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NEW SYNTHETIC METHODS FOR SILICON-NITROGEN POLYMERS

L. W. Breed and R. L. Elliott
Midwest Research Institute

TECHNICAL REPORT AFML-TR-69-20, Part I

January 1969

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-68-C-1371, "Research on New Synthetic Methods for Silicon-Nitrogen Polymers." The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (MANP), as Project Scientist. Funds for this project are supplied to the Air Force Materials Laboratory by the Office of Aerospace Research.

This technical report covers the work conducted from 23 January to 31 December 1968. The manuscript was released by the authors in December 1968 for publication as a technical report.

The work was carried out by Messrs. Richard L. Elliott and L. W. Breed, who acted as principal investigator. The authors are indebted to Mr. Dwayne Inmon and Mr. Iraj Hekmati for their contributions to the research.

This technical report has been reviewed and is approved.

W E Gibbs

W. E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Condensation polymers of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane and bis(*p*-dimethylhydroxysilylphenyl) ether and *p*-phenylenebis(dimethylsilanol) were prepared and characterized. Under various conditions of preparation, the polymers lost solubility in nonpolar solvents before high molecular weights could be achieved. The condensation of the same arylene disilanols with N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane in the presence of sodium hydride gave polymers with less tendency to lose solubility, but high molecular weight materials were not obtained. Condensation reactions of arylene disilanols with the amino-, methylamino-, and diethylaminosilyl derivatives of the cyclodisilazane monomers are also reported. Evidence is offered for the structure of the oligomers obtained by equilibrating dichlorodimethylsilane with hexamethylcyclotrisilazane under various conditions and the structure compared with that of other similarly prepared materials that have been reported by others. Additional details are offered on the synthesis of monomers and intermediates.

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I.

INTRODUCTION

The goal of this program is to develop new synthetic methods for high molecular weight silicon-nitrogen polymers. Approaches have been selected that afford the greatest probability of obtaining polymers with flexible backbones. The present report describes the results of research on this program conducted after that reported in AFML-TR-66-116, Part III, December 1967.

In earlier work, new intermediates with the trisilylamine and cyclodisilazane structures received particular attention as candidate polymer precursors. Methods were developed for preparing a number of functional trisilylamines and cyclodisilazanes, and these compounds have been screened in polymerization experiments. Condensation of silylamino derivatives of cyclodisilazane with arylenedisilanols appears to offer potentially useful materials.

Also, earlier work had shown that when molar deficiencies of dichlorodimethylsilane were heated with hexamethylcyclotrisilazane or octamethylcyclotetrasilazane, a high proportion of the monomers was converted to oligomers that were not volatile at 230°.* These oligomers had good heat stability and surprising solvolytic stability. Some evidence concerning their possible structures was offered.

This report concerns additional research on condensation polymers, particularly those derived from difunctional cyclodisilazane derivatives and arylenedisilanols, and on the earlier reported oligomeric materials.

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* All temperatures are reported in °C.

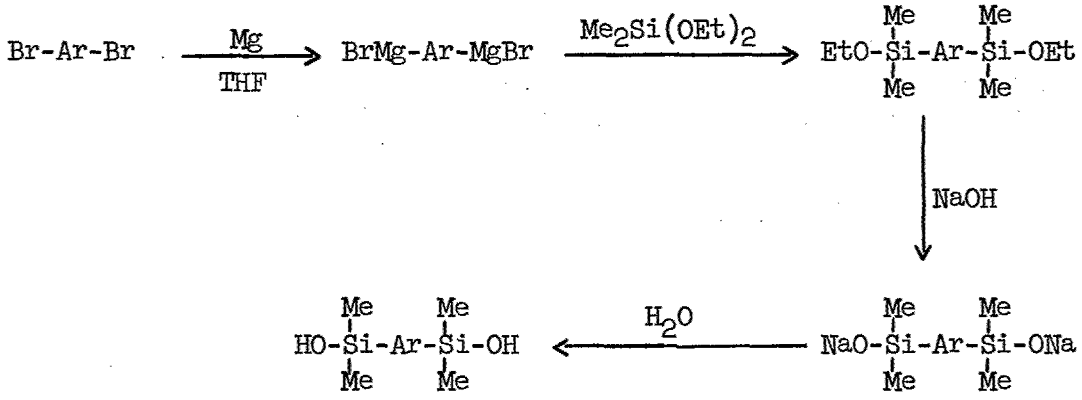
II.

DISCUSSION

A. Monomers, Intermediates, and Samples

1. N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane: This key intermediate, whose preparation has been reported a number of times in earlier reports, has been isolated by distillation from a complex mixture of compounds obtained by equilibrating hexamethylcyclotrisilazane and dichlorodimethylsilane at 175°. The compound was usually separated in the fractions that boiled between about 145° and 165° at 45 mm., and the fractions were used directly without further purification in the preparation of derivatives. Since the conversion to these derivatives was usually high, it was assumed that the intermediate had been obtained in reasonably high purity. G.l.c. data obtained during this report period indicated that fractions boiling between 145° and 160° at 45 mm. had been at least 85% pure and that a fraction could be collected at 156° at 45 mm. that was 99% pure.

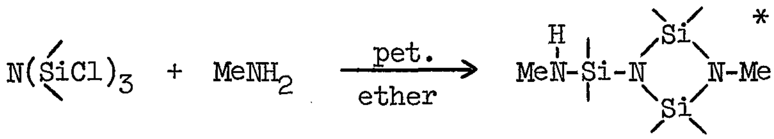
2. Arylenedisilanol monomers: Considerable time was spent on the synthesis of arylenedisilanol monomers.



By this method, the intermediates and monomers, p-phenylenebis(dimethylethoxysilane), p-phenylenebis(dimethylsilanol), bis(p-dimethylethoxysilylphenyl) ether, and bis(p-dimethylhydroxysilylphenyl) ether, could be prepared in very satisfactory yields. Although p-phenylenebis(dimethylsilanol) was easily purified, the purification of bis(p-dimethylhydroxysilylphenyl) ether offered erratic results.

After a number of the batches of bis(p-dimethylhydroxysilylphenyl) ether had polymerized spontaneously on storage after recrystallization, it was found that this monomer was particularly sensitive to the acid concentration of the buffered solution used in the hydrolysis of the sodium salt. With proper adjustment of the acidity, stable monomer could be obtained. Polymerized materials could be recovered through the use of methanolic sodium hydroxide.

3. N-Methyl-N'-dimethylaminosilyltetramethylcyclodisilazane: An attempt to prepare N-methyl-N'-dimethylmethylaminosilyltetramethylcyclodisilazane by treating tris(chlorodimethylsilyl)amine with methylamine afforded a poorly defined product under the conditions that had given good conversions of N-methyl-N'-trimethylsilyltetramethylcyclodisilazane from methylamine and bis(chlorodimethylsilyl)trimethylsilylamine.



If this monomer could be prepared, it could probably be homopolymerized by ring expansion and condensation under acid conditions. The product of the reaction appeared to contain about 80 percent of the specified cyclodisilazane. Since n.m.r. data indicated that pure tris(chlorodimethylsilyl)amine had been used [there was no indication of N,N'-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane being present], it seemed pertinent to reexamine the method reported by Wannagat for the preparation of tris(dimethylaminodimethylsilyl)amine (Ref. 1). The procedure was repeated except that the reactants were simply warmed to room temperature before the product was worked-up. Under these conditions the yield of tris(dimethylaminodimethylsilyl)amine was reduced to 20 percent as compared with the 83 percent yield that Wannagat obtained when the reactants were heated in refluxing petroleum ether for 15 hr. before they were worked-up.

It is apparent that more forcing conditions are required for an adequate conversion to obtain this monomer. On the other hand, previous work with the N-methylcyclotrisilazanes have indicated that higher temperatures in such condensations could lead to ring cleavage side reactions; therefore, the preparation may not be feasible.

4. Condensation of dimethylphenylsilanol with cyclodisilazane derivatives: Because of its structural relationship as a model compound of polymers studied during this report period, the synthesis of the condensation product of dimethylphenylsilanol and N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane was of some interest.

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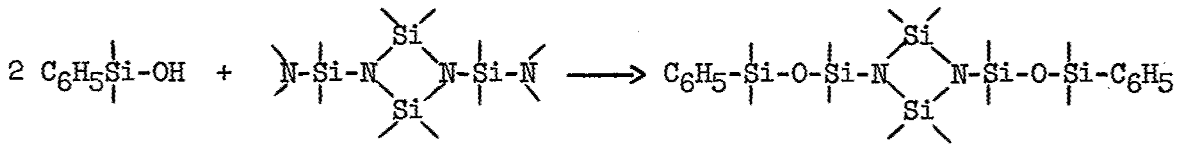
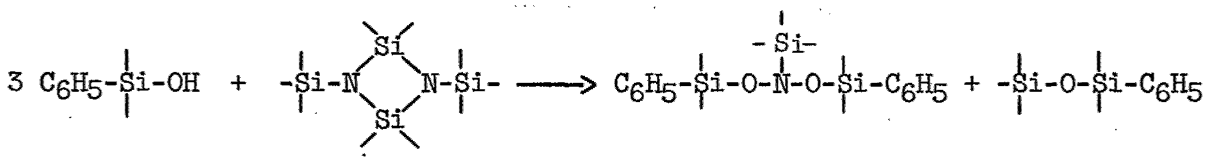
* All unfilled bonds are methyl groups.



The product was isolated by distillation in less than a quantitative conversion (66%), and the spectrum of the distillation residue showed medium strength absorption bands at 915 and 945 cm^{-1}. Also, a significant forerun was separated in the distillation. The less than quantitative conversion and the spectral evidence for the formation of trisilylamine structures indicated that ring cleavage could be a side reaction in a polymerization involving such a condensation.

In an investigation of the reaction in which the ring would be cleaved and the trisilylamine formed, the cyclodisilazane was treated with 5 moles of the silanol. However, no pure product could be isolated, apparently both because of the high boiling point of the product and the resistance of the ring to cleavage. In an alternate reaction, dimethylphenylsilanol was treated with N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane, and 19% of the trisilylamine derivative was isolated.



In the reaction, a considerable portion of the cyclodisilazane ring remained uncleaved even though the reactants were heated at 150° for 9 hr.

5. Other compounds: In addition to the repetition of the preparation of a number of monomers and intermediates reported in earlier reports, the compounds listed in Table I were also prepared.

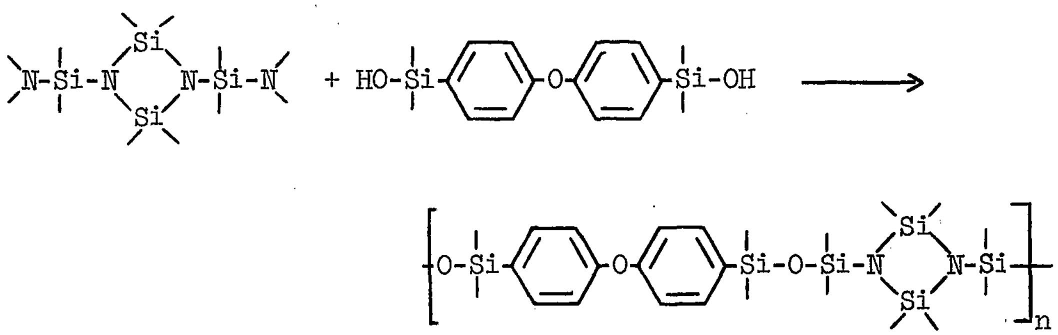
TABLE I

TABULATION OF MISCELLANEOUS COMPOUNDS SYNTHESIZED

Compound Name	Boiling Point	n_D^{20}
Bis(methylamino)dimethylsilane	108-109° (atm.)	1.4160
Bis(methylamino)diphenylsilane	103° (0.010 mm.)	1.5718
1,3-Dichlorotetramethyldisiloxane	56-57° (40 mm.)	--
1,5-Dichlorohexamethyltrisiloxane	94-95° (40 mm.)	--
1,7-Dichlorooctamethyltetrasiloxane	125-126° (40 mm.)	--

B. Condensation Polymerizations

1. Silanol-silylamine condensates: A previously reported condensation polymer from bis(*p*-dimethylhydroxysilylphenyl) ether and N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane has been found to have potentially useful properties as an elastomeric gum.



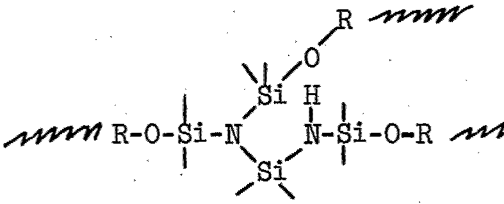
In the preliminary investigation of the polymerization variables, a series of experiments were carried out in which small amounts of the monomers were heated together under different conditions. When equimolar quantities of the reactants were heated in the absence of solvent, the polymers gelled at temperatures as low as 72°. In toluene or xylene solution, gelation occurred either during the reflux period or while the solvent was being removed from the polymer.

In the first experiments, the polymerizations were carried out by mixing the monomers cold and immersing the polymerization mixtures in a heating bath. Because the monomers were not mutually soluble, random reaction could occur in the nonhomogeneous medium. An experimental modification was therefore adopted in which the monomers were first mixed in a toluene solution and the toluene was then evaporated under reduced pressure to give an oil that could be further polymerized. However, even with this modification, the polymers became insoluble when they were heated to 95°.

The latter procedure was followed in preparing four 30-g. samples from the same monomers. The oil that was obtained by evaporating the toluene was gradually heated in a rotary evaporator with the bath temperature being slowly increased until the mixture no longer flowed. In the four experiments a final temperature of 65-75° was required. Two of the polymers, those containing molar excesses of the cyclodisilazane monomer, were soluble immediately after the polymerization was complete, but all ultimately became at least partly insoluble. Later it was found that a polymer that was heated no higher than 30° during its preparation gelled after storage for 72 hr.

Under all conditions that have been examined, the highest inherent viscosity obtained on these polymers was about 0.20, and all the polymers were subject to subsequent solubility loss. Insoluble portions of the polymers swelled extensively in toluene; therefore, the extent of cross-linking or cleavage of the cyclodisilazane ring was not great.

In AFML-TR-66-116, Part III, it was suggested that insolubility could have resulted from a minor amount of cyclodisilazane ring cleavage, which would allow a portion of the cyclodisilazane to function as a trifunctional monomer in its reaction with the arylenedisilanol.



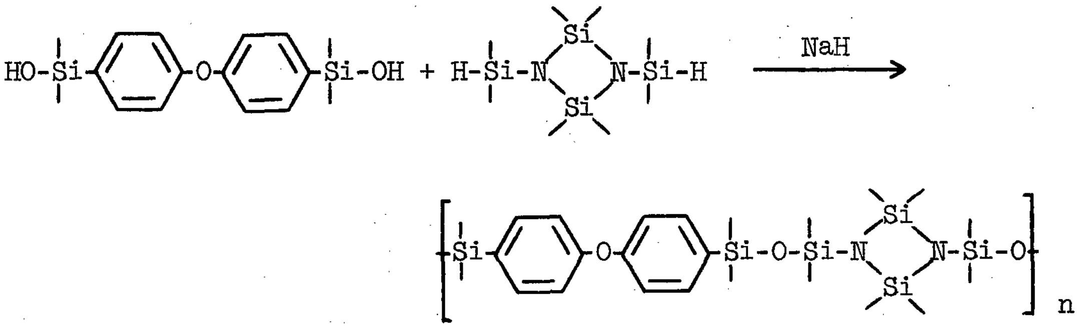
It does not seem unreasonable to assume that the cyclodisilazane ring competes with the pendant silylamine group for the silanol. Evidence that such cleavages occur is the observation of weak silazane absorption in the 900 to 950 cm^{-1} region in these polymers, which can be assigned to a disilazane or trisilylamine structure.

Except for the weak band in the 900 to 950 cm^{-1} the infrared spectra of the polymers were entirely consistent with their structures. The structures were further confirmed by the agreement of the calculated and experimental values for the elemental analyses of polymers from N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane with both p-phenylenebis-(dimethylsilanol) and bis(p-dimethylhydroxysilylphenyl) ether.

As a possible approach to increasing the relative rate of reaction at the pendant silylamine group with respect to the cyclodisilazane group, the polymerizations of the amino-, methylamino-, dimethylamino-, and diethylaminosilyl derivatives of the cyclodisilazane were compared. In this series it was found that condensation at the pendant silylamine group was favored by the more basic amine substituent. The condensation products with the amino- and methylaminosilyl derivatives had much stronger absorptions in the 900 to 950 cm^{-1} region indicating that ring cleavage had been even more favored in these condensations. The lack of reactivity of the aminosilyl derivative was demonstrated by the reprecipitation of unchanged diol after the two monomers were heated in toluene for several hours at 50°. Ring cleavage was so extensive in the polymerization that prolonged heat treatment was required for gelling the product. Rather than acting as a cross-linking agent in these examples, the ring cleavage culminated in degradation and hence lowered molecular weights.

Very recently, polymers have been reported as the product of condensing arylenediols or arylenedisilanols and N,N'-bis(diethylaminodimethylsilyl)-tetramethylcyclodisilazane (Ref. 2). Molecular weights and solubilities of the polymers were not reported, but it was stated that the polymer from N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane and p,p'-biphenol is soluble to only a minimum extent in aromatic solvents. Since the ionization constants of dimethylamine and diethylamine are 5.12×10^{-4} and 1.26×10^{-3}, respectively, it is possible that the diethylamine group functions more effectively as a leaving group in the polymerization owing to its increased basicity. Such an assumption was apparently valid, since a soluble polymer with an inherent viscosity of 0.77 was obtained from bis-(p-dimethylhydroxysilylphenyl) ether and the diethylamine-substituted monomer. Under similar conditions a polymer that was not completely soluble in toluene was obtained from the dimethylamine-substituted monomer. The polymer from the diethylamine-substituted monomer, however, became partly insoluble after eight days' storage and is thus subject to the same storage stability limitation in its solubility as the polymers from dimethylamine-substituted monomers.

2. Silanol-silyl hydride condensates: When N,N'-bis(dimethylsilyl)-tetramethylcyclodisilazane was heated with bis(p-dimethylhydroxysilylphenyl) ether in the presence of sodium hydride, hydrogen evolved smoothly above 85°. In a preliminary experiment, a polymer with an inherent viscosity of 0.21 was obtained that could be heated to 150° without gelation and remained toluene-soluble after 18 days.



Since this condensation appeared to offer a route in which higher molecular weight, soluble polymers might be obtained, a series of experiments were carried out to determine the important variables in a polymerization procedure in which the reactants were heated in xylene, the solvent was evaporated, and the finished polymer was heated under vacuum to remove the remaining solvent and complete the polymerization. Of the variables studied, two seemed to have an important effect on the properties of the finished material: The catalyst level and final temperature to which the polymer was heated.

At a low catalyst level (0.1 wt. %), a homopolymer of bis(p-dimethylhydroxysilylphenyl) ether was obtained. A copolymer was obtained with the 0.5 wt. % catalyst level, and none of the polymers prepared with this level of catalyst gelled during polymerization or after a month's storage. The higher 1.0 wt. % catalyst level was satisfactory in some experiments, but several of the polymers gelled either during polymerization or on storage for less than a month.

Significant changes in degrees of polymerization as reflected by the changes in inherent viscosities were effected by the final temperature at which the polymer was heated. However, when the final temperature was increased above 180°, the polymers lost their solubility.

Although this procedure had initially appeared promising, and polymers could be obtained that retained their solubility in toluene, the procedure ultimately proved to have the limitation of producing polymers with inherent viscosities no higher than 0.2. Some higher viscosity polymers were produced, but these also lost their solubility. An unexplained phenomenon in connection with this mode of polymerization is that in the spectra of the polymers the weak 945 cm^{-1} absorption is evident, but does not seem to be associated with insolubility.

In this condensation, the possibility exists that some homopolymerization of the silanol may occur concurrently with the polymerization reaction. This route would effectively lower the concentration of the silanol with respect to the silyl hydride and at the same time decrease the probability of ring cleavage reactions that might lead to crosslinking. The use of a molar deficiency of the diol with cyclodisilazane silylamine derivatives in earlier work had led to more soluble polymers; however, these polymers also ultimately lost their solubility.

Some evidence concerning the extent of homopolymerization can be found in various infrared spectra. The band at about 1030 cm^{-1} in N,N'-bis-(dimethylaminodimethylsilyl)tetramethylcyclodisilazane associated with the cyclodisilazane ring shifts to about 1010 cm^{-1} in the model compound, N,N'-bis(dimethylphenylsiloxydimethylsilyl)tetramethylcyclodisilazane (Figure 1,*). Siloxane absorption is centered at 1070 cm^{-1}. The homopolymer of bis(p-dimethylhydroxysilylphenyl) ether shows siloxane absorption as a broad band centered at 1050 cm^{-1} (Figure 2). Except for the relative intensities of the bands centered at 1010 cm^{-1}, and 1070 cm^{-1}, the infrared spectrum in the 1000-1100 cm^{-1} region of the model compound was similar to the spectrum of the polymer obtained by condensing bis(p-dimethylhydroxysilylphenyl) ether with N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (Figure 3). The polymer from the silyl hydride also showed the same pattern in the

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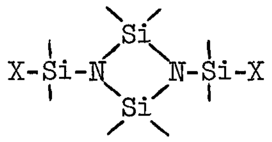
* All infrared spectra are reproduced in the Appendix, p. 59.

1000-1100 cm^{-1} region (Figure 4), but other siloxane absorptions may be present, since the valley between the two peaks is less pronounced. The predominant mode of bonding is, according to the infrared data, similar to the bonding in the model compound, but some homopolymerization cannot be precluded.

Should homopolymerization occur, some water would be formed as the product of the reaction and lead to the cleavage of silazane linkages. In only one of the sodium hydroxide-catalyzed experiments with the cyclodisilazane monomer, one with a low sodium hydride concentration, was homopolymerization actually observed to occur. Furthermore, in only one experiment was water formation observed. The latter experiment, however, was not one that was catalyzed by sodium hydride, but was a preliminary experiment in which sodium bis(trimethylsilyl)amide had been screened as a potential basic catalyst for the polymerization.

Homopolymerization of the arylenedisilanol was also observed in an attempt to extend this mode of polymerization to the sodium hydride-induced condensation of bis(dimethylsilyl)trimethylsilylamine with bis(p-dimethylhydroxysilylphenyl) ether.

3. <u>Other condensation polymerizations</u>: Another approach to the problem was to select for consideration other functional bis(silyl) cyclodisilazane derivatives in which the nature of the leaving group in the condensation polymerization was such that reaction at the pendant group would be preferred over ring cleavage. Potentially useful monomers were:



X = OC_6H_5
= NHC_6H_5
= $NHCOCH_3$
= $NHSi(CH_3)_3$

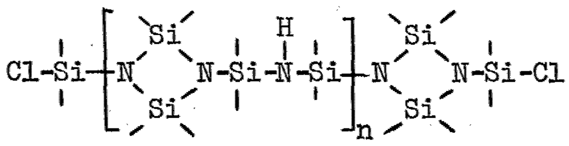
Methods had been developed previously for the synthesis of the hydrido, phenoxy, and anilino derivatives; therefore, these monomers could be readily prepared. Condensations of the anilino and phenoxy derivatives with bis(p-dimethylhydroxysilylphenyl) ether did not produce polymers. Attempts to prepare the acetamido and the trimethylsilylamino derivative by methods that have been described for similar structures in the literature were unsuccessful (Ref. 3).

A final series of condensation polymers were prepared by heating bis(p-dimethylhydroxysilylphenyl) ether in various mole ratios with an equilibration oligomer that had been treated with dimethylamine (see AFML-TR-66-116, Part II, and subsequent sections of this report.) Although most of the polymers had low inherent viscosities, intermediate concentrations gave higher molecular weight materials, several of which were not completely soluble in toluene. One polymer had an inherent viscosity of 0.31. The infrared spectra of the polymers were very similar to the spectrum of the oligomer except for the presence of Si-C_6H_5 bands, and there was ample evidence for the presence of both Si_2NH groups and cyclodisilazane rings in the polymers.

In one experiment, the replaceable nitrogen groups were determined by heating the oligomer with ethanol and titrating the liberated amine. When an equivalent amount of arylenedisilanol was used in a polymerization with the same equilibration polymer, the inherent viscosity of the product was low.

C. Equilibration Polymers and Oligomers

Earlier, in work under this contract, it had been found that oligomeric silazanes were obtained when hexamethylcyclotrisilazane or octamethylcyclotetrasilazane was heated with a molar deficiency of dichlorodimethylsilane. The work was initiated to extend the scope of the preparative reaction that had been used for the synthesis of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane. On the basis of infrared and n.m.r. data, the following structure was tentatively assigned to these materials:



The mixtures of reactants were heated at 175°, cooled, treated with dimethylamine (in solution followed by removal of amine hydrochloride) and heated to 225° in vacuum to remove the volatile components. When the ratio of Me_2SiCl_2 to Me_2SiNH groups in the polymerizations was between 1:22 and 1:6, the conversions were 66-77%. At a ratio of 1:2 and 1:1.33, the conversion to nonvolatile products was 15% or less, and at 1:44, 40%.

