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NEW METHODS FOR PREPARING SILICON-NITROGEN POLYMERS

By
Walter E. Weibrecht and Eugene G. Rochow
October, 1965

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ABSTRACT

Persistent efforts to prepare high-temperature polymers based on silicon-nitrogen frameworks have been hampered by the marked tendency to form cyclic structures instead of linear ones, and by poor yields of polymer obtained from the appropriate intermediates. This report deals with two attempts to overcome these difficulties. In the first, direct polymerization was sought at the time the nitrogen atoms were introduced into the framework, in a one-step process. In the other, a new form of polymerization by condensation of methoxy groups was attempted. Both procedures gave only limited success, but produced some leads which could be pursued.

The first project involved the reaction of our starting material, dimethyldichlorosilane, with ammonium halides as sources of nitrogen. When these experiments showed little or no interaction, ammonolysis of dimethyldichlorosilane at 200° in the presence of ammonium bromide was tried. Octamethylcyclotetrasilazane was obtained, together with some liquid polymer which was of the same cross-linked character as that obtained by Krüger's sequential ammonolysis and catalytic polymerization. No larger proportion of linear dimethylsilazane resulted, hence, there is no advantage to the procedure.

In the second project, sym-dimethoxytetramethyldisilazane and the corresponding tri and tetrasilazanes were prepared by the reaction of dimethyldichlorosilane with methanol, followed by treatment with annhydrous ammonia. The infrared and NMR spectra of these compounds have been examined. Prolonged heating of the disilazane in the presence of sodium methoxide, aluminum methoxide and isopropoxide, and potassium tertiarybutoxide led to the formation of low-molecular-weight linear silicon-nitrogen polymers, as well as to some other silicon-nitrogen substances of a more complicated nature.

TABLE OF CONTENTS

Page

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INTRODUCTION

Recently, a considerable amount of effort has been directed toward solution of the problem of preparing linear silicon-nitrogen polymers. In the silicon-oxygen system cyclic trimeric and tetrameric siloxanes of the general formula $(R_2SiO)_n$, where R represents an alkyl or aryl group, can be converted to linear polymers by treatment with certain either acidic or basic catalysts. These equilibrium processes afford a convenient method for the preparation of linear silicone polymers from readily obtained intermediates.

Ammonolysis of halogenosilanes, e. g. $(CH_3)_2SiCl_2$, leads almost exclusively to the formation of cyclic polysilazanes with the general formula $(R_2SiNH)_n$, where n=3 and 4.[1] These compounds, hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, can be prepared in good yield and have been thoroughly characterized. They should be logical starting materials for the preparation of linear dimethylsilazanes, and yet their use in that way has not been successful in the past.

By analogy to the isoelectronic siloxanes, Andrianov attempted to prepare polysilazanes by treatment of hexamethylcyclotrisilazane with potassium hydroxide.[2] At 165° some cleavage of the silicon-carbon bonds occurred with the formation of methane. Only highly crosslinked polysilazanes could be isolated from the reaction mixture.

A basic catalysis involving a base in the ammonia system, i.e., sodium amide, is also unsatisfactory. It has been shown that this reagent metalates the NH groups in the cyclic starting material rather than splitting the silicon-nitrogen bonds.[3] It is, of course, the breaking of silicon-nitrogen bonds in the small trimeric molecules and the addition of the chains formed in this way to one another that should lead to the desired linear polysilazanes, but this cleavage is not attained with sodium amide.

Krüger studied the use of ammonium halides, which are acids in the ammonia system, as possible polymerization catalysts. It had previously been noted by Anderson that silicon-nitrogen bonds could be broken in the presence of inorganic halides.[4] Krüger found that when a mixture of hexamethylcyclotrisilazane and from 1% to 45% of ammonium halide (NH_4Br or NH_4I) was heated to 160°, evolution of ammonia began. Ammonium chloride had no apparent effect. After 6 to 8 hours of treatment with ammonium bromide, a very viscous oil was obtained. This oil contained some silicon-halogen bonds but could be converted to a halogen-free silazane polymer by treatment with sodium amide in benzene or with an ethereal solution of ammonia. The polysilazanes obtained in this way were a mixture of oligomeric oils and resinous or gummy polymer. These polymers were known from analytical and spectral data to be highly crosslinked. Hydrolytic studies provided strong evidence that the crosslinking took place exclusively through the nitrogen atoms.[5]

Krüger's demonstration of the catalytic properties of ammonium halides in the polymerization of cyclic silazanes was a significant contribution. Although linear polymers could not be prepared by this method, a considerable insight into the chemical and physical properties of extended organopolysilazane frameworks was gleaned from these studies.

Since it had heretofore been impossible to obtain linear dimethyl polysilazanes from the corresponding trimer or tetramer, it was felt that it might be worthwhile to try to prepare polymeric materials directly from the dimethyldichlorosilane rather than using the very stable trimer as a starting material. It was thought that if sufficiently mild conditions for the reaction of dimethyldichlorosilane with ammonia could be found, and if this reaction were carried out in the presence of an ammonium halide polymerization catalyst, that direct conversion of dimethyldichlorosilane to linear organopolysilazanes might be achieved.

In the preparation of 2, 4, 6-trichloroborazine according to the method of Brown and Laubengayer,[6] boron trichloride reacts with ammonium chloride in a Pyrex tube at 200° to give the desired product. The decomposition of NH_4Cl at 200° furnishes the ammonia which subsequently reacts with the BCl_3 according to the following equation:

$$3BCl_3 + 3NH_4Cl \xrightarrow{200^\circ} Cl_3B_3N_3H_3 + 9\,HCl.$$

Therefore, by analogy to this system it was proposed to pass $(CH_3)_2SiCl_2$ vapor over a mixture of NH_4Cl and NH_4I (catalyst) in a Pyrex tube at 200°.

EXPERIMENTAL:

A. Continuous Ammonolysis of Dimethyldichlorosilane by Reaction with Ammonium Chloride at Elevated Temperatures:

The apparatus consisted of a Pyrex tube 2. 5 feet long and 51 mm. in diameter. The center portion of this tube was wrapped with nichrome wire and the wire-covered zone, in turn, insulated with asbestos tape. At the outlet end of the tube a bulb cooled to 0° served to trap easily condensable materials while more volatile species, if any, passed into the hood through a calcium chloride drying tube.

