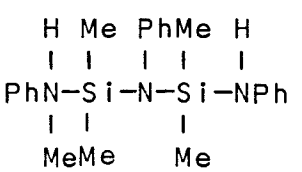
peaks of bis(methylamino)dimethylsilane and dianilinodimethylsilane. The new anilino N-H peak was slightly upfield from that of dianilinodimethylsilane. In 24 hours, more than half of the original compounds seemed to have disappeared, as judged by their Si-CH_3 peaks. During the same period, bis(methylamino)-dimethylsilane sealed alone in a tube underwent an insignificant change. The pmr spectra of IX indicated that it was not a major source of the changes observed in the mixture. The changes were tentatively attributed to amine exchange with the formation of methylaminoanilinodimethylsilane. Materials thought to be present were shown in the equation in the discussion (Section XIV.A.3.). Compounds VII, VIII, IX, and X were identified in previous studies. Compound XI was not previously known.

The existence of XI was confirmed by gas chromatography, infrared spectroscopy, and elemental analysis. For gas chromatography, 68.4 milligrams (0.28 millimole) of dianilinodimethylsilane was mixed with 60.6 mg (0.51 millimole) of bis(methylamino)dimethylsilane. The mixture became homogeneous on slight warming to about 35°C. Compounds VII, VIII, and X were identified in previous gas chromatography of the starting materials, and a peak assumed to be IX (intermediate in retention time between VII and VIII had also been seen. A new peak appeared in the first examination, 30 minutes after the compounds were mixed. It was intermediate in retention time between VIII and IX. The compound responsible for the new peak was trapped, and its infrared spectrum showed the presence of phenyl groups. Elemental analysis of the fraction further substantiated the identification of the new compound as XI, and thus, the exchange hypothesis was confirmed.

<u>Anal</u>. Calculated for $C_9H_{16}N_2Si(PhNH-SiMe_2-NHMe)$: C 59.95, H 8.94.

Found: C 60.4, H 9.2.

1,3-Dianilino-N-phenyltetramethyldisilazane,



XII.

could also be formed by self-condensation of VIII. However, it would have been less volatile than any of the other compounds discussed, so it could not have been responsible for the observations.

An attempt was made to study the exchange that occurred between bis(methylamino)dimethylsilane and dianilinodiphenylsilane, but they did not become completely liquid when mixed. When the spectrum of a benzene solution of the two was studied, changes were seen over a period of 24 hours. Such changes were not observed in benzene solutions of the individual compounds.

5. Study of special features of pmr spectra

Proton magnetic resonance spectra of three different preparations of bis(methylamino)dimethylsilane have displayed features which are not easily explained. The first spectrum, obtained in January, 1963, Figure 15, showed two $Si-CH_3$ peaks separated by 6 cps, a single $N-CH_3$ peak, and a broadened but well-defined N-H peak. Two subsequent samples of this compound prepared in July and September of 1965 gave a different spectrum, Figure 16, that showed a single $Si-CH_3$ peak, two $N-CH_3$ peaks, and N-H absorption so broad that it is best observed on the integral trace. The integrals of both types of spectra, however, fit the theoretical ratio of $N-CH_3:(N-H + Si-CH_3) = 6:8$ within experimental error.

For the 1965 preparations, spectra of the neat liquids showed that the two $N-CH_3$ peaks did not coalesce when specimens were heated to 100°C. For 50% solutions (by volume) in benzene and CCl_4, one broad peak was observed for $N-CH_3$. Subsequent dilution to 25% in these solvents, however, resulted in the reappearance of two $N-CH_3$ peaks. By contrast, the two $N-CH_3$ peaks of the 25% solution in CCl_4 coalesced when the temperature was raised to 70°C.

In 1963, two peaks were seen for the N-H absorption in dianilinodiphenylsilane, but spectra recorded for a new preparation contained only one peak. The compound melted at 161-163°C and had the following composition:

Anal. Calculated for $C_{24}H_{22}N_2Si$: C 78.65, H 6.05, N 7.64, Si 7.66.

Found: C 78.74, H 6.23, N 7.47.