The n.m.r. peaks in the spectra were complex, but were originally observed to occur in two major groups, one at τ 9.70-9.79 and the other at τ 9.88-9.97. More definitive spectra have since been obtained, and are summarized in Table II.

TABLE II

SILYLMETHYL PROTON CHEMICAL SHIFTS IN OLIGOMERIC SILAZANES

Peak	T
a	10.02 (2 peaks)
b	9.98
c	9.93
d	9.84
e	9.80 (2 peaks)
f	9.75

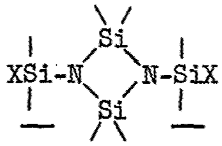
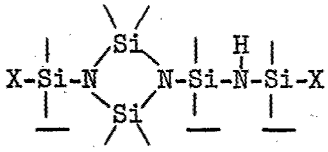
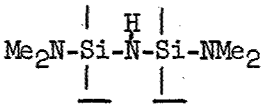
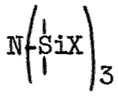
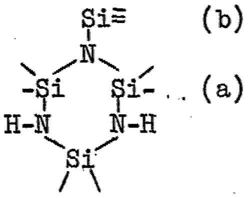
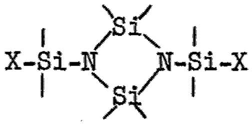
A review of the recorded chemical shifts for related silazanes in Table III allows a more precise assignment of oligomer structures. On the basis of these data, it seems apparent that three kinds of structures can be differentiated by their chemical shifts. The structures, N-SiMe$_2$-N or N-SiMe$_2$-X, where X is Me, H, or O, show shifts for the methyl protons in the τ 9.94-10.05 region. This generalization applies when the N-SiMe$_2$-N group is present in a six or larger-membered ring and when one of the nitrogens in the N-SiMe$_2$-N group is part of the strained cyclodisilazane ring. Bands a, b, and c in Table II can probably be assigned to these kinds of structures. Silylmethyl groups that are present in a trisilylamine structure have chemical shifts in the τ 9.82-9.90 region, provided the trisilylamine structure is not a part of a cyclodisilazane ring. Thus, bands d and e in Table II probably indicate trisilylamine structures. Silylmethyl protons, present in methyl groups attached directly to a cyclodisilazane ring, uniformly show shifts at τ 9.76-9.78, and band f, Table II, can be related to such a structure.

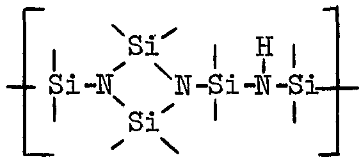
At the various mole ratios, bands b, c, and f have the greatest relative peak height. Band b retains its intensity regardless of stoichiometry, band c increases in intensity, and band f decreases in intensity with the proportion of dichlorodimethylsilane present in the equilibration.

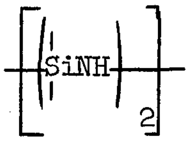
If band f is assignable to the cyclodisilazane rings, the following structures are possible in the equilibration mixtures:

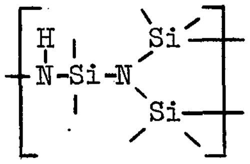
TABLE III

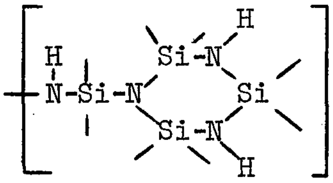
CORRELATION OF SILYLMETHYL PROTON CHEMICAL SHIFTS WITH STRUCTURE

τ	Silazane
9.94 and 9.95	$(\underline{Me}_2SiNH)_3$ and $(\underline{Me}_2SiNH)_4$
9.94-10.05	 X = CH_3, H, OR, NH_2, NHMe, NMe_2
9.95-10.03	 X = NMe_2, Me
9.98	 $Me_2N\text{-}Si\text{-}NH\text{-}Si\text{-}NMe_2$
9.82-9.87	 $N(SiX)_3$ X = OR, CH_3, H, $N(CH_3)_2$
9.85(a)-9.90(b)	
9.76-9.78	 X = CH_3, H, OR, NH_2, $NH(CH_3)$, $N(CH_3)_2$, NHPh, $OSiR_3$



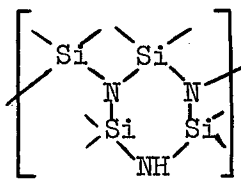




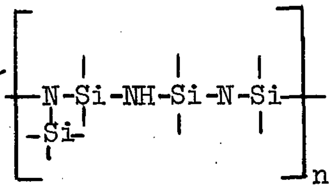


Spectral evidence, both infrared and n.m.r. indicated that cyclodisilazane, disilazanyl, and trisilylamine structures are present in the oligomers prepared at 175°, but these groups are probably randomly ordered in the polymer and the structure cannot be represented by a single formula.

In 1964, Krueger and Rochow reported that, when hexamethylcyclotrisilazane was heated with ammonium halides, silicon-nitrogen polymers were obtained, for which they proposed the following polymer structures (Ref. 4).



(A)



(B)

In their procedure, the reactants were heated at 160-190° until the calculated quantity of ammonia had evolved, cooled, treated with ammonia (in solution followed by removal of ammonium salts), and heated under reduced pressure to remove the distillable fractions, which boiled at 225-350° (1 mm.). Ammonium chloride gave only a low conversion to a polymer (11%), but when 1-45 wt. % of ammonium bromide or ammonium iodide was used, the conversions were 49-73%.

The ammonia-treated polymers were characterized by n.m.r. peaks (in carbon tetrachloride) at τ 10.02, 9.98, 9.95, and 9.74. After the mixture was pyrolyzed, two peaks remained, one at τ 9.98 and the other at τ 9.75.

Analytical data reported in their publication for polymers from various ammonium halides at different concentrations (Table IV) agreed reasonably well with the calculated values for Structures A and B.

TABLE IV

ELEMENTAL ANALYSES OF KRUEGER'S POLYMERS

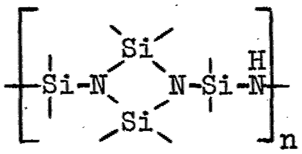
	C	H	N	Si
Calcd. for $C_8H_{25}N_3Si_2$: (Structures A and B)	34.85	9.14	15.24	40.76
Found	34.07-34.81	9.01-9.85	13.87-17.91	39.54-40.98

It is apparent that the empirical formula for the oligomers originally prepared in this laboratory and the empirical formulas for Krueger's proposed structures are the same. It is further apparent that the n.m.r. spectra of the two products are similar. Ammonium bromide in the mixture could react readily with the cyclosilazane to give a silylbromide, which could undergo the same equilibration reaction as the silylchloride with the remaining cyclosilazane.

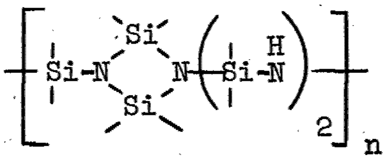
The similarity of the two reactions was verified by a parallel polymerization in which equivalent amounts of silicon-attached halogen and nitrogen were present. The spectral properties of the two products were very similar. Their elemental analyses are summarized in Table V and compared with two possible average structures.

Table V

ELEMENTAL ANALYSES OF EXPERIMENTAL OLIGOMERS



Structure C

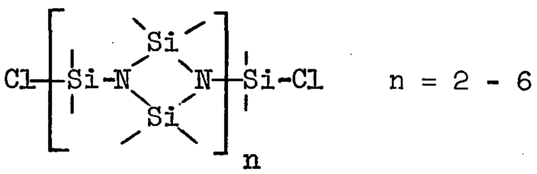


Structure D

	C	H	N	Si
Calcd. for Structure C	34.85	9.14	15.24	40.76
Calcd. for Structure D	34.43	9.25	16.06	40.26
Found for the oligomer from Me_2SiCl_2 and $(Me_2SiNH)_3$	35.39	9.38	14.93	40.24
Found for the oligomer from $(Me_2SiNH)_3$ and NH_4Br	34.97	9.44	15.66	39.88

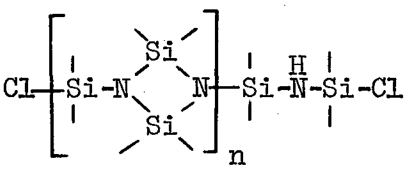
The n.m.r. spectrum of the dimethylamine-quenched polymer changed very little when it was heated to 329°. Krueger reported that the ammonia-quenched polymer retained only two n.m.r. peaks (in carbon tetrachloride) after it was heated to about 350°. Although this result was not entirely verified experimentally in this laboratory, an ammonia-quenched dichlorodimethylsilane-hexamethylcyclotrisilazane equilibration polymer that had been thermolyzed to 350° exhibited four n.m.r. peaks in CCl_4. Only two of these were major peaks, one at τ 9.97 and the other at τ 9.75. In benzene there were two peaks, one at τ 9.75 and the other at τ 9.54. It is apparent that Krueger had probably ultimately obtained the same oligomeric materials that have been just recently reported by Fink (Ref. 2).

Fink found that when the equilibration reaction of dichlorodimethylsilane and hexamethylcyclotrisilazane was carried out at temperatures above 300° rather than at 175°, the chief products were silicon-linked polycyclodisilazane derivatives.



Between 285° and 334°, the total conversion to compounds n = 2 to n = 6 was 65-80%, with the proportion of the higher oligomers being increased as the final temperature of the equilibration was increased. The conversion to N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (n = 1) in the product mixture was reduced from 32.5-10.9%, when the final temperature was increased from 285°-334°. These oligomers were characterized by their n.m.r. spectra, elemental analyses, and through the preparation of derivatives.

A second series of compounds with the following structures were also isolated from the complex product mixtures:



No infrared data were reported, but n.m.r. data were used in the determination of structure of the compounds. Because the n.m.r. data were obtained in benzene rather than carbon tetrachloride, the data could not be immediately compared with Krueger's data or the data obtained here. Therefore, a similar equilibration mixture was fractionally distilled. Gas-liquid chromatographic data indicated that most of the fractions were complex mixtures, but three of the fractions were reasonably pure and were characterized by their infrared spectra and n.m.r. spectra in both benzene and carbon tetrachloride solutions and by elemental analyses. The results of the n.m.r. determinations are shown in Table VI. These data show that the chain-of-rings structure cannot be eliminated on the basis of the n.m.r. spectrum in carbon tetrachloride as a possible structure for Krueger's polymer or for the polymer prepared here earlier, since the n.m.r. spectra do not differentiate the number of rings in the chain in that solvent.

The downfield shifts and the better resolution of the peaks from spectra taken from benzene solutions do allow the correlation of the spectra of the oligomers with their structure in the way pointed out by Fink. In benzene, the progressive downfield shift of the ring-substituted methyl protons is particularly useful in determining chain length. The chemical shift for the same methyl groups in the oligomers obtained in the 175° equilibration reaction is τ 9.54, which would indicate a chain of several rings.

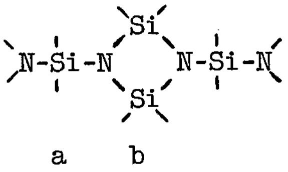
A phenomenon not reported in Fink's publication concerns the infrared spectra of these oligomers. A band that is usually observed at about 1030 cm^{-1} in cyclodisilazanes occurs as a multiplet when two or more rings are present in the chain. For example, the compound with two rings in the chain shows strong absorption at 1010 and 1040 cm^{-1}. More bands occur when more rings are present, but they are less well-defined.

This feature of the infrared spectra provides a second criterion for determining the presence of several cyclodisilazane rings in a chain. When the infrared spectra of the oligomers obtained at 175° are examined, only a single strong band is found in this region. The apparent inconsistency of the infrared and n.m.r. data has not been resolved.

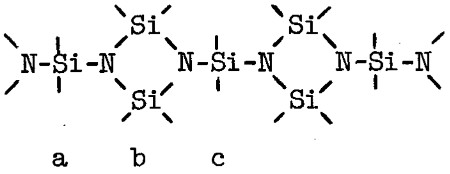
If any one of the oligocyclodisilazanes could be obtained in a reasonable conversion in an equilibration reaction, the compound would make an attractive monomer for condensation polymerizations. In the reaction above 300° with a 1:1 mole ratio of dichlorodimethylsilane to hexamethylcyclotrisilazane, the products were all extremely complex mixtures with the individual components difficult to separate and purify by distillation. The oligomers with the chlorotetramethyldisilazanyl-terminating groups were particularly difficult to separate from the α,ω-bis(chlorodimethylsilyl)-oligocyclodisilazanes. An equilibration above 300° with a 2:1 mole ratio of hexamethylcyclotrisilazane gave, as expected, an equally complex mixture with fewer volatile components. The infrared spectrum of the nonvolatile

TABLE VI

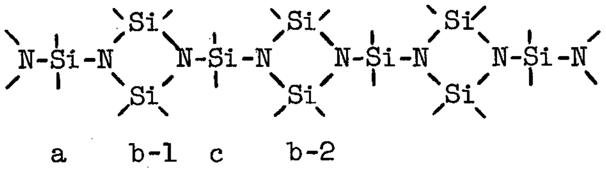
PROTON CHEMICAL SHIFTS OF CYCLODISILAZANE OLIGOMERS IN BENZENE AND CARBON TETRACHLORIDE



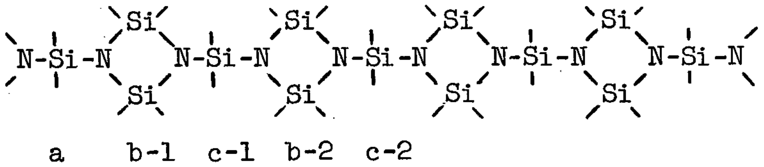
	a	b
C_6H_6	9.90	9.67
CCl_4	10.01	9.78



	a	b	c
C_6H_6	9.89	9.61	9.83
CCl_4	10.02	9.76	10.02



	a	b-1	b-2	c
C_6H_6	9.86	9.58	9.54	9.81
CCl_4	10.02	9.76	9.74	9.99

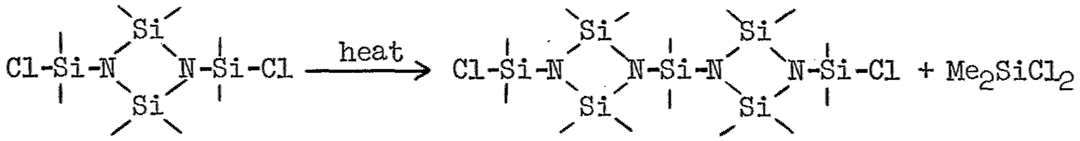


	a	b-1	b-2	c-1	c-2
C_6H_6	9.86	9.57	9.52	9.80	?
CCl_4	?	(9.75-9.77)		?	?

portion did not differ greatly from the spectrum of the equilibration product obtained at 175°.

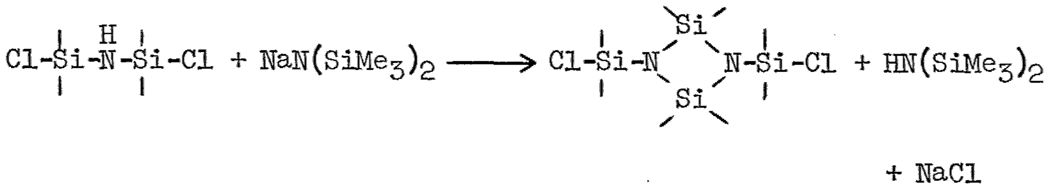
The possibility that an equilibration product could be chemically modified to produce a purer product was considered. The requirements for the modification would depend on the mechanism for the formation of chains of silicon-linked cyclodisilazane rings. Little has been clarified in the literature on the mechanism of ring formation or oligomerizations.

One possible mode of formation of the oligocyclodisilazanes could be the simple disproportionation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane or its condensation products.

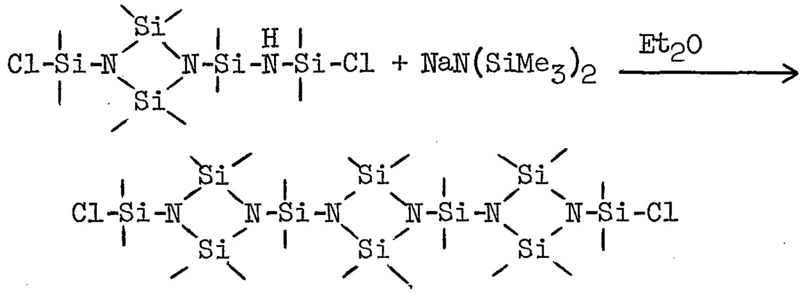


If an equilibrium existed, it could be upset by distilling the dichlorodimethylsilane from the mixture as it was formed. One attempt at such a disproportionation indicated that very little or no oligomerization occurred at 250°. This result cannot be considered as conclusive, since oligomerization occurs in the equilibration reactions above 300° and in the presence of a Lewis acid in the form of ammonium halides. Several additional experiments would clarify whether or not this route is important.

An alternate mechanism that is possible is chain extension through the base-catalyzed condensation of the terminal chlorotetramethyldisilazanyl groups. Such a reaction could proceed in a way analogous to the method described by Geymayer (Ref. 5) for the preparation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane.

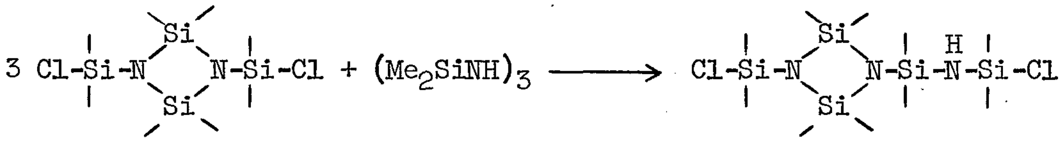


When the same base was used with N-(3-chlorotetramethyldisilazanyl)-N'-chlorodimethylsilyltetramethylcyclodisilazane at room temperature, the major product of the reaction was the cyclodisilazane oligomer (n = 3).



Again, the results of this experiment were not entirely definitive because of the lack of a pure sample of the chlorotetramethyldisilazanyl-substituted starting material and the necessity of determining the products of the experiment by g.l.c. Nonetheless, the condensation product constituted about 75% of the volatile portion of the product.

The only available source of the chlorotetramethyldisilazanyl derivatives has been from the high boiling portions of the equilibration products obtained in the preparation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, so the resources for examining this approach as a preparative method have been limited. Also lacking is the information as to how the chlorotetramethyldisilazanyl derivatives arise in the equilibration mixtures. Fink's work suggests that they might form when 1,5-hexamethyltrisilazane participates in the condensation reactions. They could also form by the reaction of chlorodimethylsilyl-terminated cyclodisilazanes with hexamethylcyclotrisilazane.



Although this question has not been thoroughly investigated experimentally, one experiment indicates that the latter reaction does occur to some extent at 175°. Additional experiments along these lines could lead to a better understanding of the equilibration and oligomerization reactions.

In view of the somewhat successful attempt at effecting ring closure by treating the disilazanyl derivative with sodium bis(trimethylsilyl)amide, an oligomer containing disilazanyl groups was treating with sodium bis(trimethylsilyl)amide under similar conditions. There was some evidence in the infrared spectrum that some ring closure had been effected, but the polymer was brittle.

III.

FUTURE WORK

On the basis of the results in this report, the following laboratory work is recommended:

1. Additional work on the arylenedisilanol-N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane condensation products in order to assure repeatability of the polymerization results when the polymeric products are not completely soluble in nonpolar solvents.

2. Other condensation reactions between arylene disilanols and functional cyclodisilazane derivatives will continue to be studied in order to obtain high-molecular-weight, soluble polymers. Structural modifications of the silazane monomer may include arylation and the use of oligomeric materials.

3. Attempts will continue to find new reactions of trisilylamines that will allow their incorporation in polymeric structures.

4. Some work will continue on the equilibration and oligomerization reaction that will lead to new information useful in preparing thermally and hydrolytically stable polymers.

IV.

EXPERIMENTAL

All chlorosilanes were redistilled before being used. Reactions were carried out in glass equipment that had been flame-dried and flushed with dry nitrogen before use. Reactants were protected from atmospheric moisture with Drierite-packed tubes or a positive pressure of dry nitrogen as needed. Elemental analyses were conducted by Spang Microanalytical Laboratory. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer and n.m.r. spectra were determined with a Varian Associates Model A60 spectrometer using cyclohexane as an internal standard.

A. Synthesis of Miscellaneous Organosilicon Monomers, Intermediates, and Samples

1. Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane: To 700 ml. of ammonia in 6,000 ml. of petroleum ether, b.p. 35-60°, cooled in a Dry Ice-isopropyl alcohol bath was added dropwise 1,161 g. (9 moles) of dichlorodimethylsilane in 2,000 ml. of petroleum ether. After the mixture was stirred overnight at room temperature and the ammonium chloride was filtered off, the solvent was distilled from the filtrate. Hexamethylcyclotrisilazane (268.5 g., 41%) distilled at 183-184° and octamethylcyclotetrasilazane (211 g., 32%) at 146-151° (35 mm.), m.p. 96-97°. Repetitions of the preparation are summarized in Table VII.

2. Hexamethyl-N-(trimethylsilyl)cyclotrisilazane: When 23 g. (1.0 g.-atom) of sodium in 500 ml. of refluxing dioxane was treated with 193 g. (0.91 mole) of hexamethylcyclotrisilazane, 125 ml. of redistilled styrene, and 109 g. (1.0 mole) of chlorotrimethylsilane by the procedure described in AFML-TR-66-116, Part II, p. 28, 173 g. (65%) of hexamethyl-(N-trimethylsilyl)cyclotrisilazane, b.p. 113° (10 mm.), n_D^{20} 1.4628, was obtained [reported b.p., 112-113° (10 mm.); n_D^{20} 1.4596] (Ref. 6).

3. Bis(methylamino)dimethylsilane: About 900 ml. (excess) of methylamine was collected in a 12-liter flask (previously flame dried under nitrogen) cooled in an isopropyl alcohol-Dry Ice bath. The amine was diluted with 3 liters of petroleum ether, b.p. 35-60°, and 645 g. (5.0 moles) of dichlorodimethylsilane in 2.5 liters of petroleum ether was added in 5 hr. The mixture was allowed to warm to room temperature and stored overnight. After the salts were filtered off and washed with petroleum ether, the solvent was distilled through a 45-cm. vacuum-jacketed column packed with berl saddles and fitted with a partial reflux head. The residue was fractionally distilled on a 1-meter spinning band column to give 394 g. (67%) of bis(methylamino)dimethylsilane boiling at 107-108°. Redistillation

TABLE VII

PREPARATION OF HEXAMETHYLCYCLOTRISILAZANE AND OCTAMETHYLCYCLOTETRASILAZANE

	Dichlorodimethylsilane	Hexamethylcyclotrisilazane			Octamethylcyclotetrasilazane		
Experiment No.	Wt. g., (moles)	Wt. g., (% yield)	b.p., °, (mm.)	n_D^{20}	Wt. g., (% yield)	b.p., °, (mm.)	m.p., °
1	1,161 (9)	351 (53)	183-184 (atm.)	1.4454	128 (19)	140 (34)	94
2	1,161 (9)	306 (47)	183-184 (atm.)	1.4454-1.4461	226 (34)	140-142 (36)	95-97
3	774 (6)	238 (54)	186-188 (atm.)	1.4452	127 (29)	136-138 (33)	96-98
4	1,161 (9)	332 (50)	188 (atm.)	1.4460	194 (30)	135-136 (30)	96

gave the pure compound boiling at 108-108.5°; n_D^{20} 1.4150; infrared spectrum, Figure 5. Nuclear magnetic resonance peaks (CCl_4) at τ 7.57 (6H, doublet, J = 7 c.p.s., $NHCH_3$) and τ 10.07 [6H, singlet, $Si(CH_3)_2$]; g.l.c. analysis (Table VIII, Method A-1) a single peak at 2.7 (reported b.p. 107-108°) (Ref. 7).

Anal. Calcd. for $C_4H_{14}N_2Si$: C, 40.62; H, 11.93; N, 23.69; Si, 23.75. Found: C, 40.81; H, 11.84; N, 23.81; Si, 23.55.