The hot zone was loosely packed with a mixture of 150 g. of NH_4Cl, 50 g. of NH_4I and 20 g. of asbestos fiber between glass wool plugs. A chromel-alumel thermocouple and a potentiometer served to measure the temperature. The apparatus was continuously flushed with nitrogen which had been passed through sulfuric acid and a mercury bubbler. Tygon tubing was used throughout. When the tube reached a temperature of 200-225°, dimethyldichlorosilane addition was initiated. Nitrogen was bubbled through a reservoir of dimethyldichlorosilane and served to carry the vapor through the tube. At 200° the formation of some iodine, presumably by decomposition of the ammonium iodide, was observed. After 5 hours, 86 g. of dimethyldichlorosilane had been exposed to the hot zone. The tube was then cooled to room temperature and sealed at both ends.

A purple solution had collected in the 0° bulb at the outlet of the reaction tube. This purple liquid distilled at 69° without leaving a residue. Since the boiling point of dimethyldichlorosilane is 70°, the purple solution collected at 0° may have simply been iodine dissolved in unreacted dimethyldichlorosilane.

Silazanes, in general, and also Krüger's polymers are soluble in cyclohexane. Therefore, the material left behind in the reaction tube was washed with 750 mls. of cyclohexane. The resulting solution had a faint purple color due to the presence of a small amount of iodine. The cyclohexane was then distilled to determine whether or not anything had been dissolved in it. The entire sample boiled at 80.5° and left no residue. The boiling point of cyclohexane is 81.4°. Therefore, no less volatile substances soluble in cyclohexane were present in the tube. Thus, it must be concluded that dimethyldichlorosilane does not react with a mixture of ammonium chloride and ammonium iodide at 200° under the conditions of this experiment.

B. Continuous Ammonolysis of Dimethyldichlorosilane in the Presence of Ammonium Bromide:

Apparently the conditions of the preceding experiment were too mild. Since it was still felt that there might be some merit in attempting the polymerization in situ before the trimer and tetramer had a chance to form, the hot tube method was modified in the following way.

The tube described above was also used in this experiment. However, in this case the tube was packed with 100 g. of NH_4Br and 20 g. of asbestos. At the inlet there was one tube for the addition of nitrogen or a mixture of nitrogen and dimethyldichlorosilane, and another tube extending into the hot zone. This tube was fitted with a fritted glass disc and was used for the addition of ammonia. It was hoped that the dimethyldichlorosilane would react with the ammonia in the presence of the catalyst and form large polymers rather than trimer and tetramer. The tube was continuously swept with dry nitrogen and heated to 175°. At this point the ammonia and dimethyldichlorosilane addition was begun and the exothermicity of the reaction caused the temperature to rise to 197° where it was maintained. Ninety g. of dimethyldichlorosilane passed into the tube in three hours. Eight g. of $(CH_3)_2SiCl_2$ was collected in the 0° bulb at the outlet of the tube. Since dimethyldichlorosilane does have a significant vapor pressure at 0° and nitrogen was continuously passed over it, it is reasonable to assume that more than 3 g. passed through the tube unchanged.

The contents of the tube were washed with 700 mls. of n-hexane. Any polymeric materials should have been dissolved by the hexane. When the hexane was removed from the resulting solution by distillation, a colorless, crystalline solid and a light yellow oil remained behind. The solid was recrystallized from hexane and identified as the tetramer, $(CH_3)_2SiNH)_4$. Both its melting point and infrared spectrum were identical to those of a known sample of octamethylcyclotetrasilazane. The oil which was present in small amounts relative to the tetramer had an infrared spectrum and boiling range in agreement with those obtained by Krüger for his oligomeric oils. The absence of a significant NH absorption in the infrared spectrum of the oil compared to that of the trimer or tetramer provides a further indication of the cross-linking through the nitrogen in these polysilazanes.

Since it was apparent that this hot tube method did not give rise to linear organopolysilazanes, it was abandoned. Furthermore, the type of polymer that was obtained could be made with an equal effort and in greater yield according to Krüger's method.

C. Acid Catalyzed Polymerization in Solution:

Before abandoning the ammonium halide catalyzed polymerization as a method of obtaining linear organopolysilazanes, the reaction was studied in the solvent tri-n-butylamine. An amine was chosen to maximize the acidity of the ammonium halide. Tri-n-butylamine, b. p. =214°, made it possible to achieve the desired polymerization temperature. In a preliminary experiment, approximately equal weights of trimer and tri-n-butylamine were mixed in a small bulb connected to two bubblers, the second of which contained mineral oil. In this way a closed system was achieved. The mixture was heated to 180° for 24 hours. Upon cooling, it was observed that the internal pressure at the end of the reaction was somewhat lower than at the beginning. This suggested disappearance of the trimer. The reaction mixture had been exposed to vapor phase chromatography before heating and was again analyzed by this method after heating. There was an approximately 30°/o diminution in the trimer peak while the tri-n-butylamine peak remained essentially constant.

The second experiment in this series was carried out in exactly the same manner as the first with the addition of an equimolar amount of ammonium bromide to determine its catalytic effect under these conditions. The reaction mixture was again heated at 180° for 24 hours, and at the end of this period essentially no trimer was present as determined by vapor phase chromatography. The reaction mixture which still contained all of the original tri-n-butylamine was very viscous. Some sort of reaction had definitely taken place.

Since there was a reaction in experiment two, the reaction was run again at the same conditions on a larger scale so that the products could be studied. 0.064 mole of trimer, 0.066 moles of tri-n-butylamine and 0.109 mole of ammonium bromide were mixed and heated as before. During the heating there was some effervescence, and when the apparatus was opened the characteristic odor of ammonia was observed. The reaction mixture was treated with 200 mls. of hexane and the ammonium bromide removed by filtration. The hexane, tri-n-butylamine and any unreacted trimer were removed by distillation. The residue consisted of a colorless, crystalline solid and a light yellow oil. The solid was identified as tetramer by its melting point. The oil was again identical to Krüger's oligomeric oils. The evolution of ammonia during the polymerization was also consistent with his observations in the absence of a solvent.