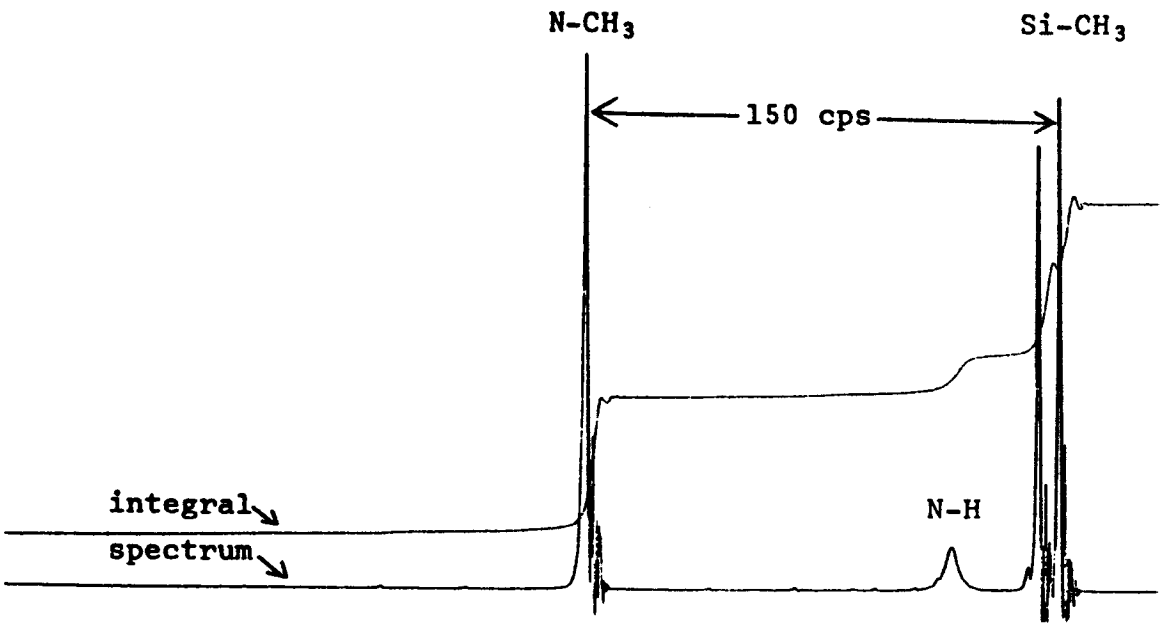


Figure 15. Pmr Spectrum of Bis(methylamino)dimethylsilane (Prepared January, 1963)