TABLE VIII

GAS-LIQUID CHROMATOGRAPHIC PROCEDURES

Method	Column	Temperature (°)	Carrier Flow
A-1	Two-Meter Column Packed With 5% SF 96 on 100/120 Mesh Gas Chrom Q	50	He, 82 ml/min
A-2		180	He, 61 ml/min
A-3		160	He, 44 ml/min
B-1	One-Meter Column Packed With 5% SE 30 on 80/100 Chromport XXX	150	N, 52 ml/min
B-2		175	N, 52 ml/min
B-3		200	N, 52 ml/min
B-4		230	N, 52 ml/min

4. Bis(methylamino)diphenylsilane: About 400 ml. (excess) of methylamine was collected in a 5-liter flask (previously flame-dried under nitrogen) in an isopropyl alcohol-Dry Ice bath. The amine was diluted with 1 liter of petroleum ether, b.p. 35-60°, and 506 g. (2.0 moles) of dichlorodiphenylsilane in 1 liter of petroleum ether was added with stirring in 2.5 hr. The mixture was allowed to warm to room temperature and was stored overnight. The salts were filtered off and washed with petroleum ether. The filtrate was stripped of solvent and the residue distilled through a 45-cm., vacuum-jacketed column to obtain 453 g. (94%) of crude bis(methylamino)diphenylsilane boiling at 122° (0.11 mm.). Fractional

distillation through a 1-meter spinning band column gave 382 g. (79%) of bis(methylamino)diphenylsilane, b.p. 103° (0.010 mm.); n_D^{20} 1.5718; infrared spectrum, Figure 6. Nuclear magnetic resonance peaks (CCl_4) at τ 2.31-2.87 (10H, multiplet, C_6H_5), τ 7.38 (6H, doublet, J = 7 c.p.s., $NHCH_3$), and τ 9.08 (broad, NH); g.l.c. analysis (Table VIII, Method A-2) a single peak at 6.2 min. [reported b.p. 108-112° (0.1 mm.); n_D^{28} 1.5690] (Ref. 7).

Anal. Calcd. for $C_{14}H_{18}N_2Si$: C, 69.37; H, 7.48; N, 11.56; Si, 11.59. Found: C, 69.20; H, 7.55; N, 11.62; Si, 11.64.

5. α,ω-Dichlorosiloxanes: After a mixture of 296 g. (2.00 moles) of diethoxydimethylsilane, 1,132 g. (8.78 moles) of dichlorodimethylsilane, and 3.0 g. of ferric chloride was heated at 71° for 10 hr., ethyl chloride was no longer evolved. Upon distillation, 555 g. of dichlorodimethylsilane was recovered, and 396 g. of oligomers boiling between 53 and 140° (40 mm.) was obtained. Fractional distillation of the oligomers gave the following compounds: 1,3-Dichlorotetramethyldisiloxane, 85 g., b.p. 56-57° (40 mm.) [reported, 41° (20 mm.)] (Ref. 8), n.m.r. peaks (CCl_4) at τ 9.49 [singlet, $Si(CH_3)_2$]; 1,5-dichlorohexamethyltrisiloxane, 154 g., b.p. 94-95° (40 mm.) [reported, 79° (20 mm.)] (Ref. 8), n.m.r. peak (CCl_4) at τ 9.83 [6H, singlet, $OSi(CH_3)_2O$] and τ 9.56 [12H, singlet, $ClSi(CH_3)_2O$]; and 1,7-dichlorooctamethyltetrasiloxane, 82 g., b.p. 125-126° (40 mm.) [reported, 111° (20 mm.)] (Ref. 8), n.m.r. peaks (CCl_4) at τ 9.86 [12H, singlet, $OSi(CH_3)_2O$] and τ 9.56 [12H, singlet, $ClSi(CH_3)_2O$].

6. Dimethylphenylsilanol: A solution of dimethylethoxyphenylsilane [prepared by treating 65.6 g. (0.38 mole) of chlorodimethylphenylsilane with 80 ml. of dry ethanol and purging the mixture for 2 hr. with nitrogen to remove hydrogen chloride] was added to a solution of 153 g. (3.83 moles) of sodium hydroxide in 255 ml. of methanol and 300 ml. of water. After the solution was stirred for 1 hr., it was added dropwise to 346 g. of 85% phosphoric acid in 3 kg. of ice and 1.5 liters of water. Fractional distillation of the ether extract of the hydrolysate afforded 48.3 g. (83%) of dimethylphenylsilanol, b.p. 100-102° (13 mm.); n_D^{20} 1.5139; infrared spectrum, Figure 7; n.m.r. peaks (DMSO) at τ 9.63 [6H, singlet, $Si(CH_3)$], τ 4.06 (1H, singlet, OH), and τ 2.20-2.65 (5H, multiplet, C_6H_5) [reported b.p. 101-101.5° (14 mm.), n_D^{25} 1.5100] (Ref. 9). In a second smaller scale experiment, the yield from 17.1 g. (0.10 mole) of chlorodimethylphenyl silane was 61%.

B. Synthesis of Arylenedisilanols

1. p-Phenylenebis(ethoxydimethylsilane): A solution of 500 g. (2.13 moles) of p-dibromobenzene in 1,100 ml. of dry tetrahydrofuran was added in rapid drops to 105 g. (2.42 g.-atoms) of previously activated

magnesium covered with 200 ml. of tetrahydrofuran. The reaction proceeded exothermally. After the addition was complete, the mixture was refluxed for 2 hr., then treated with 635 g. (4.26 moles) of diethoxydimethylsilane in rapid drops. An additional exothermic reaction occurred during the addition. The product was refluxed overnight, cooled to room temperature, and filtered to remove the unchanged magnesium. After the filtrate was extracted exhaustively with petroleum ether, b.p. 60-90°, evaporation of the combined filtrate and petroleum ether extracts on a rotary evaporator and flash distillation of the residue afforded 355 g. (59%) of the crude product. Fractional distillation gave 292 g. (49%) of p-phenylenebis-(ethoxydimethylsilane), b.p. 112-113° (2 mm.), n_D^{20} 1.4780, [reported, b.p. 119-120° (3.6 mm.), n_D^{20} 1.4782] (Ref. 10).

2. p-Phenylenebis(hydroxydimethylsilane): A solution of 292 g. (1.04 moles) of p-phenylenebis(dimethylethoxysilane) in 300 ml. of 95% ethanol was added to a solution of 208 g. of sodium hydroxide in 730 ml. of methanol and 83 ml. of water. To this mixture was added a solution of 208 g. of sodium hydroxide in 810 ml. of water. After 1 hr., the solution was added to a stirred mixture of 4 kg. of ice, 3.3 liters of water, and 870 g. of syrupy phosphoric acid. When the precipitate diol was stored overnight, filtered off, and dried under reduced pressure, 229 g. (98%) of the crude material was obtained. Two recrystallizations from toluene afforded 109 g. (72%) of p-phenylenebis(hydroxydimethylsilane), m.p. 135°, (reported, 136-137°) (Ref. 10).

3. Bis(p-ethoxydimethylsilylphenyl) ether: A solution of 350 g. (1.07 moles) of bis(p-bromophenyl) ether in 550 ml. of dry tetrahydrofuran was added to 57.3 g. (2.36 g.-atoms) of previously activated magnesium covered with 100 ml. of dry tetrahydrofuran at a rate which maintained an exothermic reaction. After the addition was complete, the mixture was refluxed for 1 hr., treated with 317 g. (2.14 moles) of diethoxydimethylsilane over a period of 20 min., and then refluxed overnight. After the mixture was filtered to remove the remaining magnesium, the solvent was evaporated in a rotary evaporator and the residue was washed exhaustively with petroleum ether, b.p. 60-90°. The extracts were evaporated and flash-distilled to obtain the crude ethoxysilane. Fractional distillation afforded 191 g. (47%) of bis(p-ethoxydimethylsilylphenyl) ether, b.p. 136-140° (0.04 mm.), n_D^{20} 1.5200 [reported, b.p. 141-142° (0.1 mm.) n_D^{20} 1.5213] (Ref. 10).

A repetition of the experiment, but with twice the quantities of reactants, afforded 405 g. (51%) of bis(p-ethoxydimethylsilylphenyl) ether, b.p. 163-167° (0.3 mm.), n_D^{20} 1.5202.

A final preparation with 500 g. (1.53 moles) of bis(p-bromophenyl) ether gave 240 g. (42%) of bis(p-ethoxydimethylsilylphenyl) ether, b.p. 141-143° (0.06 mm.), n_D^{20} 1.5195.

4. Bis(p-dimethylhydroxysilylphenyl) ether: Bis(p-ethoxydimethylsilylphenyl) ether [191 g. (0.511 mole)] in 100 ml. of ethanol was treated with 102 g. (2.55 moles) of sodium hydroxide in 350 ml. of methanol and 40 ml. of water, followed by 102 g. (2.55 moles) of sodium hydroxide in 370 ml. of water. When the resulting sodium salt was hydrolyzed with 4 kg. of ice and 2 liters of water containing 475 g. of syrupy phosphoric acid, 157 g. (98%) of crude bis(p-dimethylhydroxysilylphenyl) ether was obtained. In an attempt to purify this material by recrystallizations from mixtures of toluene and petroleum ether, it polymerized during a third recrystallization, to 100 g. of a rubbery material. In each of two other experiments, 203 g. of bis(p-ethoxydimethylsilylphenyl) ether was hydrolyzed and quantitative conversions to the crude diol were obtained. Recrystallization of the latter afforded 150 g. and 166 g. of bis(p-dimethylhydroxysilylphenyl) ether, respectively. These samples were similarly vacuum-dried at 50° for seven days and found to exhibit siloxane groups. To a solution of 232 g. (4.13 moles) of potassium hydroxide in 2 liters of 95% ethanol was added 262 g. (0.825 mole) of the partially polymerized bis(p-dimethylhydroxysilylphenyl) ether. The mixture was heated to reflux for 120 min. to effect solution. The soluble portion was transferred to an additional funnel and added slowly to a solution of 422 g. (3.10 moles) of monobasic potassium phosphate in a mixture of 3 liters of water and 3 kg. of ice. After the mixture had warmed to room temperature overnight, the crude product was filtered off, mixed and subsequently filtered three times from 2-liter portions of distilled water. The residue was air-dried overnight, and dried under reduced pressure at room temperature to remove the remaining water. A total of 249 g. (95%) of bis(p-dimethylhydroxysilylphenyl) ether, m.p. 101-103°, was obtained. Recrystallization of the material in three portions from 1 liter of petroleum ether, b.p. 60-90°, and 1.5 liters of toluene gave 219 g. (84%) of bis(p-dimethylhydroxysilylphenyl) ether, m.p. 103-105°; differential thermal analysis trace, a single endotherm at 104°. The infrared spectrum is reported in Figure 8.

Repetition of the procedure with 129 g. of the impure diol gave 60.4 g. of bis(p-dimethylhydroxysilylphenyl) ether, m.p. 103-104°.

C. Synthesis of Cyclodisilazanes

1. N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane: A mixture of 158 g. (0.721 mole) of hexamethylcyclotrisilazane and 139 g. (1.078 mole) of dichlorodimethylsilane was heated at 175° for 77 hr. To the mixture was added 200 ml. of petroleum ether, b.p. 30-60°, and the

soluble portion was separated from the ammonium chloride and distilled. N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane (159.5 g., 60%) boiling at 151-164° (45 mm.) was collected. The fractions, boiling points, weights, and g.l.c. analyses are reported in Table IX.

Repetition of the procedure in which 155.5 g. (0.5325 mole) of octamethylcyclotetrasilazane and 137.4 g. (0.165 mole) of dichlorodimethylsilane were heated at 175° for 65 hr., gave 171.0 g. (65%) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane. The fractions, weights, boiling point ranges, and g.l.c. analyses are reported in Table X.

A mixture of 65.7 g. (0.30 mole) of hexamethylcyclotrisilazane and 77.4 g. (0.60 mole) of dichlorodimethylsilane was heated under nitrogen to 225° in 24 hr. The portion soluble in 125 ml. of petroleum ether (60-90°) was stripped of solvent and after a short-path distillation, gave 55.9 g. (50% based on hexamethylcyclotrisilazane) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, boiling range 150-163° (45 mm.), and 21.2 g. of higher boiling material, boiling range 92-166° (0.1 mm.). The latter contained N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (17%), N-(3-chlorotetramethyldisilazanyl)-N'-(chlorodimethylsilyl)tetramethylcyclodisilazane (52%), and oligo-α,ω-(chlorodimethylsilyl)tetramethylcyclodisilazane (n = 2) (31%), as well as other peaks as determined by g.l.c. analysis (Table VIII, Method B-3).

In other preparations, the results recorded in Table XI were obtained.

2. N,N'-Bis(dimethylsilyl)tetramethylcyclodisilazane: To 3.9 g. (0.102 mole) of lithium aluminum hydride in 250 ml. of diethyl ether was added 33.8 g. (0.102 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 100 ml. of ether in 2 hr. The temperature was maintained below 30° during the addition. After the mixture was stirred overnight at room temperature and the solvent was removed at reduced pressure, the residue was distilled at 37-39° to obtain 22.6 g. of the crude product, which was collected in a Dry Ice trap. The distillation residue was not heated above 60°. Fractional distillation gave 17.4 g. (65%) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane, b.p. 79° (14 mm.), n_D^{20} 1.4309 [reported b.p. 65-66° (8 mm.), n_D^{20} 1.4312] (Ref. 11); g.l.c. analysis (Table VIII, Method A-3), a single peak at 1.2 min. The infrared spectrum is reported in Figure 9.

In another experiment, to a suspension of 5.7 g. (0.150 mole) of lithium aluminum hydride in 330 ml. diethyl ether was added 49.8 g. (0.150 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 2 hr. After the mixture was stirred overnight at room temperature and the solvent removed at atmospheric pressure, 17 g. of a liquid, b.p. 45-60° (1 mm.), was collected in a Dry Ice trap.

TABLE IX

G.L.C. ANALYSIS OF N,N'-BIS(CHLORODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE (Experiment No. 1)

Fraction	B.P.	Weight	G.L.C.[a] Peak No. and Area Percentage				
No.	(45 mm.)	(g.)	1[b]	2[c]	3[b]	4[b]	5[d]
1	151-152°	19.0	< 1	98	< 1	< 1	1
2	152°	15.0	-	--	-	-	-
3	154°	12.7	7	89	1	< 1	3
4	154°	10.5	< 1	99	< 1	< 1	< 1
5	154°	9.8	6	90	< 1	< 1	4
6	154-156°	10.1	-	98	< 1	-	2
7	156°	8.1	-	99	-	-	< 1
8	156°	10.3	-	99	< 1	-	< 1
9	156°	8.7	-	99	< 1	-	< 1
10	158°	8.4	-	97	1	-	2
11	160°	9.3	-	97	1	-	2
12	160°	10.1	-	96	1	-	3
13	160°	9.7	-	95	1	-	4
14	160-162°	8.5	-	89	2	1	8
15	164-166°	9.3	-	80	2	2	16

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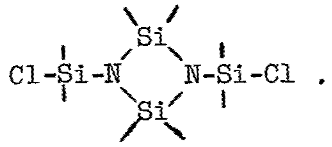
[a] G.l.c. method: Table VIII, Method B-1.

[b] Unidentified.

[c] 

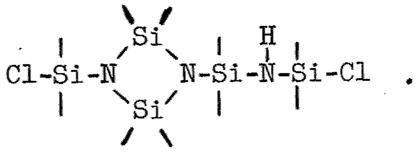
[d] 

TABLE X

G.L.C. ANALYSIS OF N,N'-BIS(CHLORODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE
(Experiment No. 2)

Fraction No.	B.P. (45 mm.)	Weight (g.)	G.L.C.[a] Peak No. and Area Percentage				
			1[d]	2[c]	3[b]	4[b]	5[d]
1	140-145°	45.0	17	72	3	1	6
2	146-153°	20.9	5	88	3	2	3
3	154-156°	42.9	3	89	4	1	4
4	156°	17.3	< 1	91	4	1	4
5	158-160°	22.0	< 1	84	6	1	9
6	160-168°	22.9	< 1	77	7	1	15

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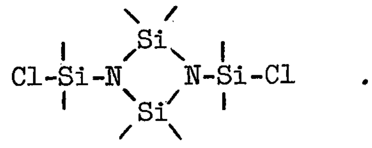
[a] G.l.c. method: Table VIII, Method B-1.

[b] Unidentified.

[c]



[d]

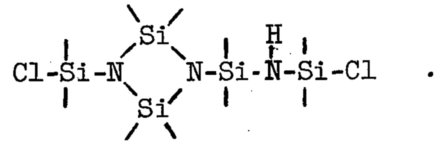


TABLE XI

PREPARATION OF N,N'-BIS(CHLORODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE

Experiment No.	Dichlorodimethylsilane Wt., g.; (mole)	Hexamethylcyclotrisilazane (A) or Octamethylcyclotetrasilazane (B) Wt., g.; (mole)	N,N'-Bis(chlorodimethylsilyl)-tetramethylcyclodisilazane Wt., g.; (% yield); b.p., °; (mm.)
1	140 (109)	(A) 158 (0.72)	179 (67) 148-169 (43)
2	137 (107)	(B) 156 (0.53)	161 (61) 150-163 (45)
3	137 (1.07)	(B) 156 (0.53)	163 (62) 154-162 (45)
4	61.2 (0.47)	(B) 69.1 (0.24)	66 (56) 150-166 (45)
5	137 (1.07)	(B) 155 (0.53)	126 (48) 146-164 (45)
6	139 (1.08)	(A) 158 (0.72)	190 (71) 146-173 (45)

Repetition of the procedure with 46.5 g. (0.140 mole) of N,N'-bis (chlorodimethylsilyl)tetramethylcyclodisilazane and 5.30 g. (0.140 mole) of lithium aluminum hydride gave 19.1 g. of a liquid boiling at 32-35° (0.5 mm.). When the unpurified products from the two experiments were combined and distilled on a 3-ft. spinning band column, 29.8 g. (39%) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane boiling at 77-78° (14 mm.) was obtained, n_D^{20} 1.4310, g.l.c. (Table VIII, Method A-3), a single peak at 1.2 min.

Repetition of the procedure with 34.3 g. (0.1037 mole) of N,N'-bis-(chlorodimethyl)tetramethyldisilazane and 3.9 g. (0.1037 mole) of lithium aluminum hydride gave 14.2 g. (52%) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane, b.p. 71-72° (10 mm.), n_D^{20} 1.4302, g.l.c. analysis (Table VIII, Method A-3), a single peak at 1.3 min.

3. N,N'-Bis(aminodimethylsilyl)tetramethylcyclodisilazane: Repetition of the procedure described in AFML-TR-66-116, Part II, p. 34, with 61.3 g. (0.19 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane afforded 23.9 g. (44%) of N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane, b.p. 95° (5 mm.), m.p. 36-38° (sealed tube) [reported, b.p. 99-100° (7 mm.), m.p. 33-35°] (Ref. 11); g.l.c. (Table VIII, Method A-3), a single peak at 3.2 min. An additional 9.2 g. of less pure material was also obtained. The infrared spectrum of the pure material is reported in Figure 10.

In another experiment, when 23.3 g. (0.0705 mole) of distilled N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane was treated with ammonia, 11.7 g. (57%) of N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane boiling at 98-100° (6 mm.), m.p. 35-37°, was obtained; g.l.c. analysis (Table VIII, Method A-3) showed N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane at 3.0 min., 92%, and an unknown impurity at 3.9 min., 8.0%.

4. N,N'-bis(dimethylmethylaminosilyl)tetramethylcyclodisilazane: Repetition of the procedure described in AFML-TR-66-116, Part II, p. 34, with 62.8 g. (0.19 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane afforded 44.1 g. (73%) of N,N'-bis(dimethylmethylaminosilyl)-tetramethylcyclodisilazane, b.p. 109-110° (3 mm.), n_D^{20} 1.4515 [reported, b.p. 118° (8 mm.), n_D^{20} 1.4518, AFML-TR-66-116, Part II] ; g.l.c. (Table VIII, Method A-3), a single peak at 6.0 min. The infrared spectrum is reported in Figure 11.

When 23.4 g. (0.0708 mole) of distilled N,N'-bis(chlorodimethylsilyl) tetramethylcyclodisilazane was treated with methylamine, 15.1 g. (67%) of N,N'-bis(dimethylmethylaminosilyl)tetramethylcyclodisilazane boiling at 119-121° (8 mm.), n_D^{20} 1.4515, was obtained; g.l.c. analysis (Table VIII, Method A-3) indicated the compound was 96.8% pure with a peak at 5.2 min., and contained 3.2% of an unidentified impurity at 1.5 min.

A repetition of the experiment with 39.3 g. of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane gave 21.6 g. (57%) of N,N'-bis-(dimethylmethylaminosilyl)tetramethylcyclodisilazane, b.p. 107-109° (5 mm.), n_D^{20} 1.4517. A g.l.c. analysis indicated the material was pure. A forerun, 10.5 g., contained 72% of the bis(methylamino)cyclodisilazane.

5. N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane: A solution of 60 ml. (excess) of dimethylamine in 100 ml. of petroleum ether, b.p. 35-60°, which was cooled in a Dry Ice-isopropyl alcohol bath was treated with a solution of 60.5 g. (0.18 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 200 ml. of petroleum ether. After the addition was complete, the mixture was warmed to room temperature, the salts were filtered off, and the solvent was evaporated. After a preliminary distillation, the compound was distilled on a spinning band column to obtain 34.6 g. (54%) of N,N'-bis(dimethylaminodimethylsilyl)-tetramethylcyclodisilazane, b.p. 118-119° (4 mm.), n_D^{20} 1.4529-1.4531 [reported (AFML-TR-66-116, Part II), b.p. 122-123° (5 mm.), n_D^{20} 1.4530]. The infrared spectrum is reported in Figure 12.

When excess methylamine in 100 ml. of petroleum ether, b.p. 35-60°, was treated with 55.1 g. (0.167 mole) of distilled N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, there was obtained 26.6 g. (46%) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, b.p. 109° (2 mm.), n_D^{20} 1.4530, g.l.c. analysis (Table VIII, Method A-3), a single peak at 7.2 min.

The procedure was repeated with 63.5 g. (0.19 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane. When the product was combined with 32.5 g. of the impure cyclodisilazane derivative from previous experiments and fractionally distilled, 50.1 g. of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, b.p. 118-120° (3.8 mm.), n_D^{20} 1.4530, was obtained; g.l.c. analysis (Table VIII, Method A-3), a single peak at 8.6 min.

A mixture of 104 g. (0.80 mole) of dichlorodimethylsilane and 118 g. (0.40 mole) of octamethylcyclotetrasilazane was equilibrated at 175° for 52 hr. A solution of the soluble portion of the equilibration product in 500 ml. of petroleum ether, b.p. 35-60°, was added to a solution of 200 ml. (excess) of dimethylamine in 500 ml. of petroleum ether. After a preliminary distillation, the product was fractionally distilled on a spinning band column to obtain 88 g. (42%) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, b.p. 113-114° (4 mm.), n_D^{20} 1.4531-1.4535, g.l.c. analysis (Table VIII, Method A-3) showed a single peak at 7.1 min.

6. N,N'-Bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane: To 18.6 g. (0.254 mole) of freshly distilled diethylamine in 75 ml. of petroleum ether, b.p. 60-90°, was added dropwise 159 ml. of 1.6M butyllithium in petroleum ether while the temperature was kept below 30°. The mixture was then treated with 42.0 g. (0.127 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 75 ml. of petroleum ether in 1 hr., stirred for 0.5 hr. at room temperature, and heated at reflux for 2 hr. After the salts were filtered off in a Celite-packed filter and the solvent was evaporated, a preliminary distillation gave 35.1 g. of a liquid, b.p. 110-126° (0.7 mm.). Fractional distillation on a spinning band column gave 26.3 g. (51%) of N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane, b.p. 83° (0.1 mm.), n_D^{20} 1.4590 [reported b.p. 164° (12 mm.) n_D^{20} 1.4584 (Ref. 12)]; n.m.r. peaks (CCl_4) at τ 10.06 [12H, singlet, $Si(CH_3)_2$ pendant], τ 9.82 [12H, singlet, $Si(CH_3)_2$ring], τ 9.06 (12H, triplet, J = 7, $-CH_3$), and τ 7.13 (8H, quadruplet, CH_2); g.l.c. (Table VIII, Method A-3), a single peak at 8.8 min.; infrared spectrum Figure 13.

7. N,N'-Bis(anilinodimethylsilyl)tetramethylcyclodisilazane: Repetition of the procedure described in AFML-TR-66-116, Part III, p. 27, with 24.1 g. (0.26 mole) of freshly distilled aniline and 21.4 g. (0.065 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane afforded 7.7 g. (27%) of impure N,N'-bis(anilinodimethylsilyl)tetramethylcyclodisilazane, b.p. 170-186°, m.p. 95-104°. Recrystallization of the distillate from petroleum ether, b.p. 30-60°, gave 3.7 g. (13%) of purer material, m.p. 105-106°.

8. N,N'-Bis(dimethylphenoxysilyl)tetramethylcyclodisilazane: Repetition of the procedure described in AFML-TR-66-116, Part II, p. 36, with 22.4 g (0.70 mole) of N,N'-bis(methylaminodimethylsilyl)tetramethylcyclodisilazane and 13.2 g. (0.14 mole) of phenol afforded 13.6 g. (44%) N,N'-bis(dimethylphenoxysilyl)tetramethylcyclodisilazane, b.p. 148-150° (0.5 mm.), m.p. 44-45°.