The preceding modifications of the ammonium halide catalyzed polymerization of hexamethylcyclotrisilazane did not lead to the formation of linear organopolysilazanes. Therefore, it was not deemed worthwhile to continue investigations based on ammonium halide catalysis.

PREPARATION AND POLYMERIZATION OF DIMETHOXYTETRAMETHYLDISILAZANE:

In an investigation of the properties of some alkoxysilazanes, Bürger and Wannagat[7] found that pyrolysis of hexamethoxydisilazane at 200° in a sealed tube led to the formation of crosslinked polymers, accompanied by the evolution of tetramethoxysilane. This result provided the inspiration for the following investigation. It was felt that if a partially methoxylated methyldisilazane could be prepared, then it might be possible to achieve a polymerization similar to the above to give a linear silicon-nitrogen polymer rather than a crosslinked one. Therefore, it was proposed to prepare dimethoxytetramethyldisilazane and to find the appropriate conditions to effect the kind of polymerization reaction shown in the following equation:

$$(n+1)\ (\ (CH_3O)\ (CH_3)_2Si)_2NH \longrightarrow n\ (CH_3O)_2Si(CH_3)_2 + \\ (CH_3O)\ (CH_3)_2Si\text{-}(NH\text{-}Si(CH_3)_2\text{-})_nNH\text{-}Si(CH_3)_2(OCH_3)$$

With only one methoxy group per silicon atom, dimethoxytetramethyldisilazane could not lead to crosslinked polymers if the polymerization mechanism merely involved the splitting out of dimethyldimethoxysilane.

A. Preparation of Dimethoxytetramethyldisilazane:

The following reaction sequence was conceived for the preparation of this compound:

Step 1

$$(CH_3)_2SiCl_2 + CH_3OH \xrightarrow{\text{hexane}} (CH_3O)(CH_3)_2SiCl + HCl.$$

Step 2

$$2\,(CH_3O)\,(CH_3)_2SiCl + 3NH_3 \xrightarrow{\text{hexane}} 2NH_4Cl + (\;(CH_3O)(CH_3)_2Si)_2NH.$$

In a typical experiment 5 moles of dimethyldichlorosilane, obtained from General Electric and used without purification, were added to 1.5 l. of dry n-hexane in a 3-liter, 3-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. Five moles of methanol were added dropwise and HCl evolution began immediately. After all of the methanol had been added, the reaction mixture was refluxed for 1.5 hours and the apparatus flushed with dry nitrogen to remove traces of hydrogen chloride. The methoxydimethylchlorosilane which was presumably the product of this reaction was not isolated. Rather, ammonia gas was added directly to the hexane solution described above and ammonium chloride precipitation was observed immediately. Concurrently, there was a rapid rise in temperature which caused the hexane to reflux without external heating. Ammonia addition was continued for 4 hours until the reaction mixture began to cool.

The hexane solution was separated from the very large amount of NH_4Cl by suction filtration. The ammonium chloride was then washed with 2 l. of hexane, and the two hexane fractions were combined. Undoubtedly, this washing of the ammonium chloride was one of the most crucial steps in maximizing the yield. Much of the desired product would otherwise almost certainly have been left clinging to the NH_4Cl. The hexane was distilled out of the mixture, and when the temperature had risen to 95°, it appeared as though all of the hexane had been removed. The remaining liquid weighed 312 g. which corresponded to a 65% yield of dimethoxytetramethyldisilazane. This liquid was fractionally distilled at atmospheric pressure, 740 mm., using a short column packed with glass helices. The following reasoning was used to predict the boiling point of the dimethoxytetramethyldisilazane:

b. p. hexamethyldisilazane = 126°

b. p. hexamethoxydisilazane = 220°.

Therefore, the expected boiling point should have been approximately

$$126 + \frac{(220-126)}{3} = 157^{\circ}.$$

The first fraction boiled at 163° and the temperature rose slowly, but steadily, to 178°. Upon redistillation, this fraction (I) boiled at 162°. The second fraction (II) boiled at 178-182° while the third (III) was collected at 210-225° and the fourth (IV) at 255-265°. There was 160g. of (I), 50g. of (II), 40g. of (III), 20 g. of (IV) and 10g. of higher boiling oily material.

Analytical data obtained for compounds (I) and (II) were compared with the values calculated for dimethoxytetramethyldisilazane and dimethoxyhexamethyltrisilazane, respectively. These data are shown in Table I.

TABLE I

	Calc.	Found	Calc.	Found
			$(CH_3O)(CH_3)_2Si-NH-Si(CH_3)_2-NH-Si(CH_3)_2(O\ CH_3)$	
(I) $((CH_3O)(CH_3)_2Si)_2NH$			(II)	
% Carbon	37.25	36.82	36.02	34.93
% Hydrogen	9.90	9.90, 9.82	9.83	9.41
% Silicon	29.04	30.25	31.60	30.99
% Nitrogen	7.24	7.33	10.50	10.82
Molecular Weight	193	205	267	290
Refractive Index, n_D^{20}		1.4148		1.4315
Density, D_4^{20}		0.923		0.941

The agreement between the calculated and found percentages of the various elements, especially in the case of compound (I), leaves little doubt that this substance is indeed the desired dimethoxytetramethyldisilazane.

The infrared spectra of compounds (I) through (IV) were obtained as pure liquid films between NaCl discs, using a Perkin Elmer 137 infrared spectrophotometer. All of the spectra were identical except for the appearance of an additional absorption at 1025 cm.$^{-1}$ in the spectrum of compound (IV). Most of the peaks in the spectrum of compound (I) could be assigned by comparison to values reported by Smith[8] for some alkoxysilicon compounds and also the infrared absorption frequencies of hexamethylcylcotrisilazane discussed by Kriegsmann.[9] The infrared absorption frequencies of compound (I), their relative intensities and tentative assignments are given in Table II.

TABLE II

Frequency in cm.$^{-1}$	Intensity	Assignment
3367	m	symmetric N-H stretch
3024	s	symmetric C-H stretch, methyl
2886	m	symmetric C-H stretch, methoxy
1460	w	
1402	w	antisymmetric C-H deformation
1258	vs	symmetric C-H deformation, characteristic of Si-CH_3
1189	s	$SiOCH_3$ rock
1093	vs	C-O stretch
940	vs	Si-N-Si stretch
848	vs	Si-O stretch
807	vs	
725	m	

This infrared spectrum is entirely consistent with what might be expected for a molecule such as dimethoxytetramethyldisilazane. All of the important frequencies have been observed.