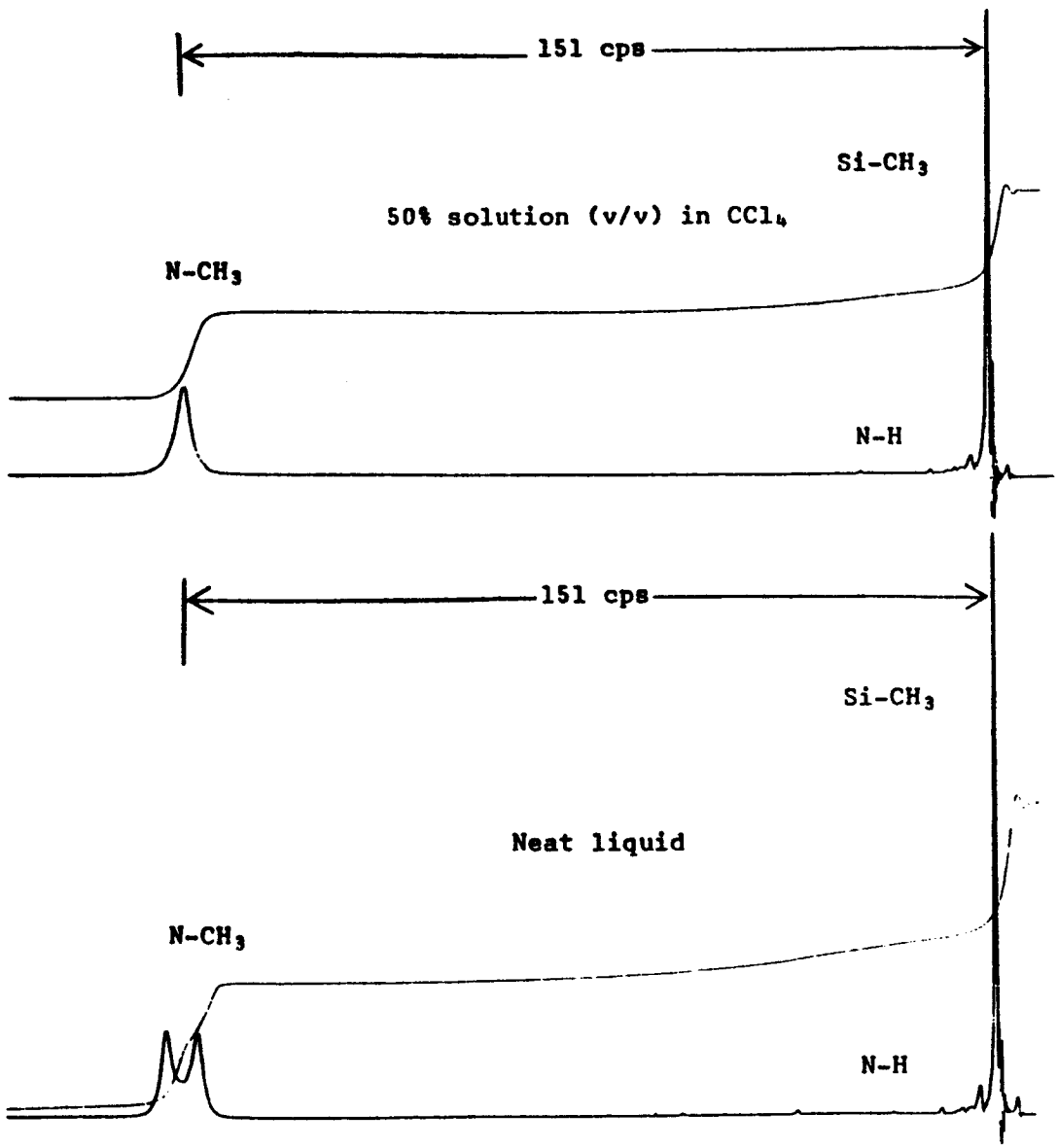


Figure 16. Pmr Spectra of Bis(methylamino)dimethylsilane (Prepared 1965)

Recently, a fresh preparation of bis(methylamino)dimethylsilane was examined and found to have only one $Si-CH_3$ peak. As it stood for 3 weeks, it acquired a second $Si-CH_3$ peak of gradually increasing intensity. Then another freshly distilled sample of bis(methylamino)dimethylsilane was sealed in a glass tube and examined periodically. It also gradually acquired the second peak even at room temperature. This gradual appearance of the second peak could be explained as progressive formation of methylamine by condensation.

Spectral characteristics of interest are summarized in Table XVI.

Table XVI. Salient Features of Proton Magnetic Resonance Spectra

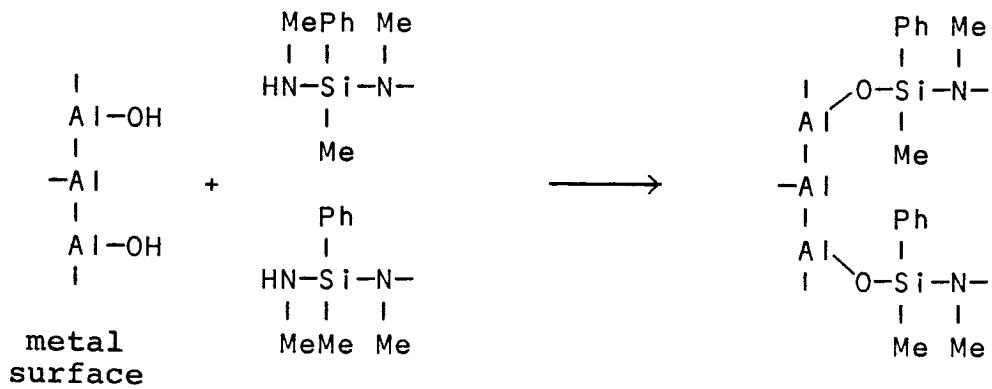
Date	Medium Solvent	Conc., %	Temp., °C	Si-R	N-H	N-R'
A.	Bis(methylamino)dimethylsilane, R = R' = CH_3					
1/63	neat	-	35-40	doublet	well defined	singlet
1/63	CCl_4	20 v/v	35-40	doublet	well defined	singlet
7/65	neat	-	34	singlet	very broad	doublet
7/65	neat	-	20	singlet	very broad	doublet
7/65	neat	-	100	singlet	very broad	doublet
7/65	C_6H_6	50 v/v	34	singlet	very broad	singlet
7/65	C_6H_6	25 v/v	34	singlet	very broad	doublet
9/65	neat	-	34	singlet	very broad	doublet
9/65	neat	-	80	singlet	very broad	doublet
9/65	CCl_4	50 v/v	34	singlet	very broad	singlet
9/65	CCl_4	25 v/v	34	singlet	very broad	doublet
9/65	CCl_4	25 v/v	70	singlet	very broad	singlet
9/65	$CDCl_3$	10 v/v	34	singlet	broad	singlet
9/65	C_6H_6	11 v/v	34	singlet	very broad	doublet
9/65	acetone-d_6	50 v/v	34	singlet	very broad	broad singlet
B.	Dianilinodiphenylsilane, R = R' = C_6H_5					
1/63	CCl_4	4 w/v	35-40	complex multiplet*	two peaks	complex multiplet*
C.	Bis(methylamino)diphenylsilane, R = C_6H_5, R' = CH_3					
7/65	neat	-	20	complex multiplet*	quartet*	doublet*
1/63	CCl_4	20 v/v	35-40	complex multiplet*	quartet*	doublet*