9. N,N'-Bis(dimethylphenylsiloxydimethylsilyl)tetramethylcyclodisilazane: To 11.8 g. (0.0340 mole) of N,N'-bis(dimethyldimethylaminosilyl)tetramethylcyclodisilazane in 35 ml. of toluene was added in 1 hr. 10.3 g. (0.0680 mole) of dimethylphenylsilanol in 35 ml. of toluene. The solution was stirred 0.5 hr. at 26°, heated slowly to 80° (1 hr.), and maintained at 80° for 1 hr. After the solvent was stripped off, fractional distillation of the residue gave 2.2 g. of an unidentified material boiling between 132-170° (0.018 mm.) and 12.6 g. (66%) of N,N'-bis(dimethylphenylsiloxydimethylsilyl)tetramethylcyclodisilazane, b.p. 178-180° (0.018 mm.), n_D^{20} 1.4869, n.m.r. peaks (CCl_4) at τ 10.02 [12H, singlet, cyclodisilazane $Si(CH_3)_2$], τ 9.78 [12H, singlet, $OSi(CH_3)_2O$], τ 9.68 [12H, singlet, $C_6H_5Si(CH_3)_2O$], and τ 2.43-2.86 (10H, multiple, C_6H_5).

Although the infrared spectrum of the distillate (Figure 1) was consistent with the structure, adsorptions were evident in the infrared spectrum of the residue (2.2 g.) indicating the presence of Si_2N (915 and 945 cm^{-1}, strong) and Si_2NH (1180 and 3360 cm^{-1}, weak) groups (Figure 14).

Anal. Calcd. for $C_{24}H_{46}N_2O_2Si_6$: C, 51.18; H, 8.23; N, 4.98; Si, 29.93. Found: C, 51.00; H, 8.12; N, 4.88; Si, 29.37.

10. N,N'-Bis(acetamidodimethylsilyl)tetramethylcyclodisilazane (attempted): To a mixture of 6.85 g. (0.116 mole) of acetamide in 40 ml. of freshly dried and redistilled triethylamine was added 19.1 g. (0.058 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 40 ml. of toluene in 1 hr. After an additional 100 ml. of toluene was added, the mixture was stirred for 4 hr. at room temperature, filtered to remove the amine salt, and the solvent was distilled off. The residue (3.9 g.) did not distill below 200° (0.5 mm.) and showed no carbonyl adsorption in its infrared spectrum.

In a modification of the experiment using 34.2 g. (0.103 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, the mixture was stirred for 1 hr. at room temperature, then heated at 90° for 1.5 hr. When the product was distilled, 4.3 g. was collected boiling between 95-165° (0.5 mm.). Carbonyl adsorption was evident in the infrared spectrum of the distillate.

A mixture of 18.5 g. (0.0530 mole) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, 6.3 g. (0.1060 mole) of acetamide, and 20 ml. of toluene was heated at 110° for 15 hr. Dimethylamine was evolved during the heating period. After the solvent was distilled off, an infrared spectrum of the residue showed bands at 1170 and 935 cm^{-1} (Si_2NH), 1010-1090 cm^{-1}, broad (SiOSi), but the cyclodisilazane bands expected at 880 and 1020 cm^{-1} were missing.

11. N,N'-Bis[dimethyl(trimethylsilyl)amino] tetramethylcyclodisilazane (attempted): After a solution of 14.6 g. (0.05 mole) of N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane in 90 ml. of toluene was treated with 14.7 g. (0.1 mole) of bis(trimethylsilyl)acetamide and the mixture was stirred 3.5 hr. at room temperature, the solvent was evaporated, and the residue was distilled rapidly to obtain 23.3 g. of product boiling in the range of 80-140° (0.4 mm.). Redistillation afforded a series of fractions boiling over the range of 90-134° (0.2 mm.). Although the infrared spectra of all the fractions contained bands that could be correlated with the desired structure, they also contained carbonyl adsorption. The n.m.r. spectra of the fractions were complex and could not be interpreted to confirm the structure.

D. Synthesis of Trisilylamines and Their Derivatives

1. Bis(chlorodimethylsilyl)trimethylsilylamine: To a solution of 71.2 g. (1.95 moles) of hydrogen chloride in 500 ml. of dry ether was added 94.5 g. (0.325 mole) of hexamethyl-(N-trimethylsilyl)cyclotrisilazane over a period of 1.5 hr. while the mixture was maintained at -60°. The mixture was warmed to room temperature, filtered, and the solvent was distilled. Fractional distillation afforded 59.8 g.(68%) of bis(chlorodimethylsilyl)-trimethylsilylamine, b.p. 99-100° (10 mm.) [reported, 104-105° (12 mm.)] (Ref. 13).

In a repetition of the experiment, a solution of 52.5 g. (0.18 mole) of hexamethyl-(N-trimethylsilyl cyclotrisilazane)in 200 ml. of ether was treated with 39.4 g. (1.08 moles) of hydrogen chloride in 200 ml. of ether to give 31.0 g. (64%) of bis(chlorodimethylsilyl)trimethylsilylamine, b.p. 103° (11 mm.).

2. N-Methyl-N'-trimethylsilyltetramethylcyclodisilazane: To a solution of 25 ml. (excess) of methylamine in 200 ml. of petroleum ether, b.p. 35-60°, was added 44.8 g. (0.155 mole) of bis(chlorodimethylsilyl)trimethylsilylamine in 125 ml. of petroleum ether while the temperature was maintained below -20°. When the mixture was warmed to room temperature, the excess methylamine distilled. The salts were filtered off, and the filtrate was evaporated on a rotary evaporator at room temperature. The residue was first distilled at a temperature sufficiently low that the pot was not heated above 40°, then fractionally distilled to obtain 28.3 g. (79%) of N-methyl-N'-trimethylsilyltetramethylcyclodisilazane, b.p. 48° (7 mm.), m.p. -43 to -40°, n_D^{20} 1.4272 [reported, b.p. 52-53° (7 mm.), n_D^{20} 1.4273] (Ref. 13).

3. N-Phenyl-N'-trimethylsilyltetramethylcyclodisilazane: To 3.16 g. (0.34 mole) of aniline in 50 ml. of ether was added 43 ml. (0.068 mole) of 1.6N n-butyllithium in hexane during 0.75 hr. The temperature of the reaction mixture was maintained at 30-34° with the occasional use of a water bath. After about one equivalent of butyllithium had been added, the reaction mixture changed from a light brown to a greenish-yellow color, and near the end of the addition, the solution developed a yellow color and a precipitate formed. The reaction mixture was stirred for 2.5 hr., and 9.3 g. (0.34 mole) of bis(chlorodimethylsilyl)trimethylsilylamine in 50 ml. of ether was then added in 1 hr. as the color of the reaction mixture changed from yellow to purple. The reaction mixture was refluxed for 2 hr. and filtered to obtain 2.9 g. (100%) of lithium chloride. When the filtrate was evaporated, 9.6 g. (96%) of crude N-phenyl-N'-trimethylsilyltetramethylcyclodisilazane remained as a reddish solid residue. Two recrystallizations from n-pentane gave 5.1 g. (51%) of the purified compound, m.p. 95-96° (reported, m.p. 95°) (Ref. 13).

4. Tris(chlorodimethylsilyl)amine: A solution of 8.25 g. (0.226 mole) of anhydrous hydrogen chloride in 100 ml. of ether was added to a solution of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 100 ml. of ether at -60°. The addition required 1 hr., and the mixture was stirred for an additional hour. After the mixture was warmed to 25°, it was filtered, stripped of solvent, and the residue was distilled to obtain 9.6 g. (55%) of tris(chlorodimethylsilyl)amine, b.p. 103° (10 mm.); m.p. 85-90°; d.t.a. transitions at 15° and 85-91°; n.m.r. peak (CCl_4) at τ 9.29 [singlet, $Si(CH_3)_2$] [reported, b.p. 105° (10 mm.), m.p. 73-75°, n.m.r. peak at τ 9.33] (Ref. 1).

5. N-Methyl-N'-dimethylmethylaminosilyltetramethylcyclodisilazane: To excess methylamine in 100 ml. of petroleum ether, b.p. 35-60°, at -60° was added 15.3 g. (0.0496 mole) of tris(chlorodimethylsilyl)amine in 100 ml. of petroleum ether in 0.5 hr. The mixture was allowed to warm to 25° and was filtered. Evaporation of the filtrate afforded 13.4 g. of a clear liquid residue. A low-temperature distillation (40° or lower) at reduced pressure gave 12.0 g. of distillable material, which was collected in a -60° bath. A second distillation gave the following fractions: (a) 0.7 g., b.p. 63-65° (5 mm.), n_D^{20} 1.4358; (b) 4.2 g., b.p. 65-66° (5 mm.), n_D^{20} 1.4398; (c) 3.4 g., b.p. 66° (55 mm.), n_D^{20} 1.4402; and (d) 2.3 g., b.p. 67° (5 mm.), n_D^{20} 1.4415. Fractions b, c, and d were identified as impure N-methyl-N'-dimethylmethylaminosilyltetramethylcyclodisilazane, 9.9 g. (81%); infrared absorptions (neat) at 3450 (-NH), 1250 and 795 (CH_3Si), 875 and 1070 (cyclodisilazane, Si_2N-CH_3), and an impurity at 930 cm^{-1} (Si_2NH); n.m.r. peaks (CCl_4) at τ 10.05 (pendant CH_3Si), τ 9.82 (cyclodisilazane ring CH_3Si), τ 7.62-7.51, four peaks (CH_3NH and NCH_3), and τ 9.94 (unidentified impurity, weak). The g.l.c. analysis (Table VIII, Method A-3) showed 10% impurity in b, 12% in c, and 24% in d.

6. Tris(dimethylaminodimethylsilyl)amine: Excess methylamine in 100 ml. of petroleum ether, b.p. 35-60°, cooled in a Dry Ice-isopropyl alcohol bath was treated by dropwise addition with a solution of 9.6 g. (0.030 mole) of tris(chlorodimethylsilyl)amine in 50 ml. of petroleum ether. The mixture was allowed to warm up to room temperature, filtered, and distilled to obtain 4.0 g. of forerun boiling at 67-110° (6 mm.) and 2.0 g. (20%) of tris(dimethylaminodimethylsilyl)amine boiling at 100-103° (0.4 mm.), n.m.r. peaks (CCl_4) at τ 9.86 [18H, singlet, $Si(CH_3)_2$] and τ 7.60 [18H, singlet, $N(CH_3)_2$] [reported, b.p. 100° (0.6 mm.) and n.m.r. peaks at τ 9.86 and τ 7.60] (Ref. 10).

7. Bis(3-phenyltetramethyldisiloxanyl)trimethylsilyl amine and pentamethylphenyldisiloxane: A mixture of 8.7 g. (0.030 mole) of N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane and 13.7 g. (0.090 mole) of dimethylphenylsilanol was heated to 150° in 1 hr. and at 150° for 4 hr. Distillation

gave the following fractions: (a) 12.8 g., b.p. 96-100° (15 mm.); (b) 5.9 g., b.p. 104-134° (0.05 mm.); and (c) 2.3 g., b.p. 138-152° (0.05 mm.). Since the infrared spectra of all fractions showed strong absorption at 885 cm^{-1} and 1025 cm^{-1} (cyclodisilazane), the fractions were combined and heated at 150° for an additional 8 hr. A second distillation gave the following fractions: (a) 10.8 g., b.p. 94-98° (15 mm.), a mixture of N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane, dimethylphenylsilanol, and pentamethylphenyldisiloxane; (b) 3.5 g., boiling at 98-114° (0.5 mm.), tentatively identified as impure 1,3-diphenyltetramethyldisiloxane; (c) 2.3 g., boiling at 118-134° (0.5-0.1 mm.), unidentified; and (d) 2.9 g. (19%), b.p. 160-166° (0.1 mm.), identified as bis(3-phenyltetramethyldisiloxanyl)-trimethylsilyl amine, n.m.r. peaks (CCl_4) at τ 9.92 [12H, singlet, $NSi(C\underline{H}_3)_2O$], τ 9.89 [9H, singlet, $NSi(CH_3)_3$], τ 9.65 [12H, singlet, $C_6H_5(CH_3)_2SiO$], and τ 2.33-2.75 [10H, multiplet, C_6H_5]; infrared spectrum Figure 15. Fraction (a) showed infrared absorptions at 3350 cm^{-1} (OH), 1420 and 1118 cm^{-1} (C_6H_5), 1050 cm^{-1} (SiOSi), and 885 and 1025 cm^{-1} (cyclodisilazane); (b) had bands at 1420 and 1118 cm^{-1} (C_6H_5), 1050 cm^{-1}, broad (SiOSi), and 925 and 950 cm^{-1} (Si_2N); and (c) had bands at 1420 and 1180 cm^{-1} (C_6H_5), and 1050 cm^{-1} (SiOSi), and 925 and 950 cm^{-1} (Si_2N).

Anal. Calcd. for $C_{23}H_{43}NO_2Si$: C, 54.58; H, 8.56; N, 2.76; Si, 27.75. Found: C, 54.60; H, 8.75; N, 2.81; Si, 27.70.

8. Tris(3-phenyltetramethyldisiloxany)amine (attempted): A mixture of 6.4 g. (0.020 mole) of N,N'-bis(dimethylmethylaminosilyl)tetramethylcyclodisilazane and 15.2 g. (0.1 mole) of dimethylphenylsilanol was heated at 110° for 18 hr. The evolution of methylamine was noted. A flash distillation gave 15.6 g. of product boiling from 86° (0.3 mm.) to 174° (0.03 mm.). Redistillation gave the following fractions: (a) 6.3 g. of impure 1,5-diphenylhexamethyltrisiloxane, b.p. 98-110° (0.03 mm.), n_D^{20} 1.5069 [reported, b.p. 178° (13 mm.), n_D^{25} 1.4913] (Ref. 14); n.m.r. peaks (CCl_4) at τ 9.96 [4H, singlet, $OSi(C\underline{H}_3)_2O$], τ 9.69 [12H, singlet, $C_6H_5Si(C\underline{H}_3)_2O$], and τ 2.37-2.83 (10H, multiplet, $C_6\underline{H}_5$); (b) 2.5 g., b.p. 120-138° (0.03 mm.), n_D^{20} 1.4868; (c) 3.4 g., b.p. 142-160° (0.03 mm.), n_D^{20} 1.4813; (d) 0.9 g., b.p. 162-164° (0.03 mm.), n_D^{20} 1.4838; and 1.2 g. of liquid residue, n_D^{20} 1.4839. Fractions (b) (c) and (d) and the residue showed infrared adsorptions decreasing in intensity at 1050 cm^{-1} (SiOSi) and increasing in intensity for the band at 885 and 1010 cm^{-1} (cyclodisilazane). A band at 940 cm^{-1} (Si_2N) was present in all fractions. Fraction (c) had n.m.r. peaks (CCl_4) at τ 10.02 [singlet, $Si(CH_3)_2$ pendant to cyclodisilazane], τ 9.97 (singlet), τ 9.80 [singlet, $Si(C\underline{H}_3)_2$ ring cyclodisilazane], τ 9.69 [singlet, $C_6H_5\text{-}Si(\underline{CH_3})_2O$], and τ 2.37-2.81 (multiplet, $C_6\underline{H}_5$).

E. Condensation Polymerization Reactions

1. Polymers from bis(p-dimethylhydroxysilylphenyl) and N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane:

a. Preliminary experiments: A mixture of 1.7445 g. (0.005001 mole) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane and 1.5928 g. (0.005001 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 10 ml. of xylene was heated at reflux for 6 hr. After being cooled, the polymer solution was filtered, the solvent was distilled and the residue was heated to 150° (0.1 mm.) for 1 hr., and 2.9 g. (100%) of an elastic solid was obtained. The polymer was not completely soluble in toluene.

Approximately 0.00500 mole of the diol and 0.00500 mole of the cyclodisilazane were mixed and heated under the conditions indicated in Table XII. The resulting polymers were screened for their solubility in toluene.

b. Preparation of polymer samples: To 19.1 g. (0.055 mole) of chromatographically pure N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane in 100 ml. of toluene was added 15.9 g. (0.050 mole) of bis(p-dimethylhydroxysilylphenyl) ether, and the mixture was stirred until the diol dissolved (1 hr.). The solution was transferred to a 250-ml. flask, placed on a rotary evaporator, and toluene was stripped off at reduced pressure while the water bath was maintained at 40° or below. The water-bath temperature was then increased slowly while the flask was rotated at water pump pressure. After 0.5 hr. (temperature 75°) the polymer foamed and ceased being fluid. The flask was removed from the rotary evaporator and 31.9 g. (110%) of a tacky, elastic polymer, with an inherent viscosity in toluene (0.5% concentration, 30°) of 0.21, was obtained. Additional polymerizations are reported in Table XIII.

c. Preparation of polymer for characterization: After 7.3105 g. (0.02096 mole) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane in 45 ml. of toluene was treated with 6.6891 g. (0.02100 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 1 hr. at 26°, the mixture became homogeneous in 0.5 hr., but was stirred for an additional 1.5 hr. The infrared spectrum of the residue that was obtained after the solvent was removed in a rotary evaporator showed absorptions at 1060 cm^{-1} (Si_2O), 1010 and 885 cm^{-1} (cyclodisilazane), and 940 and 905 cm^{-1} (Si_2N or Si_3N). When the residue was heated to 53° over a period of 0.75 hr., gelation occurred. Heating was continued to 80° over 1 hr. to obtain 12.6 g. (104%) of a rubbery solid polymer that was stored under vacuum for three days. A sample of the polymer was 4% soluble in toluene after being mixed with the solvent for 20 hr. The infrared spectrum of a sample of the polymer is reported in Figure 3.

TABLE XII

POLYMERIZATION OF BIS(p-DIMETHYLHYDROXYSILYLPHENOL) ETHER AND N,N'-BIS(DIMETHYLAMINODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE

(PRELIMINARY EXPERIMENTS)

Experiment Number	Mole Ratio Cyclodisilazane:Diol	Mixing Procedure	Heating Schedule	Polymer Appearance	Solubility in Toluene
1	1:1	a/	18 hr. at 160°	Hard and rubbery	Insoluble
2	1:1	a/	77-95° for 5 hr.	Soft and rubbery	Insoluble
3	1:1	a/	72° for 5 hr.	Soft gum, partly liquid	Insoluble
4	1.2:1	a/	95° for 6 hr.	Soft gum	Insoluble
5	1:1	b/	95° for 6 hr.	Gelled	Insoluble
6	1:1	c/	95° for 5 hr.	Soft gum	Swells
7	1.2:1	a/	95° for 5 hr.	Soft gum	Swells
8	1:1	d/	40° for 2 hr.	Very soft gum	Swells
9	1.2:1	d/	95° for 3 hr. and 160° for 5 hr.	Fluid	Soluble
10	1:1	d/	95° for 5 hr.	Hard rubber	Insoluble
11	1.2:1	d/	95° for 3 hr. and 160° for 3 hr.	Fluid	Soluble
12	1.05:1	d/	95° for 1 hr.	Hard rubber	Insoluble
13	1.1:1	d/	95° for 1 hr. and 160° for 4 hr.	Gum	Insoluble
14	1.15:1	d/	95° for 1 hr. and 160° for 4 hr.	Fluid	Swells

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a/ The solid diol and cyclodisilazane were mixed cold.
b/ The diol and cyclodisilazane were mixed in 10 ml. of toluene.
c/ The cyclodisilazane was heated to 95° and subsequently treated with the solid diol.
d/ After the cyclodisilazane and the diol were mixed in 10 ml. of toluene until the monomers were dissolved, the toluene was removed under reduced pressure.

TABLE XIII

POLYMER SAMPLES FROM BIS(p-DIMETHYLHYDROXYSILYLPHENYL) ETHER AND N,N'-BIS(DIMETHYLAMINODIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE

Experiment No.	Mole Ratio of Diol to Cyclodisilazane	Final Polymerization Temperature (°C)	Polymer Weight (g.)	Yield[a] (%)	Inherent[b] Viscosity	Infrared Spectra
1	1:1	69	30.2	105	Not completely soluble	Fig. 16
2	1:1.05	64	32.2	112	0.24	Fig. 17
3	1:1.1	75	31.9	110	0.21	Fig. 18
4	1.1:1	64	32.8	108	Not completely soluble	Fig. 19

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[a] Calculated on the basis of the limiting molar quantity of monomer.
[b] In toluene at 30°, 0.5% concentration.

The polymer was soluble to an extent of less than 20% in 1-methyl-2-pyrrolidinone, dimethylacetamide, tetrahydrofuran, hexamethylphosphoramide, dimethylsulfoxide.

Anal. Calcd. for $C_{24}H_{44}N_2O_3Si_6$: C, 49.94, H, 7.68; N, 4.85; Si, 29.20. Found: C, 49.68; H, 7.72; N, 4.71; Si, 29.00.

2. Polymers from p-phenylenebis(dimethylsilanol) and N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane:

a. Preliminary experiment: A mixture of 4.678 g. (0.0207 mole) of p-phenylenebis(dimethylsilanol) and 7.208 g. (0.0207 mole) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane in 35 ml. of toluene was stirred for 1 hr. Since about one-half of the diol remained insoluble, the contents were transferred to a one-necked 100-ml. flask and rotated on a rotary evaporator at 40°. After the diol dissolved (0.5 hr.), the solvent was flashed off, and the residue was heated to 73° in 25 min. At a temperature of 78°, the polymer bloomed. The flask was removed, cooled, and 10.0 g. (100% yield) of a tacky, elastic, clear gum was obtained. The polymer was not completely soluble in toluene.

b. Preparation of polymer for characterization: A mixture of 5.6048 g. (0.02475 mole) of p-phenylenebis(dimethylsilanol) and 8.6464 g. (0.02479 mole) of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, and 45 ml. of toluene was mixed on a rotary evaporator until the diol dissolved (4 hr.). After the solvent was evaporated and the polymer was heated at 50° for 1 hr., the residue showed infrared absorptions at 1070 cm^{-1} (Si_2O), 1020 and 885 cm^{-1} (cyclodisilazane), and 945 and 910 cm^{-1} (Si_2N or Si_3N). When heating was continued at 56° for an additional 0.25 hr., the polymer gelled. The polymer yield was 12.2 g. (102%). No significant changes were observed in the infrared spectrum of the polymer (Figure 20) after it was stored under vacuum for three days. A sample of the polymer was 38% soluble in toluene after being mixed with the solvent for 20 hr.

Anal. Calcd. for $C_{18}H_{40}N_2O_2Si_6$: C, 44.57; H, 8.31; N, 5.78; Si, 34.74. Found: C, 44.03; H, 8.26; N, 5.78; Si, 34.66.*

3. Comparative polymerizations of bis(p-dimethylhydroxysilylphenyl) ether and the amino, methylamino, and dimethylamino derivatives of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane:

a. With N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane: A mixture of 1.5925 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.7400 g. (0.00499 mole) of the cyclodisilazane, and 20 ml. of toluene was mixed in a rotary evaporator at 0° for 2.5 hr. and at 10° for 1 hr. without effecting solution. After 3 hr. at 15°, the diol dissolved. Subsequently, the toluene was evaporated at 30° to obtain a liquid residue that gelled after storage for 72 hr. at room temperature. The infrared spectrum of the liquid product is reported in Figure 21.

b. With N,N'-bis(dimethylmethylaminosilyl)tetramethylcyclodisilazane: When 1.5925 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.6000 g. (0.00500 mole) of the cyclodisilazane, and 20 ml. of toluene were mixed in a rotary evaporator at 37°, the diol dissolved after 3 hr. After the solvent was evaporated, the infrared spectrum of the clear liquid residue showed bands at 3400 cm^{-1} (SiOH), 1050 cm^{-1} (Si_2O), 1025 and 885 cm^{-1} (cyclodisilazane), and 955 and 930 cm^{-1} (Si_3N or Si_2N). The residue was heated at 38° for 1 hr. and subsequently at 80° for 1 hr. The infrared bands assignable to SiOH and cyclodisilazane became weaker and those assignable to Si_2O and Si_3N or Si_2N became stronger (Figure 22). When heating was continued 85-90° for 2 hr. and then at 130° for 1.5 hr., gelation occurred.

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* The analyst reported that this polymer was extremely refractory.

c. With N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane: A mixture of 1.5925 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.4600 g. (0.00500 mole) of the cyclodisilazane, and 20 ml. of toluene was heated in a rotary evaporator for 2 hr. at 40° and for 2 hr. at 50° before the diol dissolved. After the toluene was evaporated, some of the diol reprecipitated, but was redissolved after 2 hr. at 50°. The infrared spectrum of the viscous liquid residue showed absorptions at 3400 cm^{-1} (SiOH), 1050 cm^{-1} (Si_2O), 1025 cm^{-1} (cyclodisilazane) and at 955 and 930 cm^{-1} (Si_3N or Si_2N). This residue was heated at 80° for 2 hr. and at 130° for 1.5 hr. without gelation occurring. The final infrared spectrum is reported in Figure 23.

4. Polymers from N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane with bis(p-dimethylhydroxysilylphenyl) ether: After 2.0470 g. (0.005050 mole) of pure N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane and 1.6084 g. (0.005050 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 10 ml. of toluene were mixed in a rotary evaporator at room temperature for 1 hr., the mixture was heated slowly in the water bath to 50° to dissolve the diol. The toluene was distilled out at reduced pressure while the bath temperature was increased slowly to 85°. After 3 hr. at 85°, 3.0 g. of a gummy polymer that swelled in toluene was obtained.