NMR Spectra of Compounds (I) Through (IV):

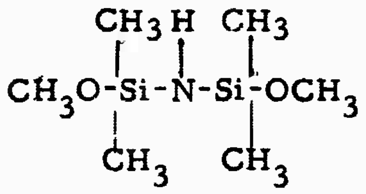
The proton nuclear magnetic resonance spectra of all of these compounds were obtained in 50^{o}/o carbon tetrachloride solution, using tetramethylsilane, (TMS), as internal standard. The instrument, a Varian A-60, was operated at a fixed frequency of 60 mc/sec.

The spectrum of compound (I) shows only 2 peaks, one of which is assigned to methyl protons at $\delta = 0.06$ upfield from TMS and the other, due to methoxy protons at $\delta = 3.4$. Integration gave a ratio of methyl protons to methoxy protons of 2.1/1. Since there was only one methyl and one methoxy peak, all of the methyl groups and all of the methoxy groups in compound (I) must find themselves in the same environment.

The spectra of compounds (II), (III), and (IV) all contain three peaks. The single methoxy peak is in the same place as for compound (I). However, the methyl peak is split into two peaks, one of which is at δ = 0.06 upfield from TMS as in compound (I) while the second is found at δ=0.04 downfield. Furthermore, this second methyl peak becomes progressively larger in going from compound (II) to (III) and finally to (IV). This illustrates that while all of these compounds contain only one type of methoxy group, structurally, there are two distinct types of methyl group. The methyl to methoxy ratios were 3.08/1, 3.9/1 and 5.4/1, respectively.

From the NMR data as well as the results of the elemental analysis and the infrared spectra, the following structures can be written for compounds (I) through (IV):

(I)



$$CH_3O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}\overset{H}{N}\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}OCH_3$$

(II) $CH_3O\text{–}(Si(CH_3)_2\text{–}NH)_2\text{–}Si(CH_3)_2(CH_3O)$

(III) $CH_3O\text{–}(Si(CH_3)_2\text{–}NH)_3\text{–}Si(CH_3)_2(CH_3O)$

(IV) A mixture of straight chain compounds composed largely of penta-and hexasilazanes.

POLYMERIZATION STUDIES ON SYM-DIMETHOXYTETRAMETHYLDISILAZANE:

I In an attempt to apply Bürger and Wannagat's pyrolysis technique to the polymerization of sym-dimethoxytetramethyldisilazane, 20 mls. of the disilazane was heated at 200-225° for 24 hours in a 25ml. stainless steel bomb. When the bomb was opened, after it had cooled to room temperature, there was no internal pressure. Volatile species such as ammonia or methane had not been produced. Furthermore, the NMR spectrum of the sample after pyrolysis was identical to that of the starting material.

The failure of this experiment to effect any noticeable changes in the disilazane indicates either that the temperature was too low to cause splitting out of dimethyldimethoxysilane or that there is an equilibrium which greatly favors the monomer.

II The following series of experiments were performed to test the catalytic effect of various nonaqueous acids and bases on the polymerization of sym-dimethoxytetramethyldisilazane. These experiments were all carried out in the absence of a solvent. The disilazane and the catalyst, under examination, were mixed and the system heated to the reflux temperature of the disilazane, 162°.

When a sample of sym-dimethoxytetramethyldisilazane was refluxed under nitrogen for 24 hours in a 100 ml. , round-bottom flask equipped with a water-cooled reflux condenser and a calcium chloride drying tube, no change was effected. Any changes in the nature of the disilazane in the presence of a foreign substance must, then, be due to the so-called catalyst and not simply to the heating in the experiments described below.

A. Ammonium Bromide Catalysis:

Thirty-one one hundredths of a mole of the disilazane and 0.031 mole of ammonium bromide were mixed and allowed to reflux for 7 days. The ammonium bromide moved up to the cool zone of the condenser, but the disilazane continuously flowed over it. It had been observed in the preparation of the disilazane that ammonium halides are somewhat soluble in it and that this solubility increases with increased temperature. This is a property of disilazanes in general and has also been observed in the case of hexamethyldisilazane.[10] After the reaction mixture had cooled, the liquid, which appeared to be unchanged, was fractionally distilled. A very small amount, 2-3 g., of a liquid boiling at 78-82° was collected. The NMR spectrum of this liquid showed one methyl and one methoxy peak in the ratio 1/1. This spectrum was identical in every detail to the spectrum of a known sample of dimethyldimethoxysilane. The boiling point of dimethyldimethoxysilane is 81°. Therefore, a very small amount of this compound was apparently formed. The rest of the reaction mixture, however, proved to be unchanged sym-dimethoxytetramethyldisilazane. Therefore, it appears as though ammonium bromide is not a catalyst for the polymerization of the disilazane under these conditions. The very small amount of dimethyldimethoxysilane that was formed could simply have resulted from the prolonged heating. Another possibility would be that the ammonium bromide played some role in its formation. It is clear, however, that the rate of formation of dimethyldimethoxysilane was so slow that ammonium bromide cannot be considered as a practical catalyst for the polymerization of sym-dimethoxytetramethyldisilazane.

B. Potassium Cyanide Catalysis:

In the previous experiment an acid, the ammonium ion, or a base, ammonia, both of which were present in the reaction mixture at 162°, did not affect the polymerization of sym-dimethoxytetramethyldisilazane. The action of the Lewis base, cyanide ion, was studied next. Sixty g. of disilazane and 5 g. of potassium cyanide were mixed and refluxed for 24 hours. The potassium cyanide did not appear to be soluble in the disilazane. Upon cooling of the reaction mixture, the liquid portion was decanted from the solid KCN and fractionated. There was no evidence for the formation of dimethyldimethoxysilane or any polymeric material Rather, the entire sample boiled at 160-163° and was, therefore, unchanged disilazane. The insolubility of the potassium cyanide in the disilazane or its weak basicity, or both of these factors, rendered it, as well as ammonium bromide, ineffective as a polymerization catalyst.