*Multiplicity resulting from spin-spin splitting

XV. SILYLAMINE COATING AGENT AS A PRIMER FOR ADHESIVES

Silylamine oligomers were previously known to have desirable properties as coatings because of their exceptional adhesion to metals and ceramics at high temperatures.[21-25] In a very brief investigation, evidence was found that they might be useful also as primers for the tough, thermally stable polyaryloxysiloxane[6] when it is used as an adhesive.

The work done was exploratory because only a small amount of time was available for it. The shear strengths of lap joints of aluminum were higher when the aluminum was primed with the methylphenyl silazane coating agent before the polyaryloxysiloxane was applied. The silazane is believed to act as a primer by forming an Al-O-Si bond with the aluminum:



The polyaryloxysiloxane, which has good shear strength, then forms a strong bond with the modified surface of the aluminum.

The experiments are summarized in Table XVII. The polyaryloxysiloxane was a polymer of a type described by Curry and Byrd,[6]

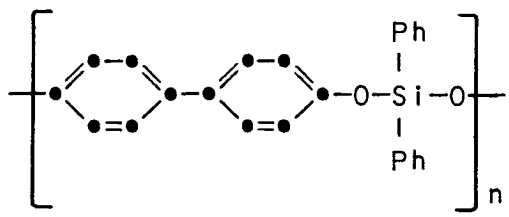


Table XVII. Effect of Silazane Primer on Shear Strength of Lap Joints on Aluminum (Methylphenyl silazane primer,[a] polyaryloxysiloxane adhesive[b])

Sample No. 3992-	Priming			Adhesive		Shear strength, psi[c]
	Material	Treatment		Method of application	Heating time at 400°C, min.	
		Time, min.	Temp., °C			
95-3	agent[d]	10	350	powder	30	1650
95-4	none	-	-	powder	30	1450
95-5	agent[d]	-	-	powder	30	1750
99-2	solution[e]	1	400	solution[f]	30	1850
99-1	none	-	-	solution[f]	30	1225
99-4	solution[e]	1	400	solution[f]	60	1350
99-3	none	-	-	solution[f]	60	750

a. References 21 and 25

b. Reference 6

c. Measured at room temperature after heating

d. The silazane, a viscous liquid, was spread on the surface with a spatula

e. A 10% solution of the silazane in benzene was spread on the surface with a spatula

f. A 25% solution of the polyaryloxysiloxane in THF was spread on the surface with a spatula

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The silazane was methylphenyl silazane, which is described in the preceding annual report.[25] Several different methods of applying the silazane appeared to be beneficial as shown by the shear strengths of the paired comparisons of Table XVII.

The silazane itself is not satisfactory as an adhesive, because it has too low shear strength. Extensive experimentation with different polyaryloxysiloxanes was not attempted because of the limited time available.

XVI. LITERATURE SURVEY

The literature on silicon-nitrogen compounds was surveyed during the contract period. The review presented here is a supplement to the similar reviews in previous annual reports. Articles pertaining to silicon-nitrogen chemistry that have been found in the past year are summarized briefly. Most of the articles appeared in 1965 or 1966, but some were found that had appeared earlier. Articles concerned principally with polymers are listed first, followed by articles on reactions, compounds, and spectra or other physical properties.

A. Polymers

Boyer[56] polymerized hexamethylcyclotrisilazane by heating it with 1% by weight of cesium at 200°C for 23 hours. A solid silazane was obtained, but no data concerning molecular weight were given.

Losev and Minsker[57] treated hexamethylcyclotrisilazane with 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane and obtained rubbery polymers with up to 15 repeating disiloxane units.

The General Electric Company[58] patented a method of curing siloxazane polymers with boric acid. The polymer was made by treating a halogen-chain-stopped poly(dimethylsiloxane) with ammonia. The polymer, 2 parts, was cured with 0.1 part of H_3BO_3.

A coating composition containing silylamines was patented by Dow Corning Corporation.[59] The product of ammonolysis of a dichloro-trichlorosilane mixture, was mixed with a silicone resin to form the coating agent.