In a similar experiment 2.0279 g. (0.005008 mole) of N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane and 1.5950 g. (0.005008 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 10 ml. of toluene were heated slowly to 50° on a rotary evaporator until the diol dissolved. Toluene was removed at reduced pressure and the residue was heated to 85° in 1 hr. and then at 85° for 1.5 hr. under reduced pressure. The toluene-soluble, gummy polymer (3.0 g.) had an inherent viscosity of 0.36 (0.5% in toluene, 30°).

In another experiment 2.0260 g. (0.005003 mole) of N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane and 1.5935 g. (0.005003 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 10 ml. of xylene were refluxed for 6 hr. The mixture was filtered, the solvent was evaporated, and the residue was heated at 150° (0.1 mm.) for 1 hr. A toluene-soluble, gummy polymer (3.0 g.) with an inherent viscosity of 0.77 (0.5% in toluene, 30°) was obtained. The infrared spectrum is reported in Figure 24.

Both of the soluble polymers became partly insoluble after storage for eight days.

Repetition of the procedures in which the monomers were heated in boiling xylene, but with a molar deficiency of the cyclodisilazane monomer, gave the following results: with a 5% molar deficiency, 86% of an elastic gum with an inherent viscosity of 0.21; with a 2% molar deficiency, 85% of an elastic gum that swelled in toluene.

5. Polymer from bis(p-dimethylhydroxysilylphenyl) ether and N,N'-bis-(dimethylsilyl)tetramethylcyclodisilazane:

a. Preliminary experiments with sodium hydride as catalyst: When 1.5924 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.3136 g. (0.00500 mole) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane, 0.0100 g. of sodium hydride (used as a 61% dispersion in mineral oil), and 10 ml. of toluene were heated at 110° for 2.5 hr., no reaction occurred. Heating was continued between 110-186° for 1 hr. after the toluene was evaporated and 145 ml. (59%) of hydrogen was collected. The residue (2.9 g., 100%) was a reddish solid that was mostly insoluble in toluene.

In a second experiment, 1.5927 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.3142 g. (0.00500 mole) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane, 0.0188 g. of sodium hydride, and 10 ml. of xylene was heated slowly to reflux. Hydrogen evolution began at 84°, and after 5 hr. at 136°, 216 ml. (88%) of the expected hydrogen was collected. When the polymer solution was filtered, and the solvent was evaporated, the residue being heated to 150° (0.1 mm.), 2.3 g. (80%) of a polymeric gum was obtained with an inherent viscosity in toluene of 0.12. The infrared spectrum is reported in Figure 25. Additional heating at 150° (0.1 mm.) increased the inherent viscosity to 0.21 without rendering the polymer insoluble. After 18 days, the polymer was still toluene-soluble.

Two repetitions of the experiment with minor experimental modifications gave essentially the same results. In one of the experiments, the silanol, sodium hydride, and xylene were heated until the sodium hydride dissolved, the mixture was cooled to 50° and then treated with the silyl hydride. The inherent viscosity of the product polymer was 0.17.

b. Preliminary experiment with sodium bis(trimethylsilyl)amide as catalyst: When 1.5925 g. (0.0050 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.3134 g. (0.0050 mole) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane, 0.010 g. of sodium bis(trimethylsilyl)amide, and 5 ml. of xylene were heated at 133° for 2.5 hr., 105 ml. (40%) of the hydrogen was collected. The formation of water was observed during the heating period. After the polymer solution was filtered, the solvent was evaporated, and the residue was heated at 150° (0.1 mm.) for 1 hr., 3.4 g. (117%) of a polymer with an inherent viscosity of 0.04 in toluene was obtained. The infrared spectrum of the product was similar to the spectrum of the homopolymer from bis(p-dimethylhydroxysilylphenyl) ether (Figure 2), except for bands at 2110 cm^{-1} (SiH), 987 cm^{-1}, 940 cm^{-1}, and 905 cm^{-1} (Si_2N), and different from the spectrum of the copolymer.

c. Polymerization series: In a series of polymerization reactions 1.5925 g. (0.005000 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.3134 g. (0.005000 mole) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane and 0.015 g. of sodium hydride (free of mineral oil) in 10 ml. of xylene were heated to reflux for 6 hr. The reaction mixture was cooled, filtered, and devolatilized at 150° (0.1 mm.). The results of this experiment and other similar experiments are reported in Table XIV.

Except for polymer No. 4, which was a homopolymer of bis(p-dimethylhydroxysilylphenyl) ether, the infrared spectra of the polymers were similar. A typical spectrum is reported in Figure 4. Solubilities and viscosities determined after specified periods are reported in Table XV.

6. Polymerization of bis(p-dimethylhydroxysilylphenyl) ether with the equilibration polymer from hexamethylcyclodisilazane and dichlorodimethylsilane: In a series of polymerization reactions 1.3170 g. of an equilibration polymer (see paragraph IV.F.2) with 0.3185 g. (0.0010 mole), 0.6360 g. (0.0020 mole), 1.2720 g. (0.0040 mole), 1.9080 g. (0.0060 mole), and 2.5440 g. (0.0080 mole), respectively, of bis(p-dimethylhydroxysilylphenyl) ether in 5 ml. xylene were heated at reflux for 6 hr. The mixtures were filtered, evaporated, and heated at 150° (0.1 mm.) for 1 hr. The experiments are summarized in Table XVI. The infrared spectra of two of the polymers, Figures 26 and 27, demonstrate the decrease in intensity of the Si_2N band at 920 cm^{-1} with increase in the diol concentration.

In another experiment, 2.000 g. of an equilibration polymer was prepared by heating 65.7 g. (0.30 mole) of hexamethylcyclotrisilazane with 38.7 g. (0.30 mole) of dichlorodimethylsilane to 319° in 48 hr., treating the cooled equilibration product with dimethylamine. The dimethylamine derivative was heated to 332° (0.15 mm.) and then heated at 80° for 7 hr. with 1.5 g. (0.035 mole) of dry ethanol and 5 ml. of benzene. Titration of the amine that distilled from the mixture indicated that 1.089 meq. of dimethylamine had been displaced by the ethanol. Subsequently, 2.000 g. of the equilibration polymer, 0.174 g. (0.00054 mole) of bis(p-dimethylhydroxysilylphenyl) ether, and 5 ml. of xylene were heated at 140° for 6 hr. After the solvent was distilled out and the residue was heated at 150° (0.1 mm.), 2.0 g. of a waxy polymer with an inherent viscosity of 0.07 in toluene (0.5% at 30°) was obtained. Except for some reduction in the intensity of the absorption due to dimethylamino groups at about 990 cm^{-1}, there was very little difference in the infrared spectra of the oligomer before and after it was treated with the diol. Broad adsorption bands in the 1000-1060 cm^{-1} region indicated the presence of oligocyclodisilazanes in both materials.

TABLE XIV

POLYMERIZATION OF BIS(p-DIMETHYLHYDROXYSILYLPHENYL) ETHER AND N,N'-BIS(DIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE IN THE PRESENCE OF SODIUM HYDRIDE

Polymer No.	Reaction Time (hr.)	Devolatilization Temp. (°C)	Devolatilization Time (hr.)	Stoichiometry (diol)	Catalyst Level (%)	Solvent	Solvent Volume (ml.)	Polymer Yield (%)	η_{inh} (0.5% in toluene)	Comment
1	6	150	1	Equimolar	0.5	Xylene	10	93	0.15	Tacky oil
2	6	150	1	Equimolar	0.5	Xylene	5	97	0.15	Tacky oil
3	6	150	1	Equimolar	0.5	Xylene	20	90	0.12	Tacky oil
4	6	150	1	Equimolar	0.1	Xylene	10	93	0.04	Oil
5	6	150	1	Equimolar	1.0	Xylene	10	100	0.18	Gum
6	6	150	1	5% Deficient	0.5	Xylene	10	90	0.12	Oil
7	6	150	1	2% Deficient	0.5	Xylene	10	83	0.17	Gum
8	6	150	1	2% Excess	0.5	Xylene	10	100	0.08	Oil
9	6	180	1	Equimolar	0.5	Xylene	10	86	0.19	Gum
10	6	120	1	Equimolar	0.5	Xylene	10	93	0.08	Oil
11	6	150	1	Equimolar	0.5	Toluene	10	93	0.12	Oil
12	24	150	1	Equimolar	0.5	Xylene	10	97	0.13	Tacky oil
13	6	150	3	Equimolar	0.5	Xylene	10	93	0.12	Oil
14	6	150	8	Equimolar	0.5	Xylene	10	93	0.13	Oil
15	6	180	1	Equimolar	1.0	Xylene	10	97	0.14	Gum
16	6	210	1	Equimolar	1.0	Xylene	10	100	0.46	Gum
17	6	180	3	Equimolar	1.0	Xylene	10	100	0.17	Gum
18	6	180	1	Equimolar	10.0	Xylene	10	-	a/	Brittle solid
19	6	180	8	Equimolar	1.0	Xylene	10	97	a/	Elastic solid
20	6	210	1	Equimolar	0.5	Xylene	10	93	a/	Elastic solid
21	6	240	1	Equimolar	0.5	Xylene	10	90	a/	Elastic solid
22	6	270	1	Equimolar	0.5	Xylene	10	86	a/	Elastic solid

---

a/ Not completely soluble after 18 hr. in toluene.

TABLE XV

STORAGE STABILITY OF POLYMERS IN TABLE XIV

Polymer No.	Initial η_{inh}	Time (days)	Final η_{inh}
1	0.15	112	0.15
2	0.15	111	0.15
3	0.12	111	0.10
4	0.04	110	0.08
5	0.18	49	0.14
		104	0.14
6	0.12	109	0.11
7	0.17	49	0.24
		104	a/
8	0.08	103	0.08
9	0.19	42	0.24
		104	a/
10	0.08	102	0.08
11	0.12	102	0.10
12	0.13	98	0.15
13	0.12	97	0.10
14	0.13	96	0.12
15	0.14	30	0.14
		90	0.15
16	0.46	25	a/
17	0.17	25	a/

---

a/ Not completely soluble.

TABLE XVI

POLYMERIZATION OF BIS(p-DIMETHYLHYDROXYSILYLPHENYL) ETHER WITH EQUILIBRATION POLYMER

Experiment No.	Bis(p-dimethylhydroxysilylphenyl) Ether		Equilibration Polymer Wt. (g.)	Solvent Vol. (ml.)	Polymer Wt. (g.)	Inherent Viscosity (0.5% in toluene at 30°)	Physical Characteristics
	Wt. (g.)	Mole					
1	0.3185	0.0010	1.3170	5	1.6	0.15[a]	Gum
2	0.6360	0.0020	1.3170	5	1.8	0.17[b]	Gum
3	0.9555	0.0030	1.3170	5	2.3	0.17	Gum
4	1.1147	0.0035	1.3170	5	2.2	Swelled	Elastic solid
5	1.2720	0.0040	1.3170	5	2.4	Swelled	Elastic solid
6	1.5925	0.0050	1.3170	5	2.7	Swelled	Elastic solid
7	1.7518	0.0055	1.3170	5	2.1	0.13	Tacky liquid
8	1.9080	0.0060	1.3170	5	2.8	0.31[c]	Tacky liquid
9	2.2296	0.0070	1.3170	5	3.2	0.12	Tacky liquid.
10	2.5440	0.0080	1.3170	5	3.2	0.14[d]	Tacky liquid

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a/ 0.17 after 21 days of storage.

b/ 0.19 after 20 days of storage.

c/ 0.38 after 10 days of storage and not completely soluble after 17 days.

d/ Not completely soluble after 9 days of storage.

7. Polymer from bis(p-dimethylhydroxysilylphenyl) ether and N,N'-bis(dimethylphenoxysilyl)tetramethylcyclodisilazane (attempted): A mixture of 1.5924 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether and 2.2341 g. (0.00500 mole) of N,N'-bis(dimethylphenoxysilyl)tetramethylcyclodisilazane was heated in a Wood's metal bath at a pressure of 25 mm. for 3 hr. at 120°, 2 hr. at 140°, and 4 hr. at 180°. The residue, 3.8 g. of a viscous liquid, solidified on standing. The formation of phenol was not detected during this experiment. An infrared spectrum of the residue showed strong bands at 1580 and 1480 cm^{-1} (C_6H_5).

8. Polymer from bis(dimethylsilyl)trimethylsilylamine and bis(p-dimethylhydroxysilylphenyl) ether: A mixture of 1.5935 g. (0.005003 mole) of bis(p-dimethylhydroxysilylphenyl) ether, 1.0282 g. (0.005003 mole) of bis(dimethylsilyl)trimethylsilylamine, 0.025 g. (1 wt. %) sodium hydride (obtained by washing 0.0420 g. of a 61% dispersion in mineral oil three times with 2-ml. portions of xylene), and 10 ml. of xylene was heated at 130° for 6 hr. during which time 78 ml. (30%) of hydrogen was collected. After the solution was filtered and the solvent evaporated, 0.8 g. (80%) of bis(dimethylsilyl)trimethylsilylamine was recovered by vacuum distillation. When the residue was heated at 180° (0.1 mm.) for 1 hr., 1.5 g. (57%) of a polymer with an inherent viscosity (0.5% in toluene) of 0.40 was obtained. The infrared spectrum, Figure 2, indicated that the residue was a homopolymer of bis(p-dimethylhydroxysilylphenyl) ether.

9. Polymer from bis(p-dimethylhydroxysilylphenyl) ether and N,N'-bis(anilinodimethylsilyl)tetramethylcyclodisilazane (attempted): To 1.5925 g. (0.00500 mole) of bis(p-dimethylhydroxysilylphenyl) ether was added 2.2247 g. (0.00500 mole) of N,N'-bis(anilinodimethylsilyl)tetramethylcyclodisilazane in 10 ml. toluene. The mixture was refluxed for 2 hr., the solvent was distilled off at atmospheric pressure, and the residue was heated at 150° (0.1 mm.) for 2.5 hr., at 180° (atm.) for 2.5 hr., at 180° (85 mm.) for 5 hr., and at 180° (0.05 mm.) for 6 hr. No aniline distilled and the residue weighed 3.6 g. (> 100% recovery of monomers).

F. Equilibration Reactions

1. Polymerization of hexamethylcyclotrisilazane with ammonium bromide at 175°: A mixture of 25.5 g. (0.11660 mole of hexamethylcyclotrisilazane and 9.8 g. (0.100 mole) of ammonium bromide was heated at 175° for 65 hr. The evolution of ammonia was noted. The soluble portion of the residue was dissolved in 50 ml. of petroleum ether, b.p. 60-90°, and added to 25 ml. of dimethylamine in 100 ml. of petroleum ether, while the mixture was cooled in an isopropyl alcohol-Dry Ice bath. The salts were filtered off, and the solvent evaporated. Distillation gave 3.1 g. of unchanged hexamethylcyclotrisilazane, b.p. 86-108° (31 mm.),and 2.1 g. of octamethylcyclotetrasilazane,

b.p. 95-110° (11-0.05 mm.), both identified by their infrared spectra. The residue, 14.0 g., was not distillable at a pot temperature of 220° (0.05 mm.). The infrared spectrum is reported in Figure 28. The molecular weight, cryoscopically in benzene, was 1500.

A 5.2-g. sample of the residue was heated at reduced pressure to a pot temperature of 329°, and 0.4 g. of oligomeric oils, boiling range 224-249° (0.06 mm.), was distilled. The polymeric residue, 4.8 g., was a viscous oil. The infrared spectrum of the sample had not changed significantly. N.m.r. peaks were observed at τ 10.03, 10.00, 9.94, 9.84, and 9.75, which are shown in Figure 37.

Anal. Found: C, 34.97; H, 9.44; N, 15.6; Si, 39.88.

A similar experiment with 22.7 g. (0.10370 mole) of hexamethylcyclotrisilazane and 2.2 g. (0.02250 mole) of ammonium bromide gave on distillation 2.4 g. of unchanged hexamethylcyclotrisilazane, b.p. 92-106° (31 mm.), and 0.5 g. of octamethylcyclotetrasilazane, b.p. about 90° (3 mm.), both identified by their infrared spectra. The residue, 15.7 g., was not distillable at a pot temperature of 220° (0.06 mm.). The infrared spectrum was similar in all respects to the spectrum of the first sample. The molecular weight, cryoscopically in benzene, was 1905.

In another experiment, the equilibration polymer was quenched with ammonia and subsequently thermolyzed in order to compare the properties of a material prepared in this manner with the properties of the material reported by Krueger (Ref. 4). A mixture of 21.9 g. (0.10 mole) of hexamethylcyclotrisilazane and 6.45 g. (0.050 mole) of dichlorodimethylsilane was heated at 175° for 65 hr. The portion soluble in 50 ml. of petroleum ether, b.p. 60-90°, was added to excess ammonia in 100 ml. of petroleum ether previously cooled in an isopropyl alcohol-Dry Ice Bath. The mixture was filtered, the solvent was distilled, and the residue was heated to 350° in a short-path distillation apparatus. The distillate, 11.7 g., which boiled in the range of 92° (10 mm.) to 246° (0.36 mm.), was separated, and the gummy residue, 9.4 g., was examined. The infrared spectrum of the residue differed from the spectrum of the dimethylamine-quenched polymer only in the absence of a band at 985 cm^{-1} $[N(CH_3)_2]$ and the strengthening of the band at 1010 cm^{-1} (oligocyclodisilazane). N.m.r. peaks were observed in CCl_4 at τ 10.01, τ 9.97 (strong), τ 9.92, and τ 9.75 (strong) and in benzene at τ 9.74, and τ 9.54. Krueger observed peaks in CCl_4 at τ 9.98 and τ 9.75.

2. Polymerization of hexamethylcyclotrisilazane and dichlorodimethylsilane at 175°: After 21.9 g. (0.100 mole) of hexamethylcyclotrisilazane and 6.45 g. (0.050 mole) of dichlorodimethylsilane were heated at 175° for 65 hr., the soluble portion of the residue was dissolved in 50 ml. of petroleum ether, b.p. 60-90°, and added to 25 ml. of dimethylamine in 100 ml.

of petroleum ether, while the mixture was cooled in an isopropyl alcohol-Dry Ice bath. The salts were filtered off and the solvent evaporated. Distillation gave 3.5 g. of material boiling at 86° (8 mm.) to 167° (0.04 mm.) with an infrared spectrum (neat) similar to the spectrum of N-(3-dimethylaminotetramethyldisilazanyl)-N'-dimethylaminodimethylsilyltetramethylcyclodisilazane). The residue, not distillable at a temperature of 220° (0.04 mm.), weighed 19.3 g. The infrared spectrum is reported in Figure 29. The molecular weight, cryoscopically in benzene, was 1036.

A 7-g. portion of the residue was heated to a pot temperature of 325° and 1.8 g. of an oligomeric oil, boiling range 195-274° (0.04 mm.), was collected. The polymeric residue, 5.2 g., was a viscous oil. The infrared spectrum had not changed significantly. N.m.r. peaks were observed at τ 10.02, 9.99, 9.96, 9.85, 9.82, and 9.74 (Figure 38) in CCl_4 and at τ 9.87, 9.81, 9.73, 9.64, 9.60, and 9.54 in C_6H_6.

<u>Anal</u>. Found: C, 35.39; H, 9.38; N, 14.93; Si, 40.24.

A similar experiment with 21.9 g. (0.10 mole) of hexamethylcyclotrisilazane and 2.27 g. (0.0182 mole) of dichlorodimethylsilane (mole ratio, 5.5:1) gave on distillation 4.8 g. of unchanged hexamethylcyclodisilazane, b.p. 90-105° (30 mm.) and 1.5 g. of octamethylcyclotetrasilazane, b.p. about 100° (3 mm.), both identified by their infrared spectra. The residue, 12.7 g. of a viscous liquid, was not distillable at a pot temperature of 220° (0.04 mm.). The infrared spectrum (Figure 30) showed a somewhat broader and stronger Si_2NH band in the 900-950 cm^{-1} region and weaker cyclodisilazane bands at 880 and 1030 cm^{-1} than were observed in the previous experiment in which a 1:2 mole ratio of reactants was used. The molecular weight, cryoscopically in benzene, was 1627.

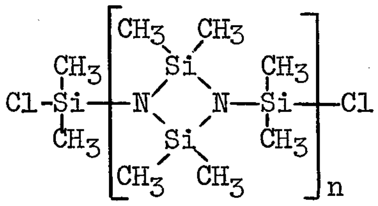
The following describes the preparation of an oligomer that was used in condensation reactions with ethanol and arylene disilanols.

After 43.8 g. (0.20 mole) of hexamethylcyclotrisilazane and 12.9 g. (0.10 mole) of dichlorodimethylsilane were heated at 175° for 65 hr., the portion of the residue soluble in 100 ml. of petroleum ether, b.p. 60-90°, was added to 30 ml. of dimethylamine in 100 ml. of petroleum ether, while the mixture was cooled in an isopropyl alcohol-Dry Ice bath. The salts were filtered off and the solvent evaporated. Distillation to a pot temperature of 320° gave 23.1 g. of oligomers, boiling range 58° (200 mm.) to 310° (0.07 mm.) and 26.5 g. of a viscous liquid polymer. The infrared and n.m.r. spectra were not different from the spectra of the oligomer that had been obtained by equilibrating the same mole ratios of monomers.

A mixture of 6.6 g. (0.0050 mole, molecular weight, 1317, calculated on the basis of the n.m.r. spectrum assuming two NMe_2 groups per molecule) of the oligomers and 2.7 g. (0.06 mole, a 12-fold excess) of dry ethanol was refluxed at 77° for 24 hr. The mixture became homogeneous when it was heated. Distillation gave 2.0 g. (74% recovery) of ethanol, b.p. 78°, and no other distillate when the residue was heated to 225° (0.035 mm.). The residue, 6.5 g., was slightly colored; the infrared spectrum (Figure 31) was similar to the spectrum of the original material except for the disappearance of the band at 990 cm^{-1} [$N(CH_3)_2$] and the appearance of new bands at 1075 and 1105 cm^{-1} ($SiOC_2H_5$). N.m.r. peaks (CCl_4) were not changed in the τ 9.70-10.05 region but the peak at τ 7.57 [$N(CH_3)_2$] was replaced by peaks at τ 8.80 (triplet, CH_3) and τ 6.27 (quadruplet, CH_2-O).

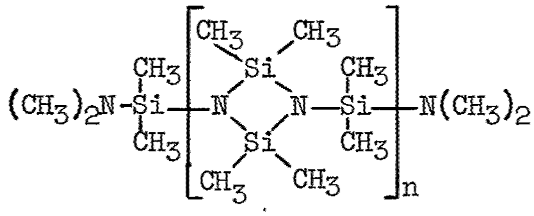
3. Polymerization of hexamethylcyclotrisilazane and dichlorodimethylsilane above 300°:

a. α,ω-Chlorodimethylsilated oligomeric cyclodisilazanes:



By the procedure described by Fink (Ref. 12), 43.8 g. (0.20 mole) of hexamethyclclotrisilazane and 25.8 g. (0.20 mole) of dichlorodimethylsilane were heated at 280-303° for 48 hr. The residue solidified on cooling. When the portion of the residue soluble in 25 ml. of petroleum ether, b.p. 60-90°, was distilled through a short-path column, the following fractions were obtained: (1) 12.0 g. of impure N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (n = 1), b.p. 144-164° (44 mm.), m.p. 64-70°; (2) 5.0 g. of impure oligomer (n = 2), b.p. 108-130° (0.04 mm.), m.p. 57-65° [reported b.p. 118° (0.05 mm.), m.p. 43.5] (Ref. 12); (3) 10.3 g., a mixture of oligomers (n = 2 and n = 3) and -NH-$Si(CH_3)_2Cl$ terminated oligomers (n = 2) boiling at 132-165° (0.04 mm.), liquid [reported b.p. 118° (0.05 mm.), 186° (0.01 mm.), and 144° (0.01 mm.), respectively] (Ref. 12); (4) 5.1 g. of a mixture of oligomers boiling at 166-189° (0.04 mm.); (5) 8.9 g. of impure oligomer (n = 3) boiling at 196-235° (0.04 mm.), melting at 71-87° [reported b.p. 186° (0.01 mm.), m.p. 109-110°] (Ref. 12); (6) 6.3 g. of impure oligomer (n = 4) boiling at 238-281° (0.04 mm.) [reported b.p. 248° (0.01 mm.), m.p. 93°] (Ref. 12); and (7) 7.0 g. of a waxy solid residue. The infrared spectra of the fractions were similar in that the cyclodisilazane bands at 1040 and 880 cm^{-1} were present in all fractions. An additional band appears at 1010 cm^{-1} in fraction 2 which becomes progressively stronger and broader as the boiling temperature increases. The cyclodisilazane band at 880 cm^{-1} also becomes broader.

b. *α,ω-Dimethyldimethylaminosilated oligomeric cyclodisilazanes:*



A mixture of 65.7 g. (0.30 mole) of hexamethylcyclotrisilazane and 38.7 g. (0.30 mole) of dichlorodimethylsilane was heated to a final temperature of 319° in 48 hr. The portion soluble in 100 ml. of petroleum ether, b.p. 60-90°, was added to 75 ml. (excess) of dimethylamine in 100 ml. of petroleum ether in an isopropanol-Dry Ice bath. The mixture was filtered, the solvent was evaporated from the filtrate, and the residue distilled through a short-path column to obtain: (1) 9.5 g. of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (n = 1) boiling at 89-102° (0.24 mm.), n_D^{20} 1.4530 [reported, b.p. 123-125° (5 mm.), n_D^{20} 1.4530]; (2) 4.3 g. impure oligomer (n = 1) boiling at 104° (0.34-0.06 mm.), n_D^{20} 1.4535; (3) 2.1 g. boiling at 104-146° (0.08 mm.), n_D^{20} 1.4547; (4) 11.3 g. of impure oligomer (n = 2) boiling at 152-174° (0.09 mm.), n_D^{20} 1.4642; (5) 11.5 g. of a mixture of oligomers (n = 2 and n = 3) boiling at 174-224° (0.09 mm.), n_D^{20} 1.4662; (6) 7.9 g. of a mixture of oligomers (n = 3 and n = 4) boiling at 224-246° (0.10 mm.), solid; (7) 11.6 g. of impure oligomer (n = 4) boiling at 252-305° (0.10 mm.), solid; and (8) 20.2 g. of waxy solid residue.