C. Alkoxide Catalysis:

In the search for an effective polymerization-inducing substance, the possibility of crosslinking during polymerization made it imperative that the most specific catalyst be found. Under very rigorous conditions it might have been possible to obtain a polymer, but almost certainly not a linear one. Therefore, there was a reluctance to employ very strong bases such as methoxide ion without first testing the effectiveness of the considerably weaker base, aluminum isopropoxide.

Sixty g. of sym-dimethoxytetramethyldisilazane was mixed with 2 g. of aluminum isopropoxide and the reaction mixture refluxed for 24 hours. The aluminum isopropoxide did not appear to dissolve nor was it noticeably changed during the course of the reaction. Nevertheless, the reaction mixture did turn a rosy orange color. After cooling, the liquid fraction was decanted from the aluminum isopropoxide and was fractionated. In this case 9g. of dimethyldimethoxysilane was collected. In addition to a considerable amount of unchanged disilazane, there was a small amount of a higher boiling liquid fraction, composed primarily of tri-and tetrasilazane. This was the first indication of polymerization. Unfortunately, no high molecular weight polymers were formed.

The next alkoxide that was tried, also in the relatively weak class of aluminum compounds, was aluminum methoxide. Four-tenths mole of the disilazane and 0.08 mole of aluminum methoxide were mixed in the absence of a solvent and refluxed for 24 hours in exactly the same manner employed in all of the previous polymerization studies. The solid aluminum methoxide which appeared to have been slightly soluble in the hot disilazane was separated from the liquid fraction by filtration. Fractionation of this liquid showed it to have been composed of 10g (0.08 mole) of dimethyldimethoxysilane, unchanged starting material and a very small amount of a liquid whose NMR spectrum and boiling point were identical to those of the dimethoxyhexamethyltrisilazane. Therefore, in this experiment as well as in the previous one involving aluminum isopropoxide catalysis, there was definite evidence of polymerization. However, no more than dimerization or trimerization to give the tri- and tetrasilazanes, respectively, took place. Crosslinking through the nitrogen also did not take place as evidenced by the NMR spectra and the absence of ammonia among the reaction products. Therefore, it must be concluded that under the conditions described above, aluminum methoxide and aluminum isopropoxide do catalyze the polymerization of sym-dimethoxytetramethyldisilazane to give low molecular weight linear polymers. Nevertheless, there is some factor in this polymerization process which makes it impossible to obtain higher linear polysilazanes.

Therefore, the catalytic properties of the strong base, sodium methoxide, were studied in an effort to form higher polysilazanes. An experiment of the type described above was performed using sodium methoxide as a catalyst and it was found that rather than remaining unchanged, the sodium methoxide entered into a reaction with the disilazane. A significant amount of dimethyldimethoxysilane was formed accompanied by polymerization of the disilazane. A detailed description of the system, sym-dimethoxytetramethyldisilazane, sodium methoxide is given below.

Forty-four one-hundredths of a mole of disilazane was mixed with 0.1 mole of sodium methoxide. No solvent was used. The reaction mixture was refluxed for 24 hours. Ammonia was identified as a product of this reaction, but, unfortunately, the amount of ammonia given off was not determined. After 24 hours, NH_3 evolution had ceased. The sodium methoxide which was insoluble in the disilazane had disappeared, and at reflux temperature there was only a clear, slightly yellow liquid. Upon cooling and standing for several hours, a crystalline solid separated from the liquid. The liquid fraction was decanted from these crystals and the two unknowns were studied separately.

The solid was recrystallized from hexane in which it was moderately soluble. It was also soluble in benzene but not in carbontetrachloride. This substance was very sensitive to hydrolysis, even by atmospheric moisture. A flame test indicated the presence of sodium, and the usual qualitative test for amine nitrogen was also positive.

Samples of the solid were hydrolyzed in aqueous methanol. The resulting solution was alkaline and was boiled to remove all of the ammonia. Excess standard hydrochloric acid was added and back titrated with standard sodium hydroxide to determine the amount of sodium as sodium hydroxide that had been present in the original samples. Standard Kjeldahl procedures were followed to determine the amount of nitrogen. Table III gives the analytical data compared to the values calculated for $((CH_3O)(CH_3)_2Si)_2N^-Na^+$, (A), and $((CH_3O)(CH_3)_2Si)_2N^-Na^+ \cdot C_6H_{14}$, (B).

TABLE III

	Calculated		Found
	(A)	(B)	
moles of Na	1.65×10^{-3}	1.18×10^{-3}	1.23×10^{-3}
°/o Nitrogen	6.52	4.65	4.69

The agreement between the calculated and found percentages of Na and N is good if it is assumed that the solid material recrystallized from hexane contains one mole of hexane of solvation per mole. Furthermore, the percent nitrogen is slightly low and the percent sodium slightly high which is consistent with slight hydrolysis of this very moisture-sensitive compound. These data indicate strongly that the crystalline reaction product is the sodium compound of sym-dimethoxytetramethyldisilazane. The NMR spectrum of this solid was identical to that of the disilazane except that the methyl protons were shifted 0.24 ppm upfield. This spectrum was taken in benzene. For the disilazane methyl protons $\delta = 0.28$ ppm upfield from TMS while $\delta = 0.52$ ppm upfield from TMS for the methyl protons of the solid dissolved in benzene. This shows the carbon and, therefore, the nitrogen to be less electronegative in the somewhat ionic sodium compound than they are in the disilazane itself. This seems totally reasonable and provides further proof of the identity of the solid.

The liquid fraction was distilled at atmospheric pressure and boiled at 78-82°. Thirty three g. of a solid residue was left behind. The NMR spectrum of the volatile liquid showed it to be pure dimethyldimethoxysilane.

The polymeric material which was left behind as a residue in the above distillation was soluble in benzene but insoluble in hexane and carbontetrachloride. The polymer could not, however, be purified by reprecipitation from benzene, because it would not precipitate. As the benzene slowly evaporated, the solution became increasingly more viscous until finally a very brittle, clear, glassy solid was obtained after prolonged heating to remove traces of benzene. The polymer was also insoluble in water or dilute acids. Concentrated sulfuric acid did, however, decompose it easily. The NMR spectrum of this substance, dissolved in benzene, showed no methoxy protons and two very broad methyl proton peaks at $\delta = 17$ ppm and $\delta = 0.33$ ppm, both upfield from TMS and is attributed to the cross-linked polymer. The infrared spectrum of this polymer does show a peak corresponding to the N-H stretching frequency, but this peak is rather small. The analytical data are given in Table IV.