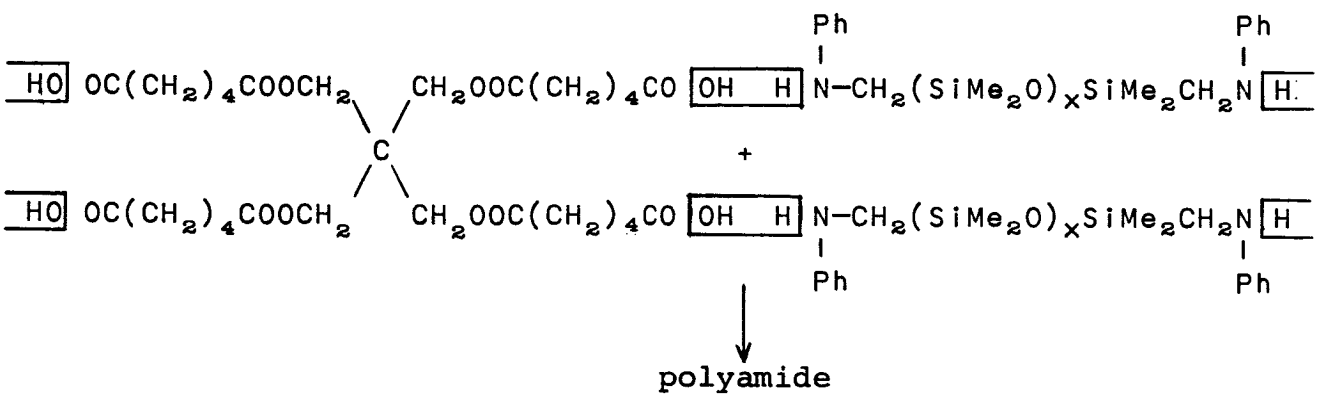
Lienhard, working with Rochow,[60] prepared silicon-nitrogen polymers based on ethylenediamine. These have been described previously in other publications.

Model, Redl, and Rochow[61] used broadline nuclear magnetic resonance spectra to study internal motion in organosilicon polymers. They found that reorientation of methyl groups about C-Si bonds occurred even at -196°C in dimethylsilazane and dimethylsiloxane polymers. Their silazane polymer had an average weight of 1200.

Minne[62] studied coordination compounds formed with beryllium and aluminum compounds and the polymer made from ethylenediamine and dimethyldichlorosilane. A polymer made from diphenyldichlorosilane and ethylenediamine was reported to have interesting adhesive properties and good resistance to hydrolysis.

Fekete[63] prepared polymers with P-O-P and P-O-Si linkages by hydrolyzing the product obtained by treating aminosilanes with PCl_3 or its derivatives. The polymers were said to be useful as lubricants or as flame and solvent resistant protective coatings.

Andrianov, Emelyanov, and Raigordskii[64] studied the polycondensation of half-acid esters of pentaerythritol and amine-containing derivatives of siloxanes. Although their siloxanes did not contain silicon-nitrogen bonds, their work is noted here because of interest in the methods they used for synthesis or complex siloxane structures. They obtained gels.



Andrianov, Khaiduk, and Khananashvilli[65] described the formation of a small amount of bicyclic and polymeric material by the reaction of dimethyldichlorosilane with ammonia. The polymer was obtained as a still residue in about 7% yield and was said to contain some chains of cyclic silazanes. No data were given on molecular weights.

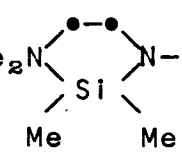
Andrianov and his coworkers[66] cured an epoxy resin with bis(phenylaminomethyl)tetramethyldisiloxane. While this compound did not contain a silicon-nitrogen bond, it served as a means of introducing silicon into a resin. Strength and thermal stability were not outstanding.

Andrianov and Ismailov[67] caused a partial rearrangement polymerization of hexamethylcyclotrisilazane by treating it with catalytic amounts of aluminum chloride at 140-240°C.

Aylett and Burnett[68] obtained a patent on polymers containing $-SiH_2NR-$ as repeating units. The polymers were prepared by condensation of silylene iodide with primary amines at -60°C to 0°C, reaction of a bis(dialkylamino)silane with a primary amine at temperatures up to 120°C by ultraviolet irradiation of an alkyldisilylamine, or by pyrolysis of alkyldisilylamine at 400-600°C. No physical data on the polymers were given.

Kummer and Rochow[69] reported on their studies of polymers made from ethylenediamine and dimethyldichlorosilane to form chains containing linear and cyclic units:

$-SiMe_2NH(CH_2)_2NH-$ and



B. Reactions

Zhinkin, Morgunova, and Andrianov[70] studied the reaction of hexamethyldisilazane with phenyl isocyanate and phenyl isothiocyanate. At 120°C, they obtained disproportionation with the formation of trimethylsilyl isocyanate and trimethylsilyl isothiocyanate.