Fractions 4 through 7 were fractionally redistilled through a vacuum-jacketed Claisen head in a series of distillations in which the succeeding fraction was added to the residue of the previous distillation. The boiling ranges, weight, and g.l.c. analyses of the principal fractions are reported in Table XVII. Fractions 8-15 were liquids and fractions 16-21 solids. The infrared spectra of fractions 11, 17, and 21 are reported in Figures 32, 33, and 34. The n.m.r. spectra of the same three fractions in CCl_4 are reported in Figures 39, 41, and 43, and in benzene in Figures 40, 42, and 44, respectively.

Fractions 10, 11, and 12, Table XVII, when redistilled at 0.05 mm., gave 1.4 g. of a center cut, b.p. 153°; g.l.c. (Table VIII, Method B-3) indicated the fraction contained 95% of a single component.

Anal. Calcd. for $C_{18}H_{54}N_6Si_7$ (n = 2): C, 39.21; H, 9.87; N, 15.25; Si, 35.67. Found: C, 39.38; H, 9.87; N, 15.18; Si, 35.58.

TABLE XVII

G.L.C. OF DISTILLATION FRACTIONS[a]

Fraction No.	Boiling Point, °C (0.03 mm.)	Wt. (g.)	Component 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1[b]	89-102[c]	9.5	14	86	-	-	-	-	-	-	-									
8	84-122	0.6	2	19	8	38	7	26	-	-	-									
10[d]	137-146	3.4	-	0.5	-	0.5	3	90	Trace	6	-									
11[e]	149-153	3.4	-	-	-	-	-	99	-	-	-									
12	145-152	4.8	-	-	-	-	-	85	-	2	13									
13	156-170	1.2	-	-	-	-	-	42	-	-	58	Trace	Trace							
16[f]	194-198	2.8									5	-	-	Trace	2	3	-	14	67	8
17	201-205	3.2									Trace	-	-	-	1	1	1	17	67	13
19	212-225	4.4																7	55	38
21	237-257	4.5											-	-	-	-	-	-	-	99

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[a] For g.l.c. procedures see Table VIII.

[b] G.l.c. method B-1.

[c] At 0.3 mm.

[d] G.l.c. method B-2.

[e] G.l.c. method B-3.

[f] G.l.c. method B-4 .

Anal. (Fraction 17, Table XVII) Calcd. for $C_{24}H_{72}N_8Si_{10}$ (n = 3): C, 38.24; H, 9.63; N, 14.87; Si, 37.26. Found: C, 38.05; H, 9.71; N, 14.72; Si, 37.16.

Anal. (Fraction 21, Table XVII) Calcd. for $C_{30}H_{90}N_{10}Si_{13}$ (n = 4): C, 37.68; H, 9.49; N, 14.65; Si, 38.18. Found: C, 37.63; H, 9.30; N, 14.42; Si, 38.24.

In an experiment in which a 2:1 mole ratio of hexamethylcyclotrisilazane was used rather than a 1:1 mole ratio, 21.9 g. (0.10 mole) of hexamethylcyclotrisilazane and 6.45 g. (0.050 mole) of dichlorodimethylsilane were heated under nitrogen to 285° in 66 hr. After the portion of the product that was soluble in petroleum ether, b.p. 60-90°, was treated with excess dimethylamine, the salts were filtered off, and the solvent was evaporated. Distillation through a short-path column to a pot temperature of 310° gave 6.5 g. of distillate, b.p. 115-260° (0.2 mm.). G.l.c. analysis of the distillate (Table VIII, Method B-3) indicated the presence of 12 components, none of which constituted a major portion of the distillate. The infrared spectrum of the distillate exhibited bands at 3450 cm^{-1} (NH), 1180 cm^{-1} (Si_2NH), 1045 and 885 cm^{-1} (cyclodisilazane), 985 cm^{-1} $[N(CH_3)_2]$, 1010 cm^{-1} (oligocyclodisilazanes), and 930 cm^{-1} (Si_2N). The spectrum of the viscous liquid residue (17.1 g.) exhibited the same bands as the distillate.

4. Disproportionation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (attempted): When 9.3 g. (0.0281 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (90% pure by g.l.c.) was heated under nitrogen to 250° in 21 hr. and at 250° for 47 hr., no dimethyldichlorosilane distilled. Distillation gave 6.0 g. of 99% pure N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane boiling between 80° (0.2 mm.) and 100° (0.2 mm.) and a residue of 1.5 g. that contained N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, 5%; N-(3-chlorotetramethyldisilazanyl)-N'-chlorodimethylsilyltetramethylcyclodisilazane, 1%; a cyclodisilazane oligomer (n = 2), 32%; and a cyclodisilazane oligomer (n = 3), 62%.

5. Condensation of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane and hexamethylcyclotrisilazane: After a mixture of 10.3 g. (0.0311 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (99% pure by g.l.c.) and 2.28 g. (0.0104 mole) of hexamethylcyclotrisilazane was heated at 175° for 48 hr., 10.3 g. of a distillate was collected by a short-path distillation between 144° (32 mm.) and 184° (0.02 mm.). In addition, 2.2 g. of a viscous liquid residue was obtained. G.l.c. analysis (Table VIII, Method B-1) of the distillate indicated the presence of the following components in the distillate: N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane, 53%; N-(3-chlorotetramethyldisilazanyl)-N-(chlorodimethylsilyl)-tetramethylcyclodisilazane, 25%; and cyclodisilazane oligomers, 22%.

When the experiment was repeated, but with 3.9 g. (0.0305 mole) of dichlorodimethylsilane also present in the equilibration mixture, the 12.7 g. of distillate, which was collected between 64° (0.3 mm.) and 108° (0.3 mm.) contained the following components: N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane, 90%; and N-(3-chlorotetramethyldisilazanyl)-N'-(chlorodimethylsilyl)tetramethylcyclodisilazane, 6%. The distillation residue weighed 0.5 g.

In another experiment, 12.00 g. (0.0363 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (90% pure by g.l.c.) and 2.6455 g. (0.0121 mole) of hexamethylcyclotrisilazane was heated under nitrogen to 275° in 24 hr. and at 275° for 48 hr. After the portion of the equilibration product that was soluble in 20 ml. of petroleum ether, b.p. 60-90°, was treated with 10 ml. of dimethylamine cooled in an isopropyl alcohol-Dry Ice bath, the mixture was warmed to room temperature, filtered, and the solvent was evaporated. Distillation in a short-path apparatus gave 11.5 g. of product boiling between 112° (0.3 mm.) and 270° (0.3). G.l.c. analysis of the distillate indicated that the distillate contained the following components: N,N'-Bis(dimethyldimethylaminosilyl)tetramethylcyclodisilazane, 48%; N-(3-chlorotetramethyldisilazanyl)-N'-(chlorodimethylsilyl)tetramethylcyclodisilazane, 3%; the cyclodisilazane oligomer (n = 2), 32%; and the cyclodisilazane oligomer (n = 3), 9%.

6. Condensation of N-(3-chlorotetramethyldisilazanyl)-N'-(chlorodimethylsilyl)tetramethylcyclodisilazane and sodium bis(trimethylsilyl)amide: To 10.0 g. (0.020 mole) of N-(3-chlorotetramethyldisilazanyl)-N'-(chlorodimethylsilyl)tetramethylcyclodisilazane [b.p. 97-102° (0.1 mm.), g.l.c. purity, 81%, with 19% lower boiling impurities, Method B-1, Table VIII] was added 3.66 g. (0.020 mole) of sodium bis(trimethylsilyl)amide dissolved in 30 ml. of ether. The addition required 0.5 hr. and stirring was continued for 2 hr. After the mixture was filtered and the solvent distilled, short-path distillation gave 5.2 g. of a partly solid distillate in the range of 122° (0.2 mm.) to 124° (0.03 mm.). G.l.c. analysis (Table VIII, Method B-3) of the distillate showed three major and nine minor peaks: N-(3-chlorotetramethyldisilazanyl)-N'-chlorodimethylsilyltetramethylcyclodisilazane, 12%; an unidentified peak (13%); and oligocyclodisilazane (n = 3), 75%.

7. Condensation of oligomers with sodium bis(trimethylsilyl)amide: After a mixture of 21.9 g. (0.100 mole) of hexamethylcyclotrisilazane and 6.45 g. (0.050 mole) of dimethyldichlorosilane was heated under nitrogen at 175° for 48 hr., the petroleum ether-insoluble portion (ammonium chloride) weighed 2.30 g. (0.043 mole, 57% conversion to trisilylamine structures). The calculated equivalents of NH remaining in the oligomer were 0.128. One-fourth of the petroleum ether solution was treated with 5.86 g. (0.032 mole) of sodium bis(trimethylsilyl)amide in 30 ml. of diethyl ether and stirred at room temperature for 1 hr. Filtration gave 0.9 g. of salts.

When the ether was evaporated and the residue was heated to 220° (0.1 mm.), 4.1 g. of a brownish solid was obtained. The infrared spectrum of the residue is reported in Figure 35 and the infrared spectrum of the untreated petroleum ether-soluble polymer in Figure 36.

In a second experiment, the same quantities of reactants were heated at 300° for 21 hr. Separation of the petroleum ether-soluble product gave 3.0 g. (0.056 mole) of ammonium chloride. The conversion to trisilylamine structures was 75%. When one-fourth of the polymer was again treated with 3.15 g. (0.019 mole) of sodium bis(trimethylsilyl)amide in ether in a similar manner, 3.5 g. of a dark brown brittle solid was obtained. The residue from the untreated material (10.3 g.) was a soft waxy solid.

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APPENDIX

FIGURES 1 THROUGH 44, INFRARED AND N.M.R. SPECTRA

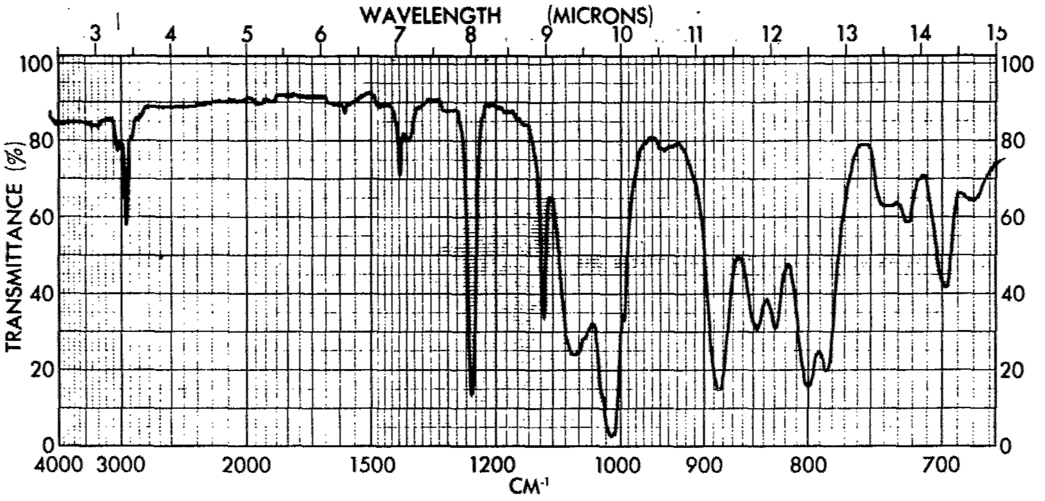

Figure 1 - Infrared Spectrum of N,N'-Bis(dimethylphenylsiloxydimethylsilyl)tetramethylcyclodisilazane (Liquid)

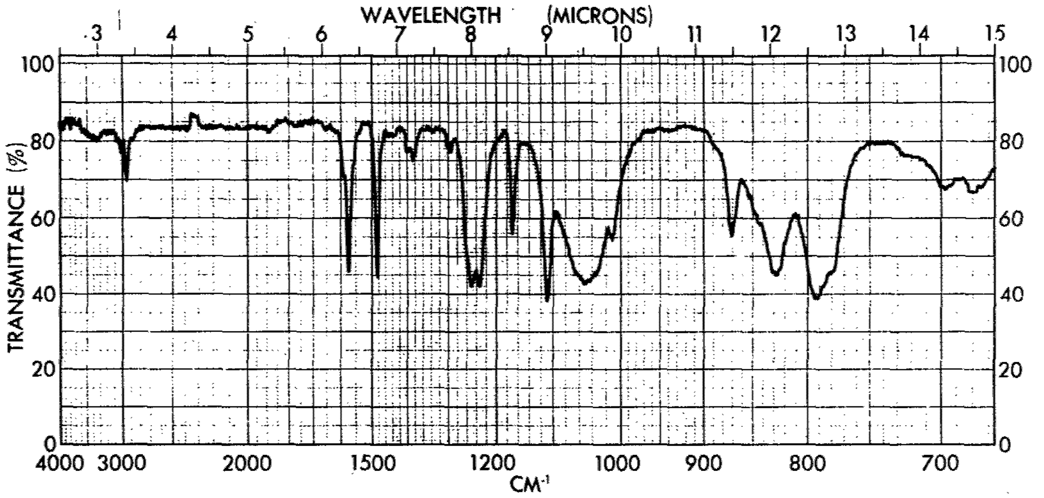

Figure 2 - Infrared Spectrum of the Homopolymer of Bis(p-dimethylhydroxysilylphenyl) Ether Obtained in the Attempted Copolymerization with Bis(dimethylsilyl)trimethylsilylamine (Film)

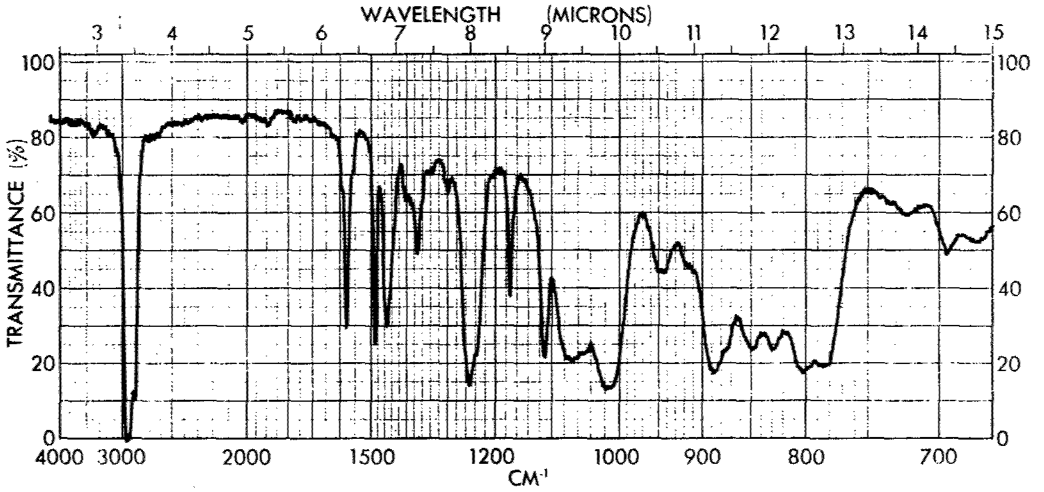

Figure 3 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, which was Prepared for Characterization (Nujol)

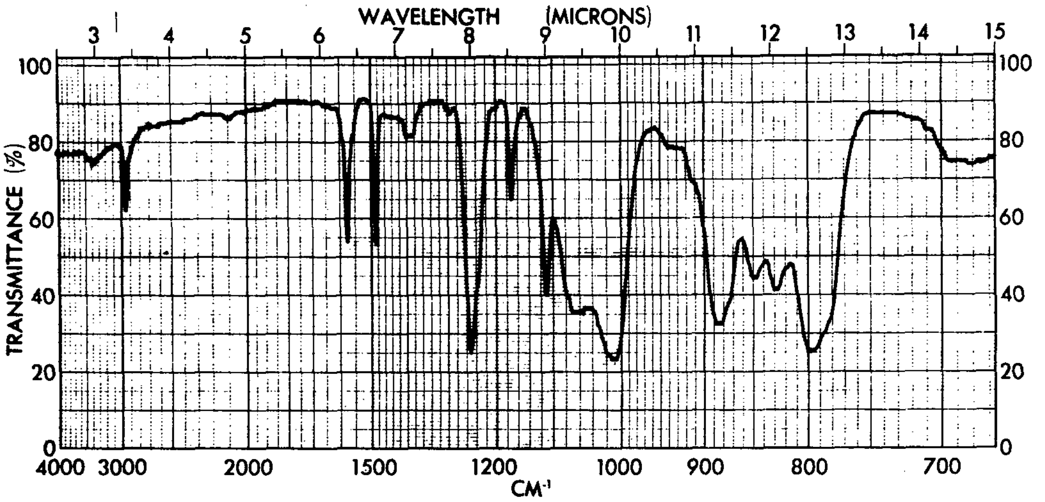

Figure 4 - Infrared Spectrum of the Copolymer from Bis(dimethylsilyl)tetramethylcyclodisilazane and Bis(p-dimethylhydroxysilylphenyl) Ether Prepared with 0.5% NaH (Film)

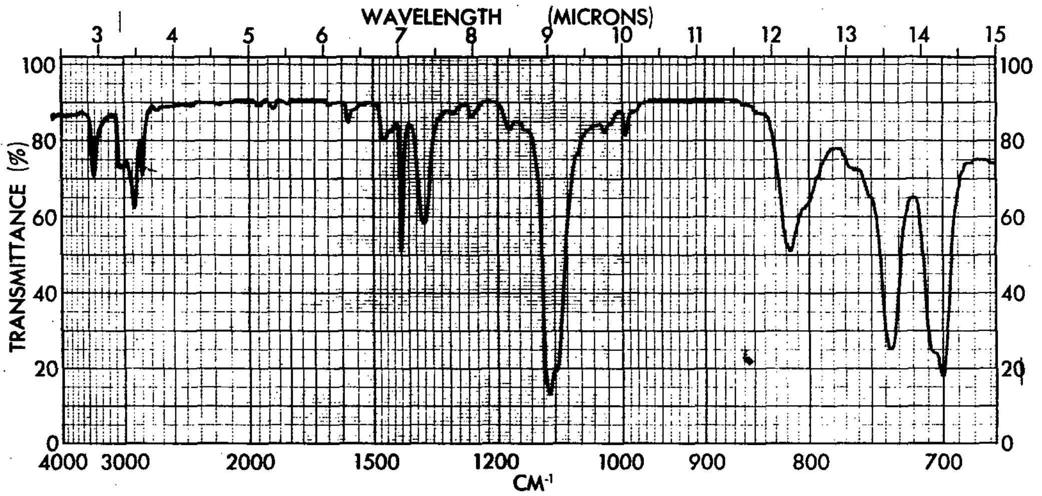

Figure 5 - Infrared Spectrum of Bis(methylamino)dimethylsilane (Liquid)

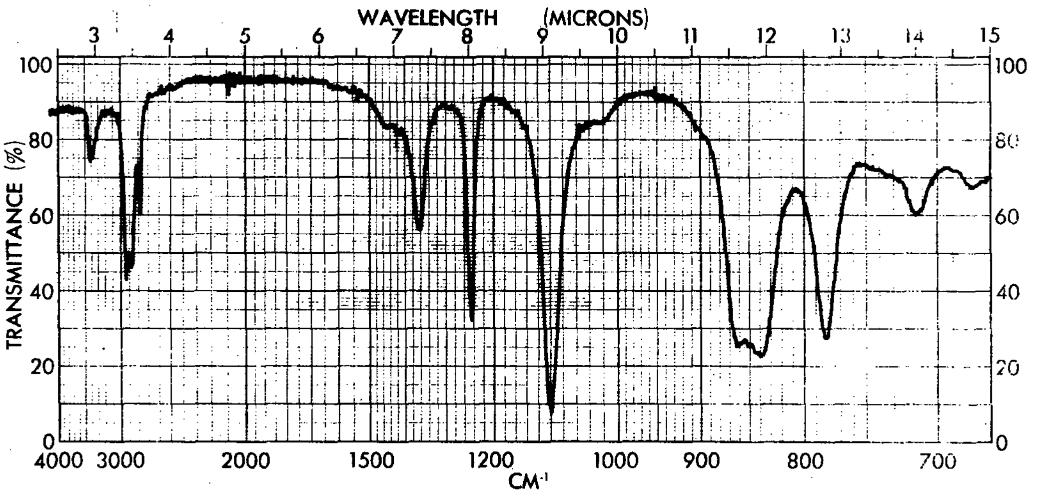

Figure 6 - Infrared Spectrum of Bis(methylamino)diphenylsilane (Liquid)

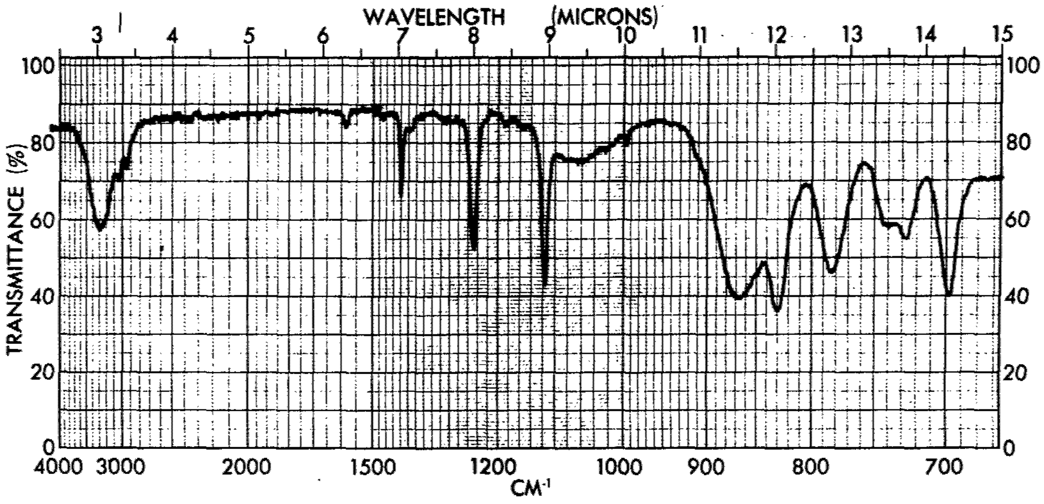

Figure 7 - Infrared Spectrum of Dimethylphenylsilanol (Liquid)

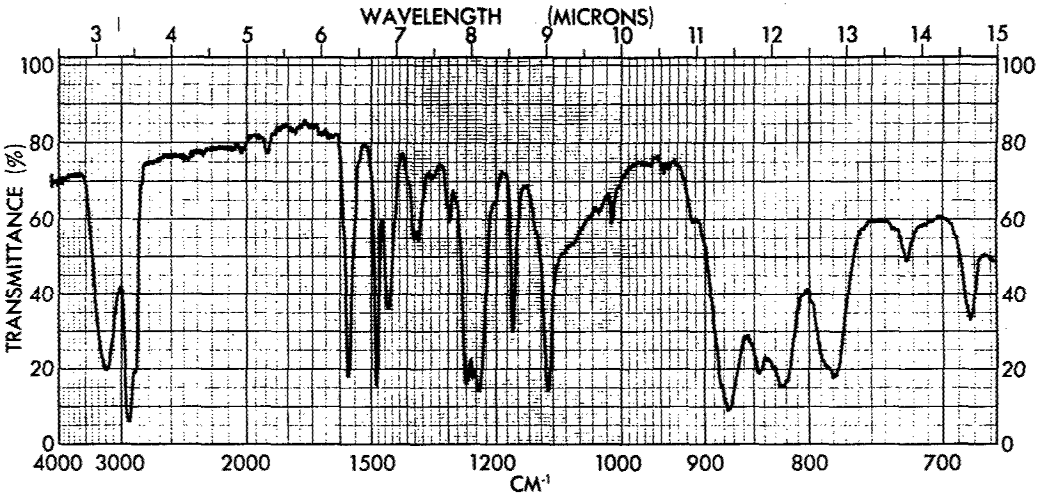

Figure 8 - Infrared Spectrum of Bis(p-dimethylhydroxysilylphenyl) Ether (Nujol)