TABLE IV

% Nitrogen	Calculated	100% linear	100% crosslinked
		19.2	13.8

Found percentages

% Carbon.....25.66

% Hydrogen....6.93

% Nitrogen....14.87

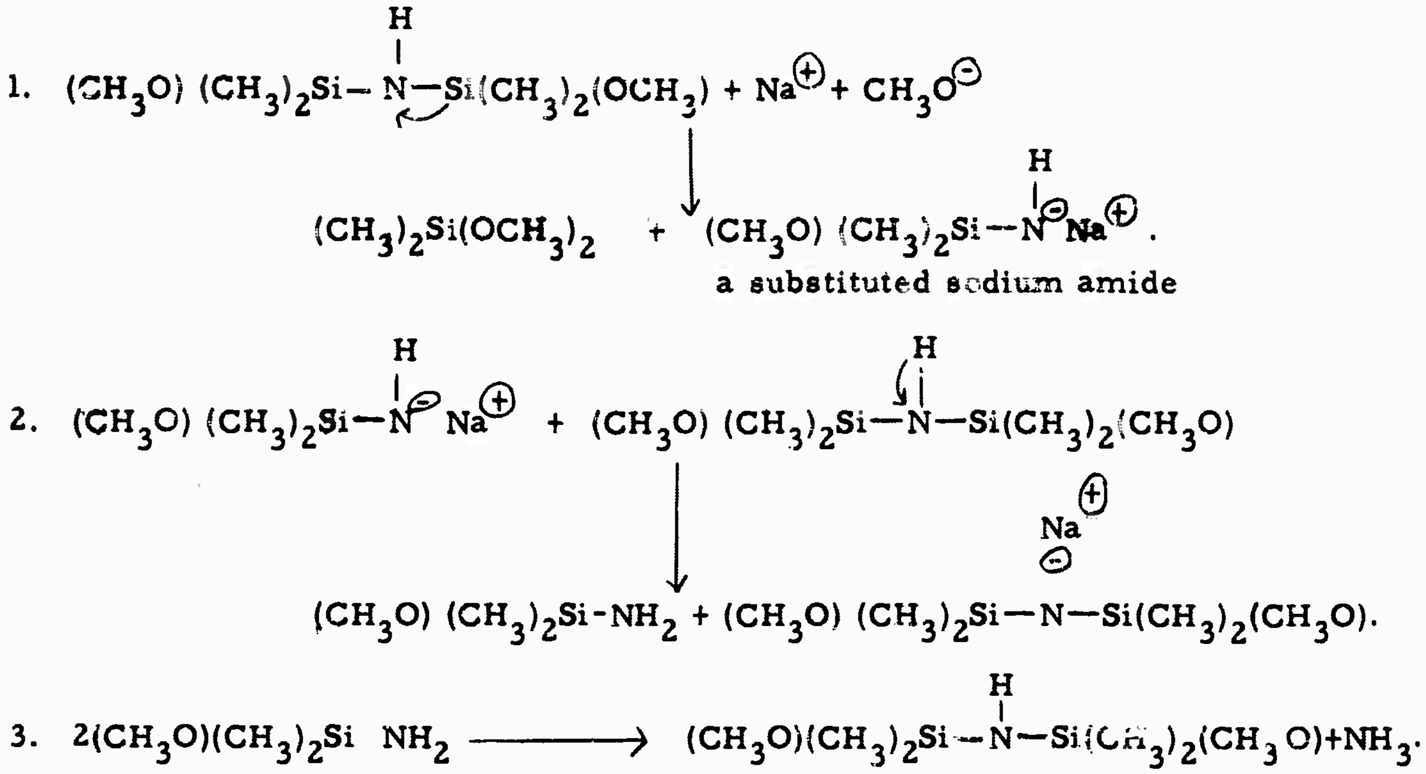
% Silicon.....38.53

Molecular Weight in ether = 2420

All of these data show that it is possible to obtain a polymer from sym-dimethoxy-tetramethyldisilazane, but that this polymer is quite highly crosslinked.

The following two competing mechanisms are suggested as a possible explanation for the formation of all of the products observed in the above polymerization process.

A POSSIBLE MECHANISM FOR THE FORMATION OF THE SODIUM COMPOUND:



1. $(CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}-Si(CH_3)_2(OCH_3) + Na^{\oplus} + CH_3O^{\ominus}$

$\downarrow$

$(CH_3)_2Si(OCH_3)_2 + (CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}{}^{\ominus}Na^{\oplus}$.

a substituted sodium amide

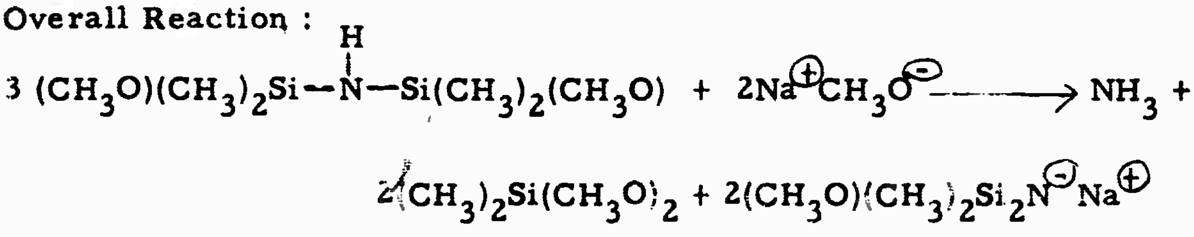
2. $(CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}{}^{\ominus}Na^{\oplus} + (CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}-Si(CH_3)_2(CH_3O)$

$\downarrow$

$(CH_3O)(CH_3)_2Si-NH_2 + (CH_3O)(CH_3)_2Si-\underset{\ominus}{\underset{Na^{\oplus}}{N}}-Si(CH_3)_2(CH_3O)$.