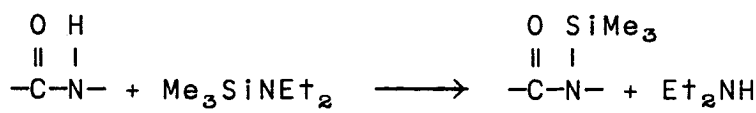
Wells and Schaeffer[71] studied the base-catalyzed elimination of silane from trisilylamine. Under certain conditions N,N',N"-trisilylcyclotrisilazane was formed. The bases used were ammonia, methylamine, and lithium hydride variously substituted with hydrogen and deuterium.

$$3\ (SiH_3)_3N \longrightarrow (-H_2SiNSiH_3-)_3 + 3\ SiH_4$$

Van Wazer and Norval[72] used nmr spectra to study exchange rates between $Si(OCH_3)_4$, $Si[N(CH_3)_2]_4$, and $SiCl_4$. The amino groups and the chlorine atoms exchanged much faster than the methoxyl groups.

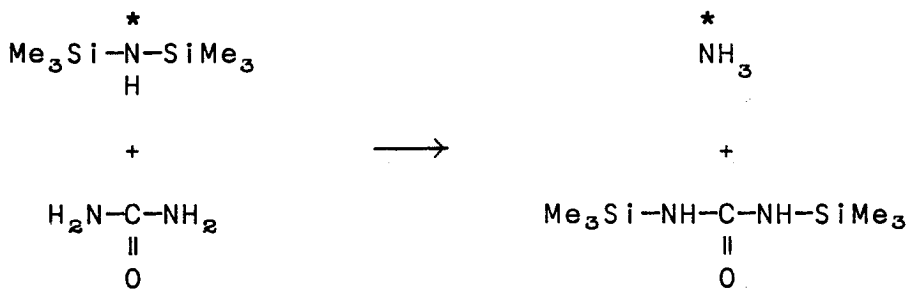
Zhinkin, Mal'nova, and Gorislavskaya[73] studied transamination reactions between Et_3SiNH_2, Me_3SiCl, NH_3, and NH_4Cl.

Ruehlmann and Rupprich[74] silylated cyclic lactams by treating them with silylamines or chlorosilanes and triethylamine.

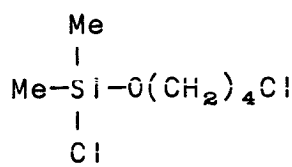


Zhinkin and his coworkers[75] studied the reactions of silazanes with organic isocyanates. They concluded that the Si-N bond splits, and the Si with its attached alkyl groups becomes attached to the N of the isocyanate.

Wannagat and his coworkers[39] demonstrated with isotopic nitrogen that the Si-N bond in bis(trimethylsilyl)amine was not attacked by sodium amide. Instead the ammonia released was initially part of the amide. In contrast, urea attacked the Si-N bond in the silylamine and joined with the silyl groups.



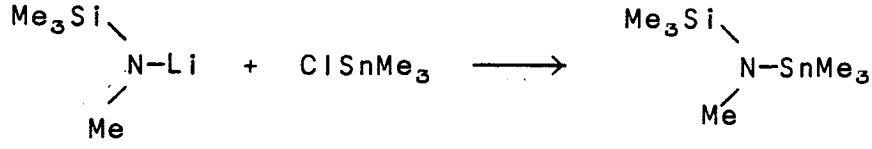
Andrianov[76] found that dimethyldichlorosilane reacted slowly with tetrahydrofuran when heated in the presence of zinc chloride to form



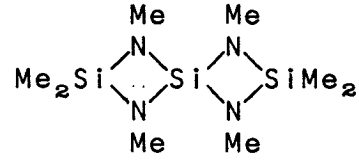
Wannagat[77] prepared a variety of sodium derivatives of alkoxy silylamines. It is interesting to note that tris(isopropoxysilyl)amine, $[(C_3H_7O)_3Si]_3N$, was extremely stable to hydrolysis in acidic and basic media.

Wiberg and Raschig[78] found that hexamethyldisilazane was converted to the N-bromo derivative when it was treated with N-bromosuccinimide in carbon tetrachloride. However, in acetone or methylene chloride, the SiN bond was cleaved and N-trimethylsilylsuccinimide was formed.