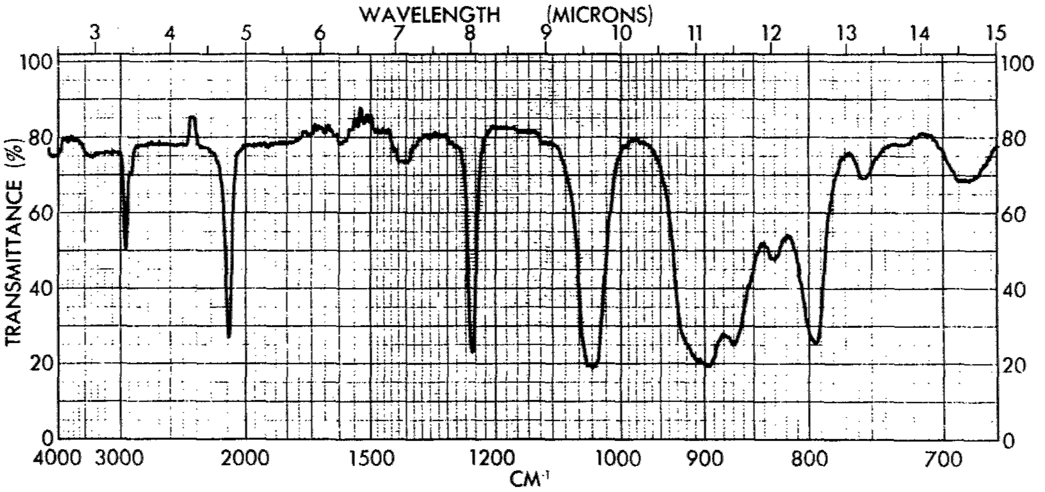

Figure 9 - Infrared Spectrum of N,N'-Bis(dimethylsilyl)tetramethylcyclodisilazane (Liquid)

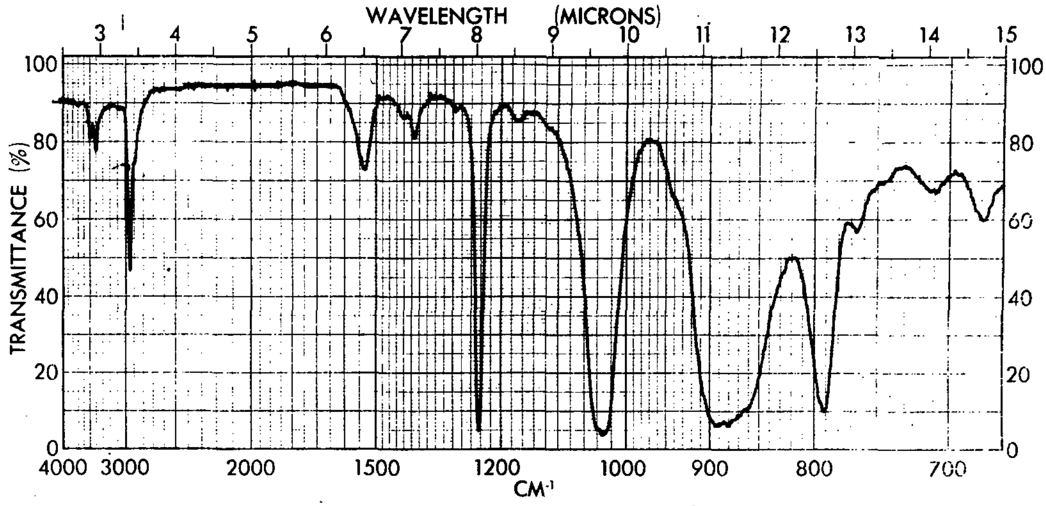

Figure 10 - Infrared Spectrum of N,N'-Bis(aminodimethylsilyl)-tetramethylcyclodisilazane (Nujol)

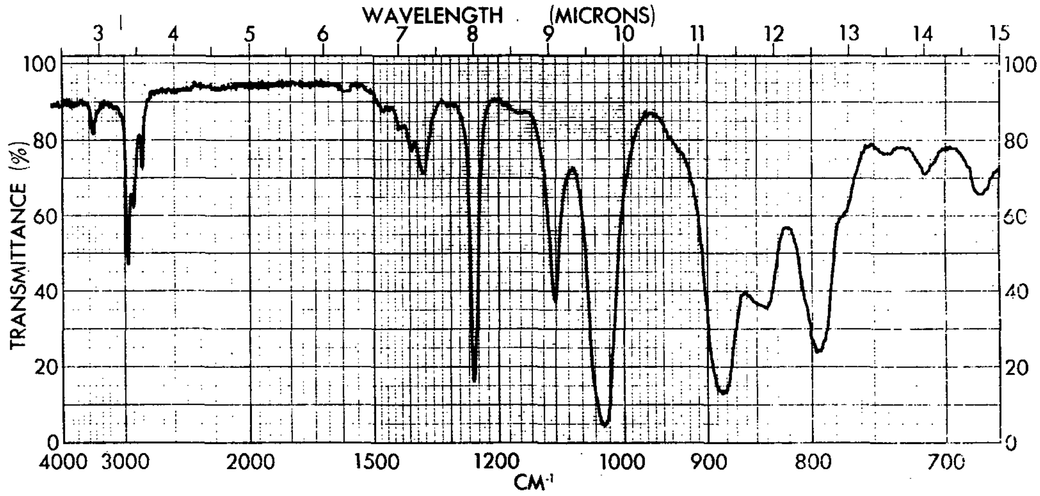

Figure 11 - Infrared Spectrum of N,N'-Bis(dimethylmethylamino-silyl)tetramethylcyclodisilazane (Liquid)

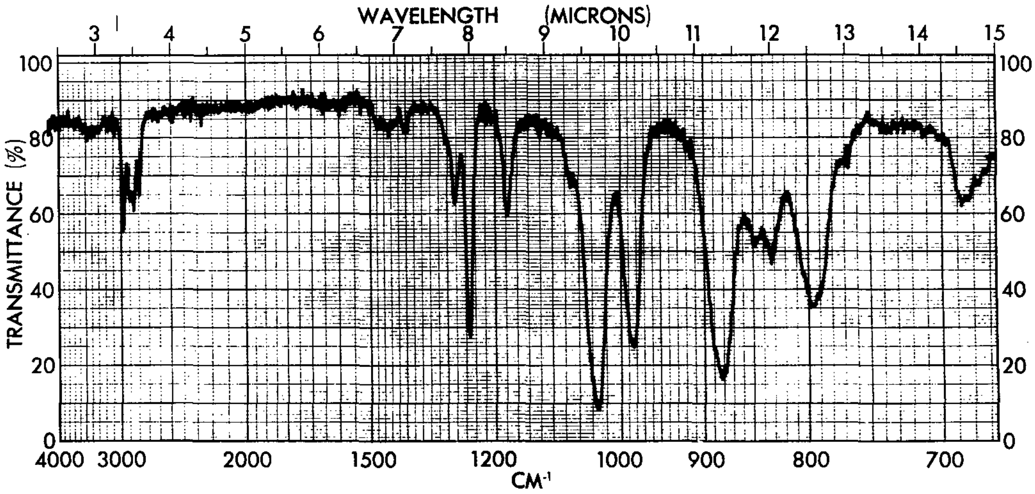

Figure 12 - Infrared Spectrum of N,N'-Bis(dimethylaminodimethyl-silyl)tetramethylcyclodisilazane (Liquid)

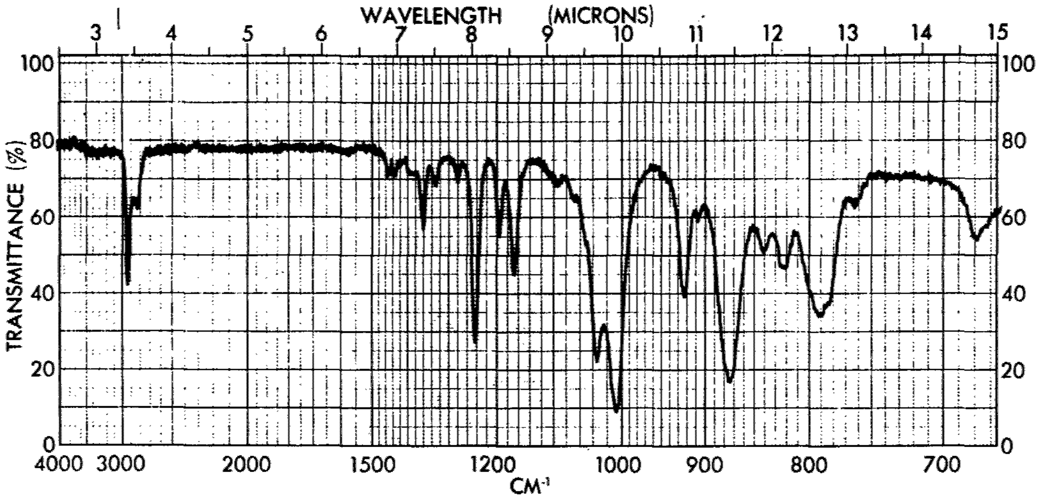

Figure 13 - Infrared Spectrum of Bis(diethylaminodimethylsilyl)-tetramethylcyclodisilazane (Liquid)

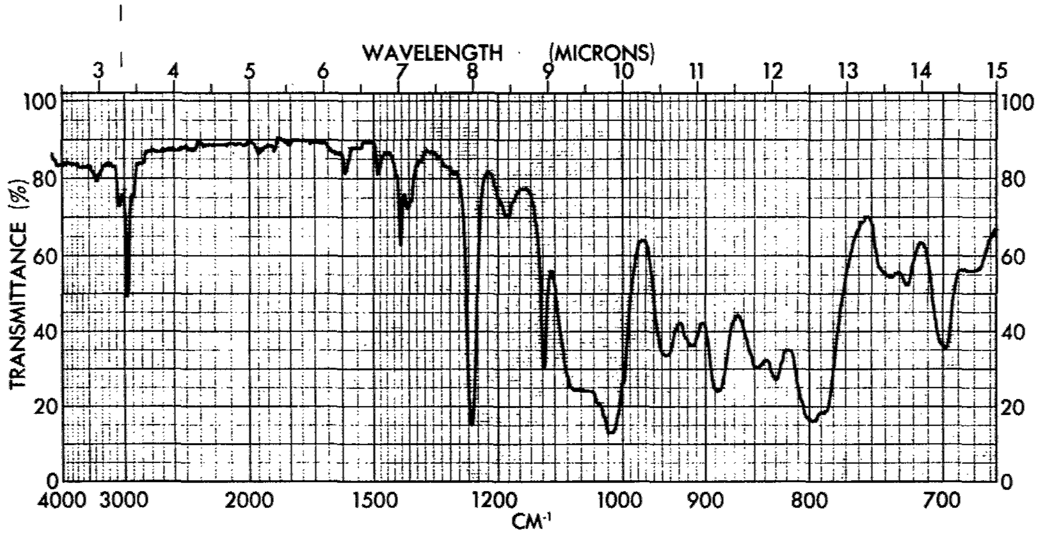

Figure 14 - Infrared Spectrum of the Residue from the Preparation of N,N'-Bis(dimethylphenylsiloxydimethylsilyl)tetramethylcyclodisilazane (Liquid)

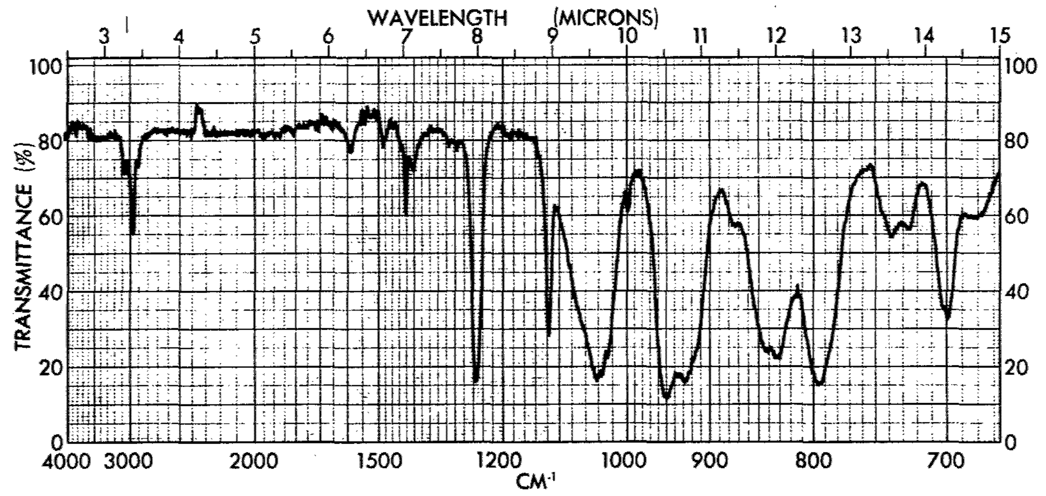

Figure 15 - Infrared Spectrum of Bis(3-phenyltetramethyldisiloxanyl)trimethylsilylamine (Liquid)

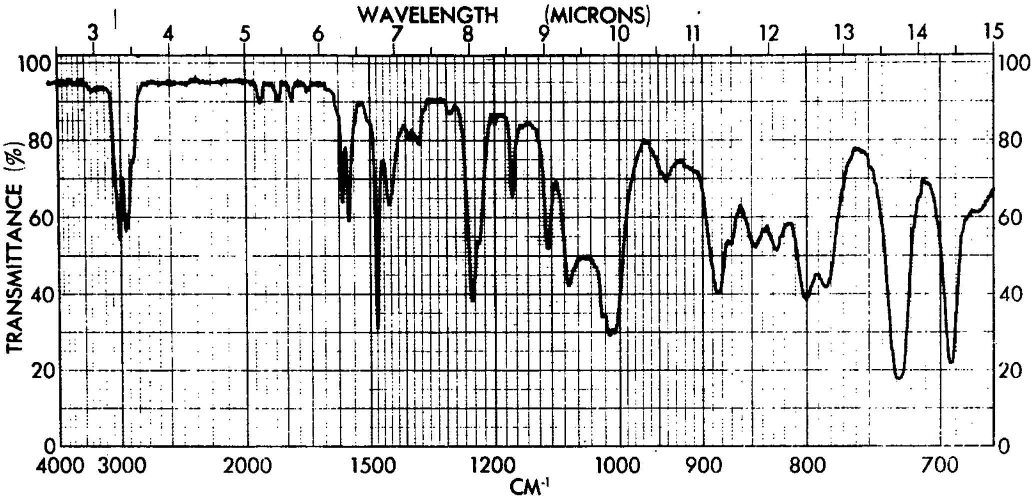

Figure 16 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (1:1) (Toluene Smear)

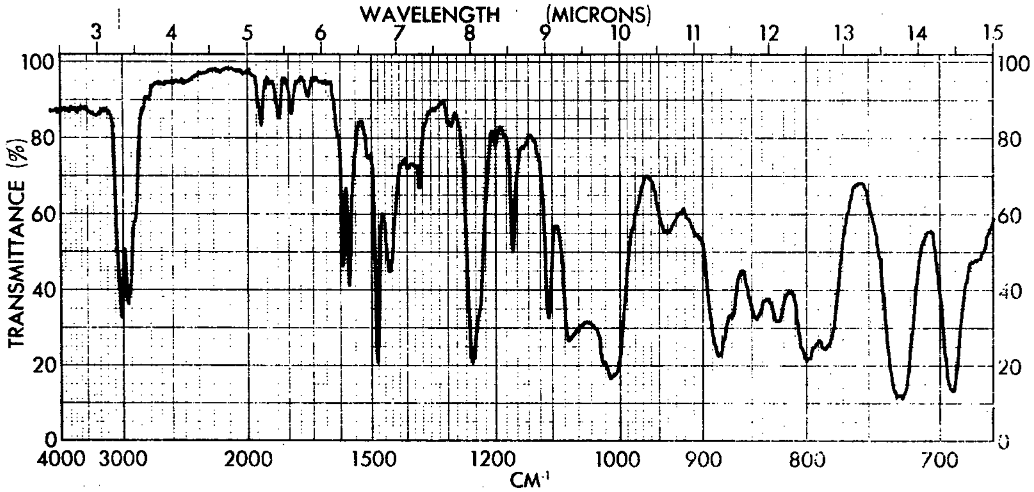

Figure 17 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (1:1.05) (Toluene Smear)

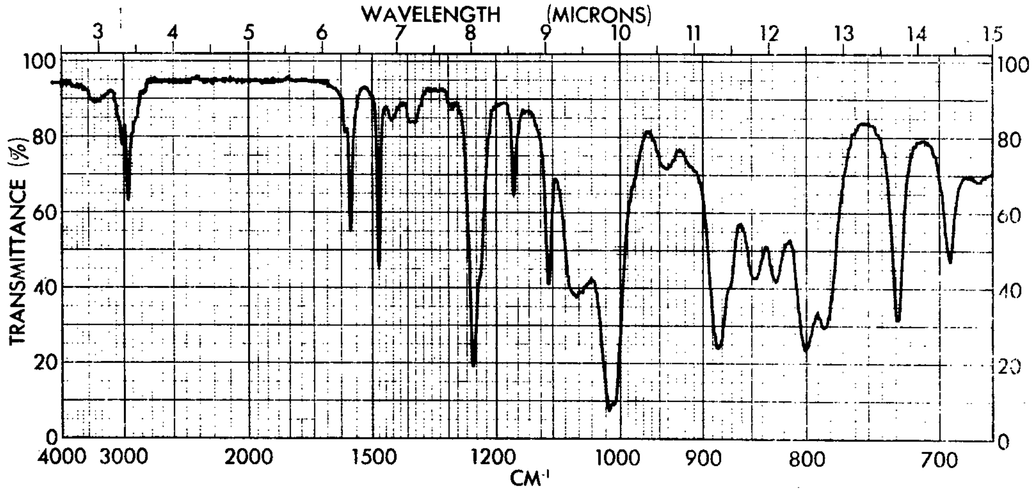

Figure 18 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (1:1.1) (Toluene Smear)

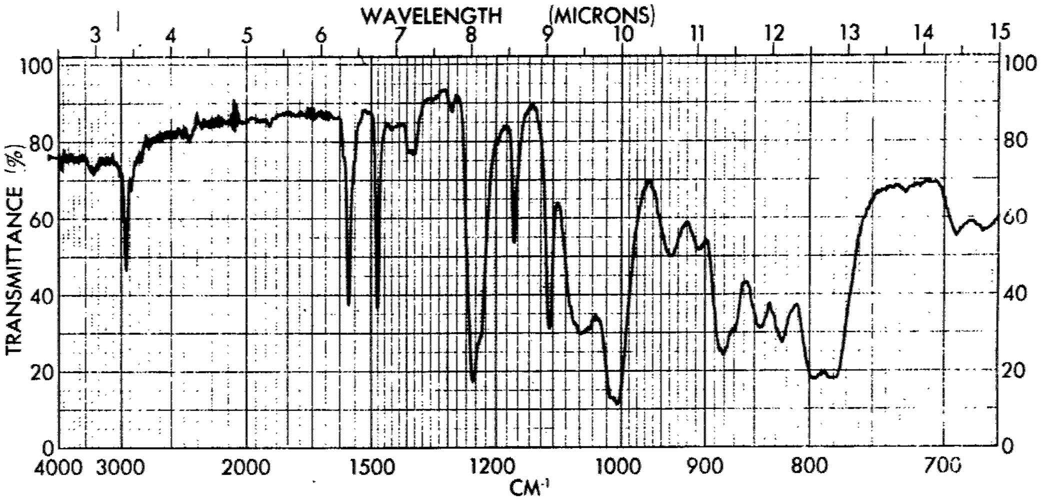

Figure 19 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (1.1:1) (Smear)

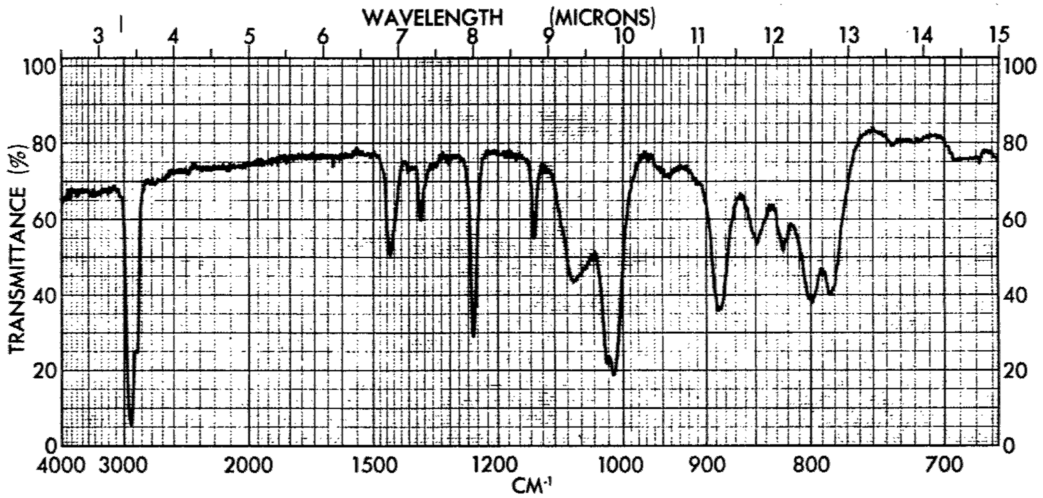

Figure 20 - Infrared Spectrum of the Polymer from p-Phenylenebis(dimethylsilanol) and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane, which was Prepared for Characterization (Smear)

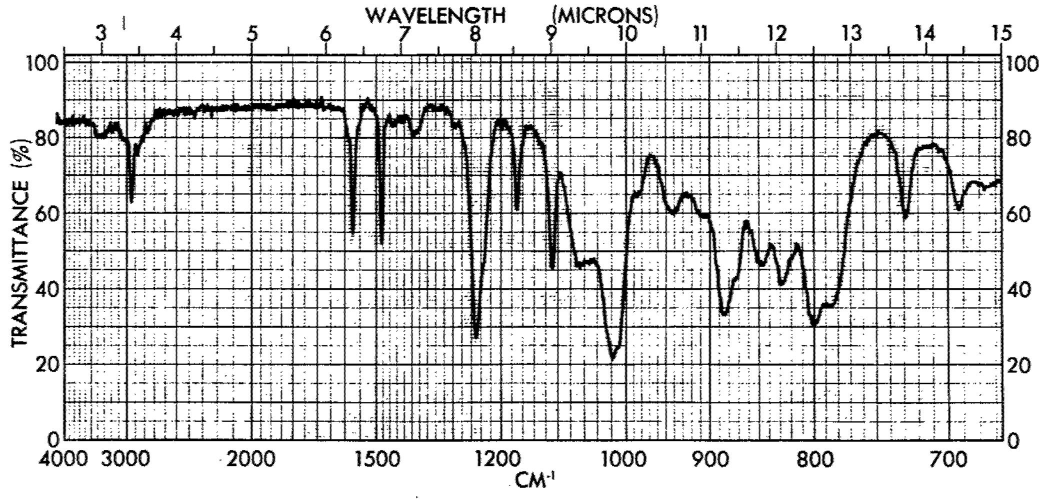

Figure 21 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane (Smear)

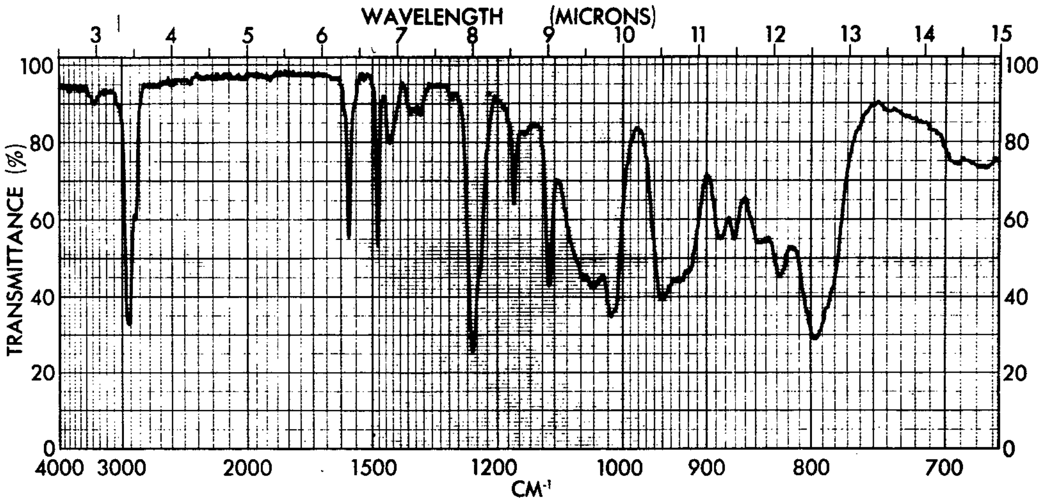

Figure 22 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylmethylaminosilyl)tetramethylcyclodisilazane (Smear)