3. $2(CH_3O)(CH_3)_2Si\ NH_2 \longrightarrow (CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}-Si(CH_3)_2(CH_3O)+NH_3$.

Overall Reaction :



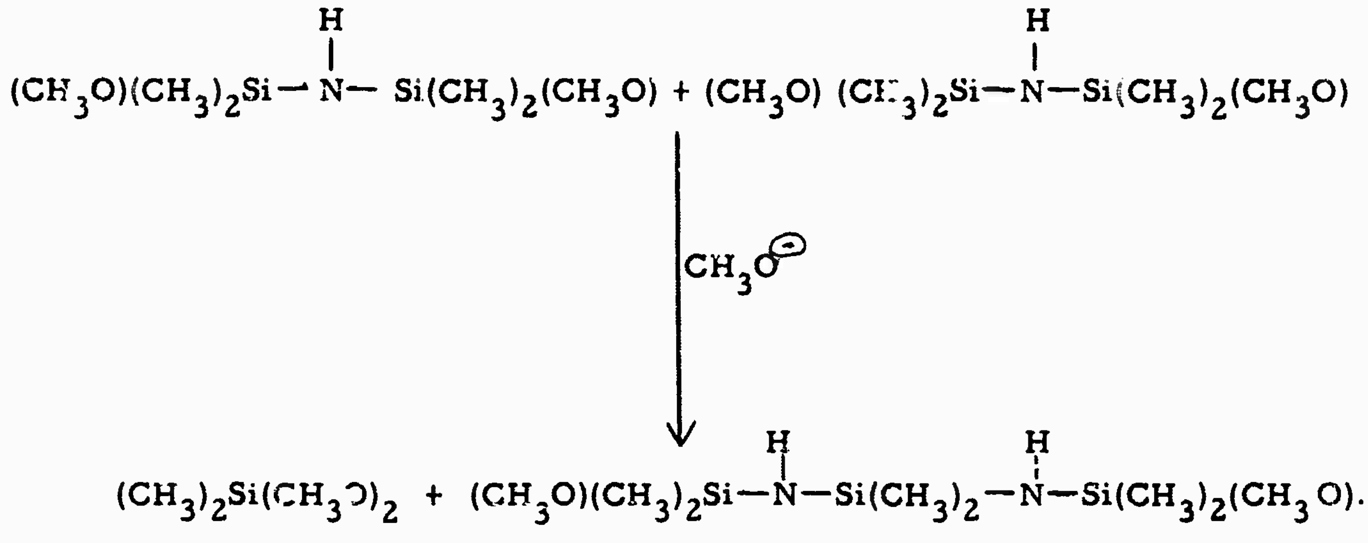
$3(CH_3O)(CH_3)_2Si-\overset{H}{\overset{|}{N}}-Si(CH_3)_2(CH_3O) + 2Na^{\oplus}CH_3O^{\ominus} \longrightarrow NH_3 +$

$2(CH_3)_2Si(CH_3O)_2 + 2(CH_3O)(CH_3)_2Si_2N^{\ominus}Na^{\oplus}$

This explains the formation of the sodium compound, ammonia and dimethyldimethoxysilane.

A POSSIBLE MECHANISM FOR THE FIRST STEP OF THE POLYMERIZATION

1.



$$(CH_3O)(CH_3)_2Si-\overset{H}{\underset{|}{N}}-Si(CH_3)_2(CH_3O) + (CH_3O)(CH_3)_2Si-\overset{H}{N}-Si(CH_3)_2(CH_3O) \xrightarrow{CH_3O^{\ominus}} (CH_3)_2Si(CH_3O)_2 + (CH_3O)(CH_3)_2Si-\overset{H}{N}-Si(CH_3)_2-\overset{H}{N}-Si(CH_3)_2(CH_3O).$$

This polymerization process is undoubtedly enhanced by the ability of the methoxide ion to break the silicon-nitrogen bond. The crosslinking reaction does not seem to be so straightforward, although it probably arises from attack by the substituted sodium amide (shown in the first mechanism) on a linear silazane in an, as yet, poorly understood manner.

It is worthy of note at this point that the methoxy groups in sym-dimethoxytetramethyldisilazane apparently have a labilizing effect on the silicon nitrogen bond, because sodium methoxide had absolutely no effect on a sample of hexamethyldisilazane which was treated in exactly the same manner.

Because sodium methoxide apparently entered into reaction with the sym-dimethoxytetramethyldisilazane by nucleophilic attack on the silicon by methoxide by an S_N2 mechanism, it was thought to try a base of equal or maybe even somewhat greater base strength, but one which was sufficiently bulky so that a bi-molecular nucleophilic substitution mechanism would be far less likely. Potassium tertiarybutoxide was chosen for this purpose.

Sixty g. of disilazane (0.3mole) was mixed with 5 g. of potassium tertiarybutoxide in the absence of a solvent and refluxed for 24 hours. The $KOC(CH_3)_3$ appeared to dissolve somewhat. Ammonia was given off during the heating process, and after 24 hours, the reaction mixture consisted of a light yellow liquid and a colorless solid. This solid was separated from the liquid by filtration, and the liquid was fractionated. At 86-90° a mixture composed largely of dimethyldimethoxysilane and a small amount of methoxy-t-butoxydimethylsilane was collected. When almost all of this volatile fraction had been removed from the material remaining in the distillation bulb, ammonia evolution began. At the end of the distillation, 32 g. of volatile liquid had been collected. Upon cooling to 25° the residue solidified into a clear, cracked, very tough, glassy material. This polymer was soluble in benzene and its NMR spectrum was obtained in benzene solution. There were no peaks corresponding to methoxy protons and only two very broad methyl proton resonances, which occurred in exactly the same place as those in the spectrum of the polymer obtained using sodium methoxide. Although the larger of these two peaks had to be assigned to methyl protons in a crosslinked environment, this polymer was less crosslinked than the polymer obtained using sodium methoxide.

In subsequent polymerizations it was possible to reduce the crosslinking further by very careful heating during removal of the volatile fractions. Nevertheless, ammonia evolution was always observed and it was not possible to obtain anything but highly crosslinked polymers by this method.