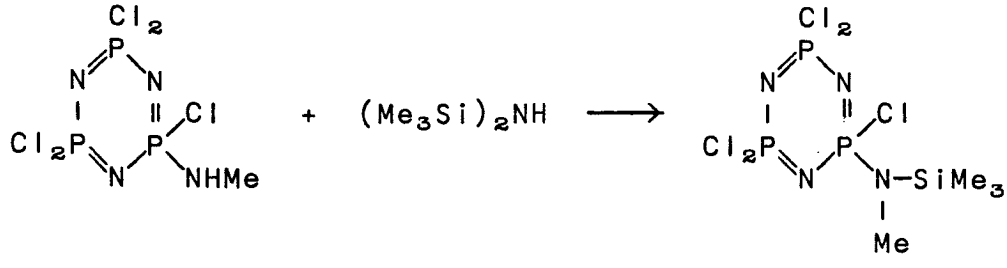
Scherer and Schmidt[79] prepared tin and lead derivatives of silylamines by way of the lithium silylamides. For example,



Lienhard and Rochow,[80] by reactions of amines, lithium silylamides, and silicon halides, prepared a variety of cyclic silazanes with N-substitution, including nonamethylcyclotrisilazane and the following bicyclic compound.



Mattogno, Monaci, and Tarli[81] studied transamination reactions of triazatriphosphorines with hexamethyldisilazane. No polymers were reported. An example of the reaction is:



Andrianov and his coworkers[82] studied the nmr spectra of variously substituted cyclic silazanes and concluded that conjugation through lone electron pairs of nitrogen does not exist in cyclic silazanes. Significant portions of the spectra resembled those of secondary amines rather than those of heterocyclic nitrogens.

Toyo Rayon Co., Ltd.[83] used tetrakis(dimethylamino)-silane and silazanes as components of catalysts for polymerizing olefins. The main components of the catalysts were aluminum alkyls and metal halides.

Ismail[84] used cyclic silazanes for silylation of hydroxy-aromatic compounds.

Andrianov and Rumba[85] studied the hydrolysis of cyclic silazanes and polymeric silazanes prepared by heating silazanes with potassium hydroxide at 170-200°C. Some polymers, of structures not described, were essentially stable in sulfuric acid and alcohol.

Andrianov[86] studied rearrangements of cyclic silazanes in the presence of electrophilic and nucleophilic reagents. Small amounts of polymers were obtained, but they evidently had low molecular weights.

Wannagat[87] studied the reactions of sodium bis(trimethyl-silyl)amide with carbon dioxide, carbon disulfide, and carbon halides. Considerable disproportionation occurred, with the formation of such compounds as hexamethyldisiloxane and tris-(trimethylsilyl)amine.

Willis[88] obtained patents on the use of silazanes to inhibit the photodegradation and thermal degradation of poly-(vinyl chloride).

Birkofer and Ritter[89] reviewed the use of silylation in organic syntheses.

Ruehlmann, Reiche, and Becker[90] described the preparation of several silicon azides by an exchange reaction between acid azides and aminosilanes.

$$RCON_3 + -\overset{|}{\underset{|}{Si}}-NR'R'' \longrightarrow RCONR'R'' + -\overset{|}{\underset{|}{Si}}-N_3$$

Krüger and Rochow[91] treated chlorine-chain-stopped oligosiloxanes with sodium bis(trimethylsilyl)amide and obtained oligomers with chlorosilyl and bis(trimethylsilyl)aminosilyl end groups. In pyridine, it was possible to hydrolyze the chlorosilane end to silanol without hydrolyzing the silylamine end.

Abel and Armitage[92] described the use of silylamines as agents for accomplishing certain types of syntheses. Alkyl and acyl halides exchanged with silylamines to form silicon halides and substituted amines or amides.

$$Me_3SiNR_2 + R'Cl \longrightarrow Me_3SiCl + R'NR_2$$

$$(Me_3Si)_2NR + 2\ R'COCL \longrightarrow 2\ Me_3SiCl + (R'CO)_2NR$$

Ethyl chlorocarbonate and nitrosyl chloride underwent similar types of exchange.

Zhinkin, Mal'nova, and Gorislavskaya[93] described several ammonolysis reactions of variously substituted triorganochlorosilanes.

Zhuzhgov and his coworkers[94] studied the formation of free radicals during ultraviolet irradiation of several silazanes including hexamethylcyclotrisilazane.

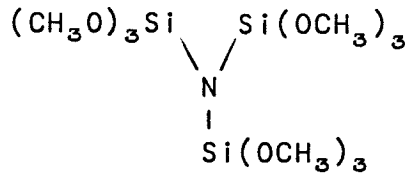
Andrianov[95] found that treatment of hexamethylcyclotrisilazane with butanol resulted in the formation of some octamethylcyclotetrasilazane and a variety of butoxylated silazanes.