The experiment was modified in such a way that the ammonia, evolved during reflux, could be measured. Also, the fractional distillation of the products was done at reduced pressure in order to avoid high temperatures and, thereby, eliminate the pyrolysis which led to the evolution of ammonia during the distillation described in the previous run. The general procedure was the same as that described above. However, the reflux condenser, rather than being equipped with a drying tube, was connected through two Leiden gas-washing bottles to a reservoir of concentrated hydrochloric acid. Any ammonia generated during the course of the reaction was trapped in this way and its amount determined by standard Kjeldahl procedures. Table V shows the results obtained in two typical experiments.

TABLE V

	1	2
Moles of disilazane	2.69×10^{-1}	3.19×10^{-1}
Moles of potassium tertiarybutoxide	6.42×10^{-3}	2.12×10^{-2}
$\frac{\text{Moles of potassium tertiarybutoxide}}{\text{Moles of disilazane}}$	2.38×10^{-2}	6.65×10^{-2}
Moles of NH_3 liberated during the polymerization	1.00×10^{-2}	2.89×10^{-2}
$\frac{\text{Moles of ammonia}}{\text{Moles of potassium tertiarybutoxide}}$	1.56	1.36
Percent of total nitrogen, as liberated ammonia	1.5	2.5

The potassium tertiarybutoxide appeared to dissolve in the disilazane. After cooling, the reaction mixture consisted of a colorless, crystalline solid which contained potassium and nitrogen as determined by qualitative tests, and a slightly yellow liquid. The crystalline material was presumably the potassium salt of the disilazane. Analytical data were not obtained, but the solubility characteristics, sensitivity to moisture and presence of potassium as well as the NMR spectrum, taken in benzene, all argue in favor of the potassium salt. No potassium tertiary butoxide could be isolated from the reaction mixture.

The liquid fraction was separated from the crystalline reaction product by filtration. This liquid was then distilled under vacuum. The first two fractions were collected at a pressure of 11 mm. while a pressure of 0.1mm. was used in the distillation of the third. Table VI shows the boiling points and amounts of the various fractions collected in runs 1 and 2.

TABLE VI

Fractions	Boiling Points		Amounts	
	1	2	1	2
A	25-27°	25-27°	17g.	24g.
B	62-70°	64-70°	10g.	13g.
C	65°	62-65°	12g.	18g.

Fraction (A) was collected in a trap at -78° because of its low boiling point. The infrared spectrum, taken as a pure liquid film between sodium chloride plates, agrees in all respects with that of a known sample of methyldimethoxysilane. The NMR spectrum of $(CH_3)_2Si(CH_3O)_2$ should contain just one methyl and one methoxy proton peak. The experimental results are in agreement with this. There was, however, one other much smaller peak which has been assigned to the protons of the tertiarybutoxy-group present in the impurity $(CH_3)_2Si(CH_3O)(C(CH_3)_3O)$. The calculated methoxy to tertiarybutoxy proton ratio, if all of the potassium tertiarybutoxide reacted with the disilazane, is 24/1. The found value was 23/1. The methyl to methoxy ratio in the dimethyldimethoxysilane was found to be 1.06/1 and 1.1/1, compared to the calculated value of 1/1. Table VII gives the analytical data obtained for this compound.

TABLE VII

	Calculated for $(CH_3)_2Si(CH_3O)_2$	Found
°/o C	39.92	40.10
°/o H	10.50	10.61
°/o Si	23.37	23.35

There can be little doubt that fraction (A) is dimethyldimethoxysilane. The presence of the calculated amount of methoxy-t-butoxydimethylsilane impurity gives credence to a mechanism of the type shown on page 27 of this report.

Fraction (B) was unreacted sym-dimethoxytetramethyldisilazane as shown both by its infrared and NMR spectra. The calculated methyl to methoxy ratio for this compound is 2/1 while the found values were 2.1/1 and 2.08/1. Table VIII gives the analytical data which also support this conclusion.

TABLE VIII

	Calculated	Found
°/o C	37.25	37.58
°/o H	9.90	9.90
°/o Si	29.04	30.25
°/o N	7.24	7.46

Fraction (C) had an NMR spectrum which contained 5 methyl peaks and one methoxy peak. They were in the ratio 4.0/1 and 4.2/1. The presence of only one methoxy peak is reasonable and shows that all of the methoxy groups are in the same environment. They are most likely attached to terminal silicon atoms, as they are in the starting material. The 5 methyl peaks suggest that there are at least 2 different kinds of methyl groups in this molecule and probably more than 2. The infrared spectrum was typical [ ] in its general features [of a polysilazane] and did show that there was a significant amount of N-H in the molecule. The relatively low boiling point of this compound suggests that it is probably not a very large molecule. The analytical data which are given in Table IX do not correspond to the calculated values for any linear polysilazane and no speculation as to its structure has been made.

TABLE IX

% C	35.05	% Si	35.27
% H	9.06	% N	10.57
		n_D^{20}	1.4385

The distillation residue was composed of a small amount of the potassium compound of the disilazane, which had been dissolved in fraction A through C and also several grams of a colorless oily liquid. The NMR spectrum of this oil showed one type of methoxy group and a broad resonance for the methyl protons, composed of a large singlet and two smaller doublets. The methyl to methoxy ratio was 6.02/1. From the analytical data shown in Table X it was obvious that this oil was not strictly a linear polysilazane. The nitrogen percentage was too low for that. The number of methyl peaks in the NMR spectrum also suggests a more complicated structure.

TABLE X

% C	34.71	% Si	42.50
% H	8.79	% N	11.90
		n_D^{20}	1.4651

CONCLUSION:

These studies involving sodium methoxide and potassium tertiarybutoxide-induced polymerization of sym-dimethoxytetramethyldisilazane clearly show that it is possible to obtain low molecular weight polymers in which a significant amount of linearity has been achieved. These polysilazanes do, however, contain the order of only 5 or 6 silicon atoms at the most and are the highest molecular weight species that can be obtained under mild conditions. If, however, these low polymers are pyrolyzed (perhaps significantly) in the presence of a small amount of dissolved sodium or potassium salt of the disilazane, high molecular weight solid polymers are obtained. These are highly crosslinked as evidenced by the evolution of ammonia. This dimethoxytetramethyldisilazane system provides another example of the great propensity that silazanes seem to exhibit to crosslink through the nitrogen rather than forming linear polymers.

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