C. Compounds

Licht and Kriegsmann[96] silylated dihydroxybenzene in high yield by treating it with hexamethyldisilazane and a small amount of trimethylchlorosilane.

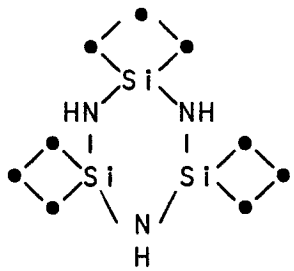
Elliott and Breed[97] prepared a variety of N-methylcyclosiloxazanes.

Wannagat, Veigl, and Bürger[98] prepared and described six new compounds with methoxysilyl groups attached to nitrogen. No stability data were given. One compound was

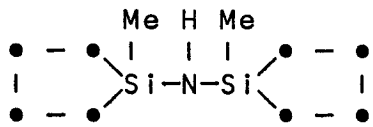


Wannagat[99] prepared a variety of silicon-nitrogen-oxygen compounds by the interaction of chlorosilanes and organyloxychlorosilanes with ammonia and methylamine.

Nametkin and his coworkers[100] prepared and studied silacyclobutylsilazanes and silacyclopentylsilazanes such as



and



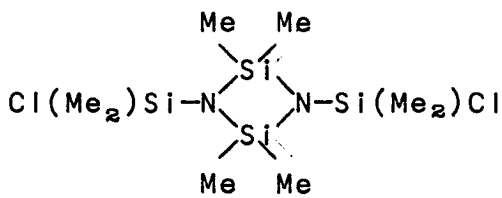
Bailey and West[101] prepared N-halo derivatives of hexamethyldisilazane, $(Me_3Si)_2NX$, in which X was chlorine, bromine, or iodine. The halo derivatives coupled with alkyl lithiums to form N-alkylhexamethyldisilazanes.

Silbiger and Fuchs[102] prepared a variety of halosilazanes, such as $ClMe_2SiNHSiMe_2Cl$.

Wannagat and Bogusch[103] prepared a new cyclic compound, $Me_{10}Si_4N_4$, by the reaction of hydrazine with 1,3-dichloropentamethyldisilazane.

Geymayer and Rochow[104] prepared N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane from octamethylcyclotetrasilazane in several steps,

$$(Me_2SiNH)_4 + Me_2SiCl_2 \longrightarrow Cl(Me_2)Si{-}NH{-}Si(Me)_2Cl \xrightarrow{(Me_3Si)_2N{-}Na}$$



Ruehlmann and Tuchtenhagen[105] described the synthesis of triisopropylcyclotrisilazane and tetraisopropylcyclotetrasilazane.

Metras and Valade[106] described several hydrogenosilylamines prepared by ammonolysis of the corresponding chlorosilanes.

Ruehlman and Hils[107] described the formation of several silyl derivatives of amino acids including

$$H_2N{-}C(HR){-}COOH + (Me_3)Si{-}NH{-}Si(Me_3) \longrightarrow H_2N{-}C(HR){-}COOSi(Me_3)$$

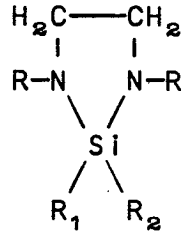
D. Spectra

Buttler and his coworkers[108] reported data on the infrared and Raman spectra of several silylamines variously substituted with C-14, C-15, D, and H.

Haiduc and Mantsch[109] assigned characteristic frequencies to specific groups in the infrared spectra of cyclic silazanes and siloxazanes.

Barrante,[110] working with Rochow, studied nuclear-magnetic-resonance spectra of siloxanes and silazanes comparing the types of internal motion present.

Abel and Bush[111] prepared several silyl derivatives of ethylenediamine and studied their reactions and infrared and NMR spectra. In addition several similar compounds with boron, phosphorus, arsenic, and sulfur were studied.



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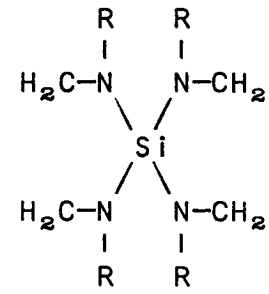

Randall,[112] with the aid of isotopic nitrogen, assigned unequivocal stretching frequencies to the Si-N bond in N-trimethylsilylaniline.

Buerger[113] also utilized isotope shift in infrared and Raman spectra to determine characteristics of aminosilanes.

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