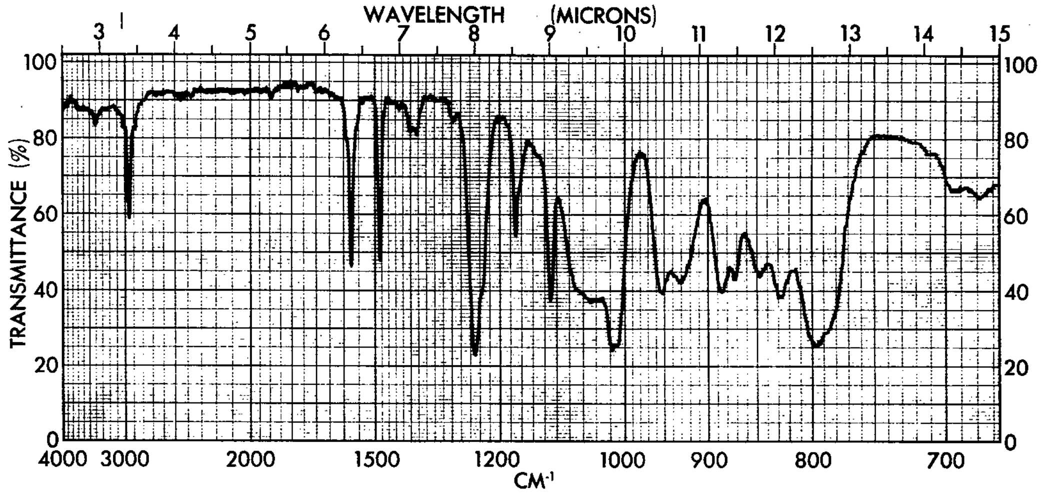

Figure 23 - Infrared Spectrum of the Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(aminodimethylsilyl)-tetramethylcyclodisilazane (Smear)

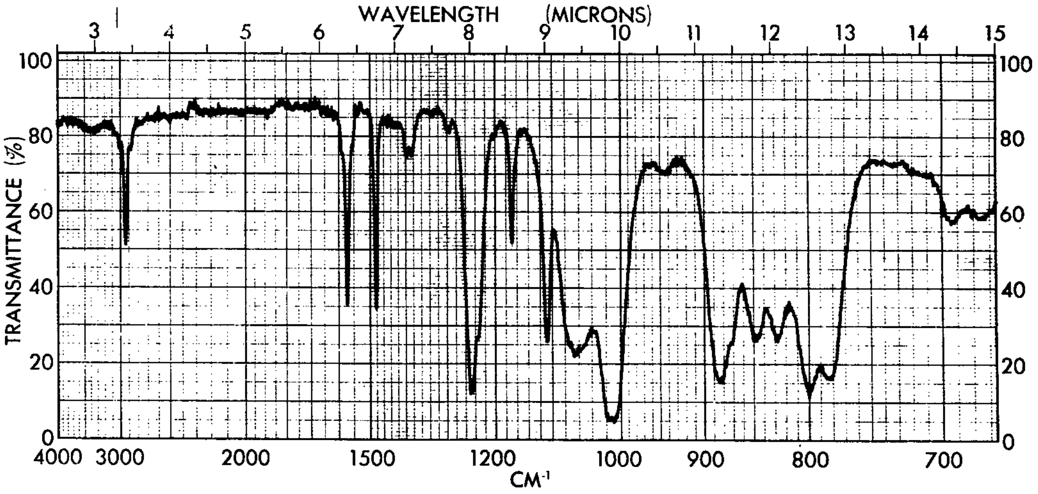

Figure 24 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane (Film)

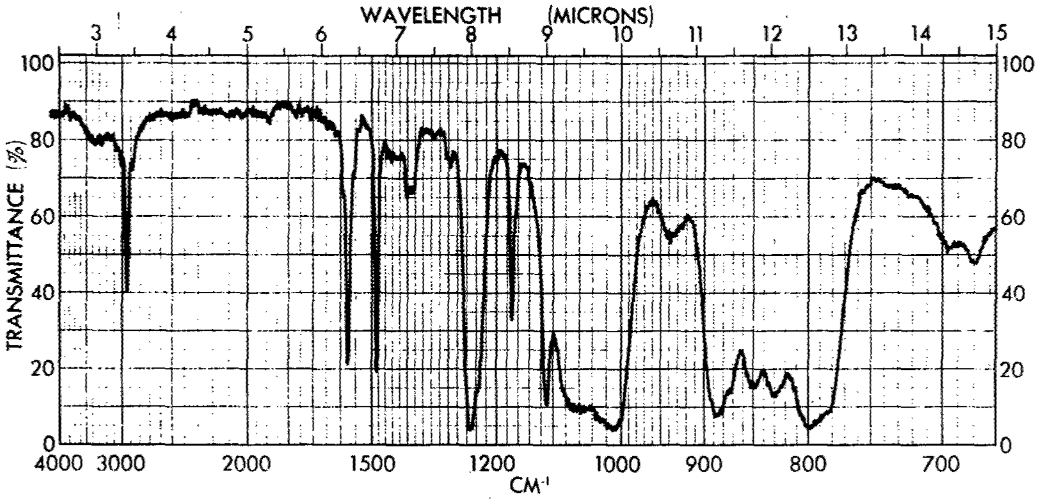

Figure 25 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis(dimethylsilyl)tetramethylcyclodisilazane (Smear)

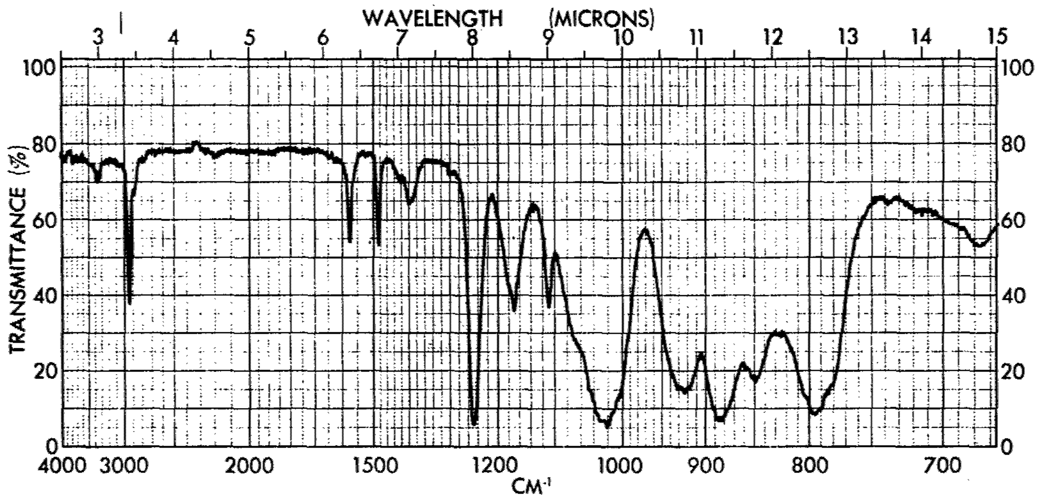

Figure 26 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and an Equilibration Oligomer (Film)

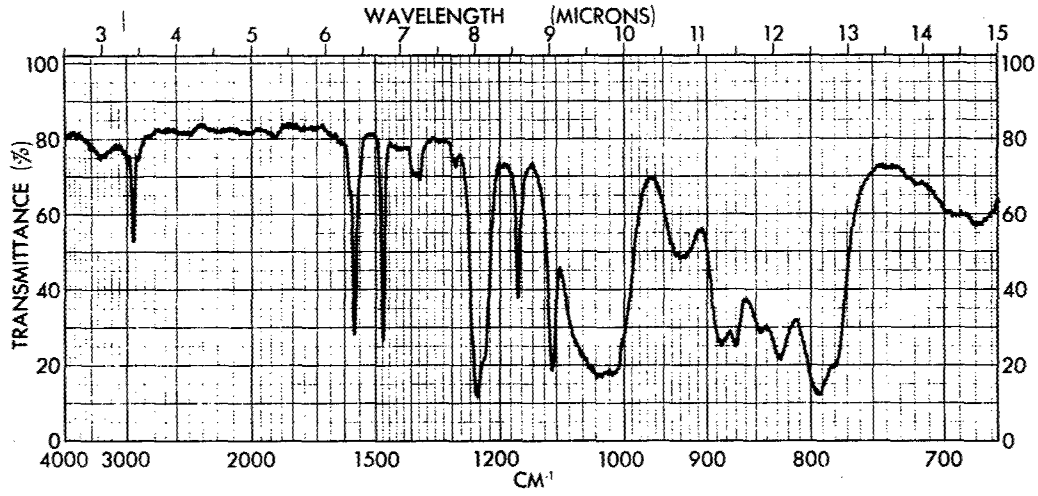

Figure 27 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and an Equilibration Oligomer (Film)

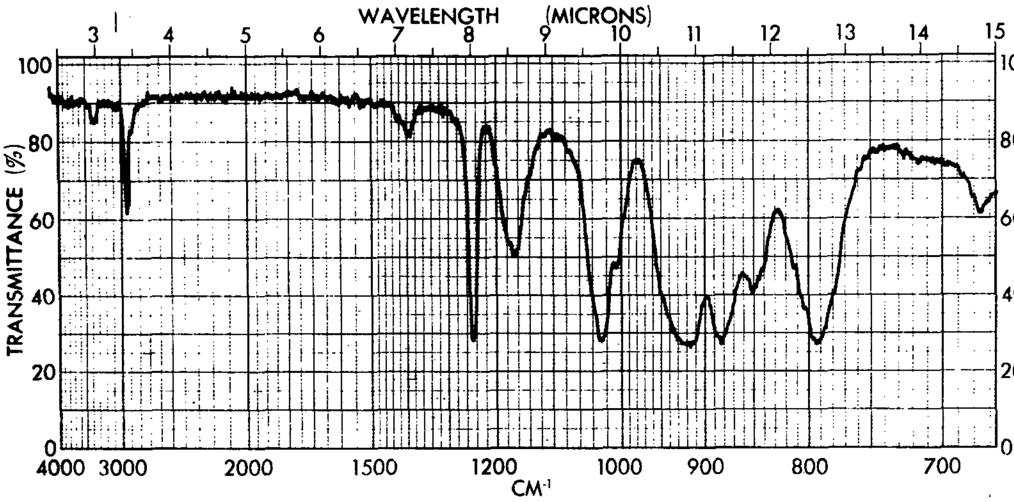

Figure 28 - Infrared Spectrum of the Oligomer from Hexamethylcyclotrisilazane and Ammonium Bromide (Film)

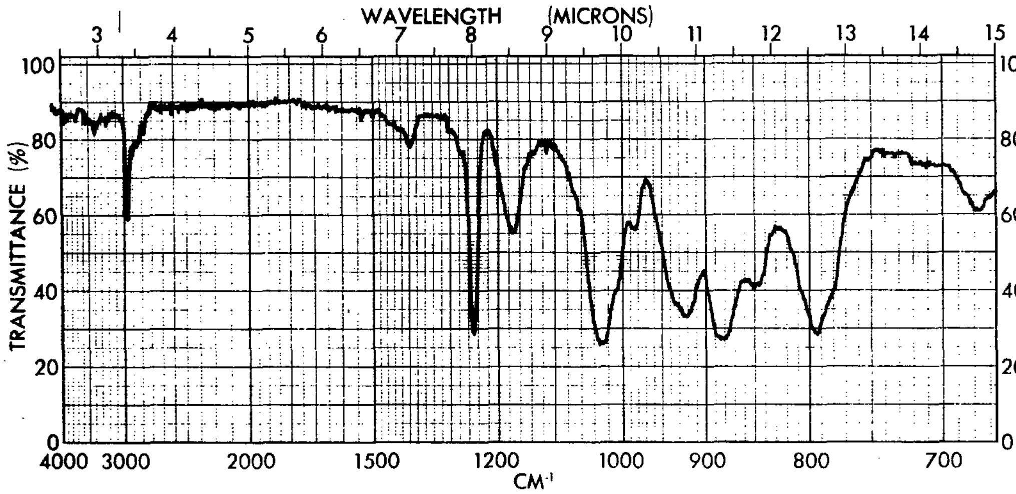

Figure 29 - Infrared Spectrum of the Oligomer from Hexamethylcyclotrisilazane and Dichlorodimethylsilane (2:1 Mole Ratio) (Film)

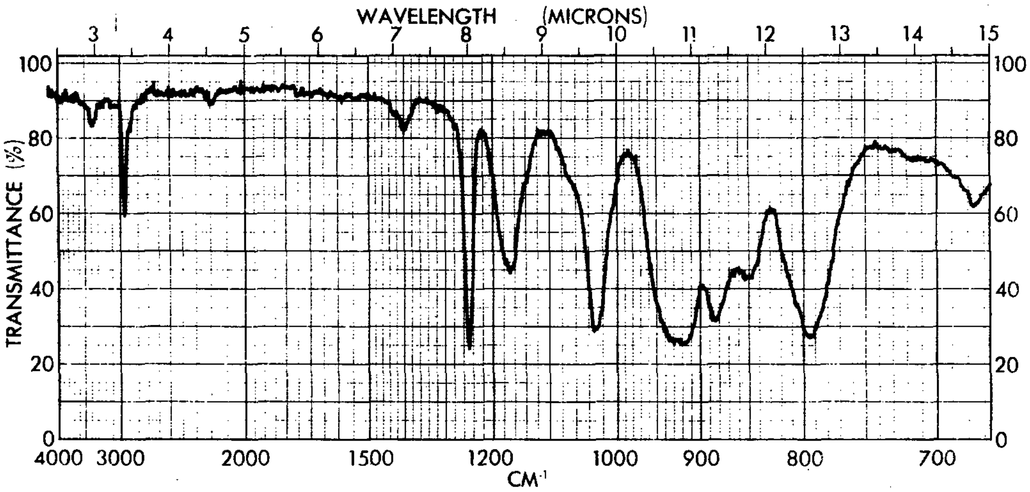

Figure 30 - Infrared Spectrum of the Oligomer from Hexamethylcyclotrisilazane and Dichlorodimethylsilane (5.5:1 Mole Ratio) (Film)

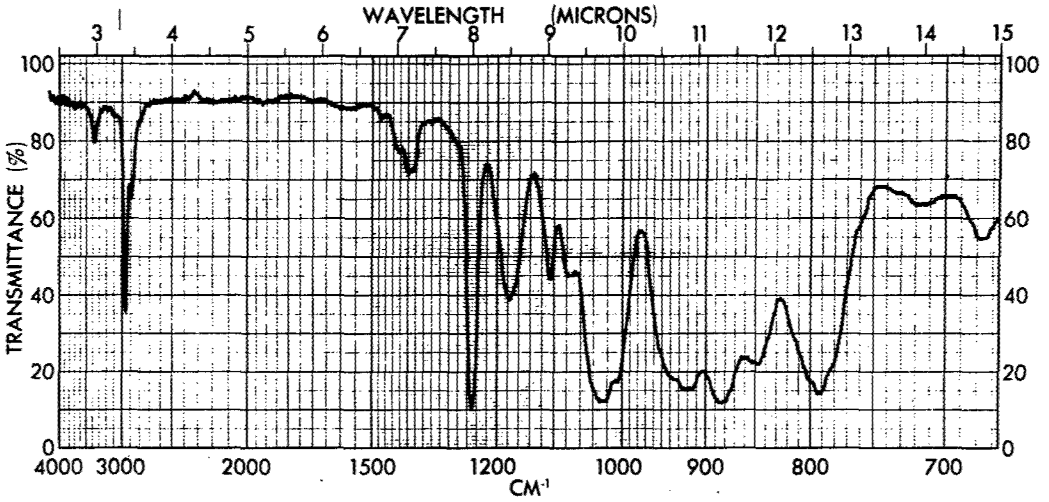

Figure 31 - Infrared Spectrum of the Product of Treating an Oligomer from Hexamethylcyclotrisilazane and Dichlorodimethylsilane with Ethanol (Film)

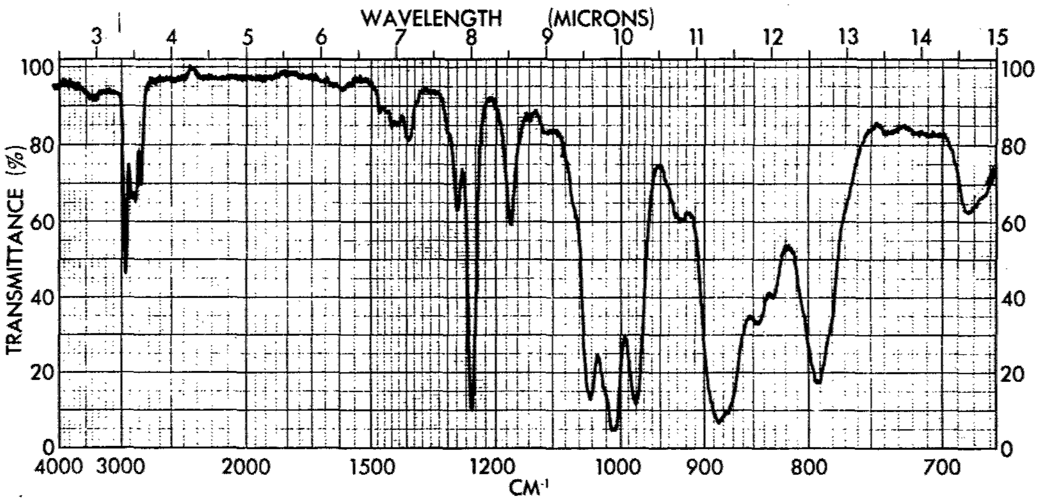

Figure 32 - Infrared Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_2SiMe_2NMe_2$ (Liquid)

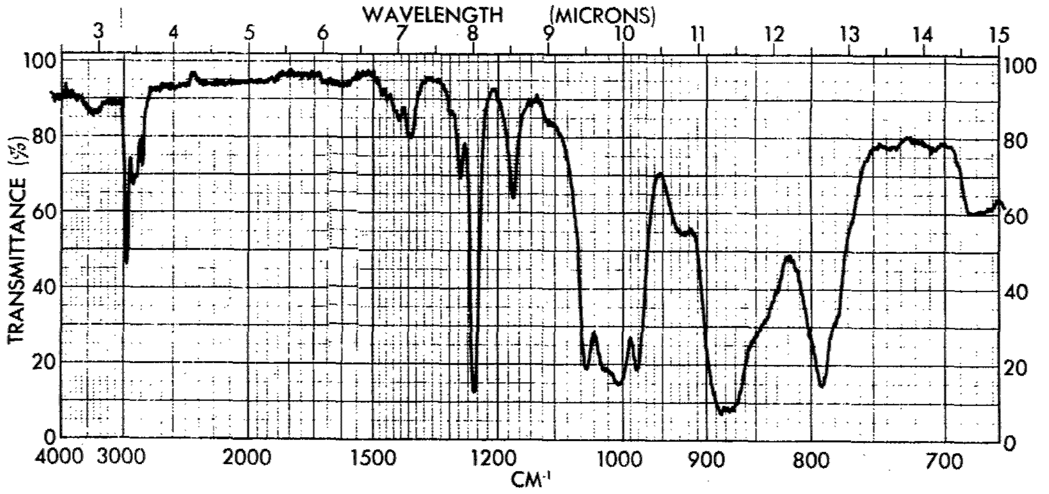

Figure 33 - Infrared Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_3SiMe_2NMe_2$ (Smear)

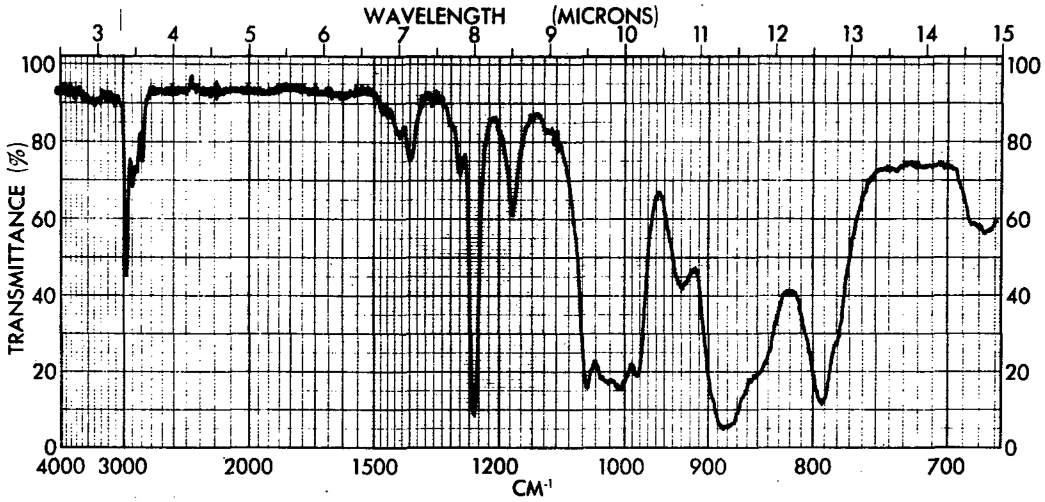

Figure 34 - Infrared Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_4SiMe_2NMe_2$ (Smear)

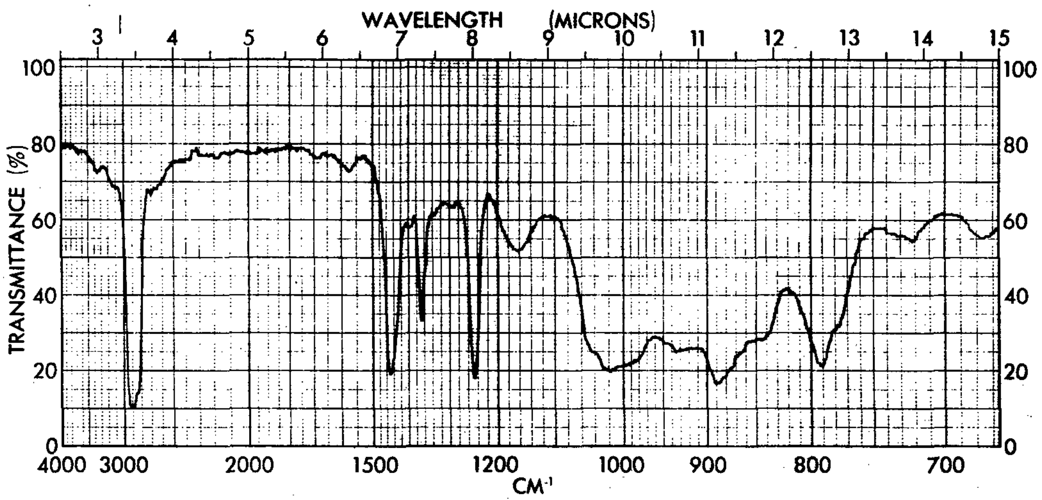

Figure 35 - Infrared Spectrum of an Oligomer After Treatment with Sodium Bis(trimethylsilyl)amide (Smear)

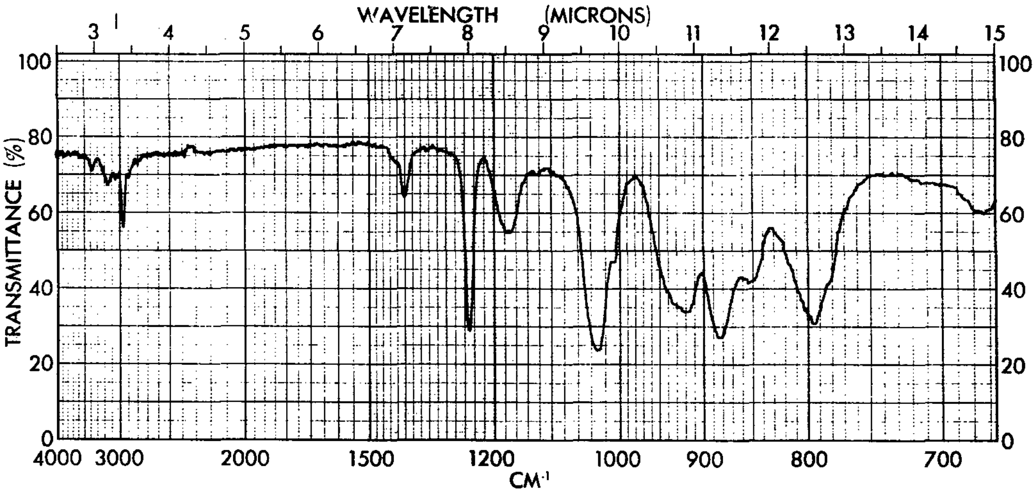

Figure 36 - Infrared Spectrum of an Oligomer Before Treatment with Sodium Bis(trimethylsilyl)amide (Smear)

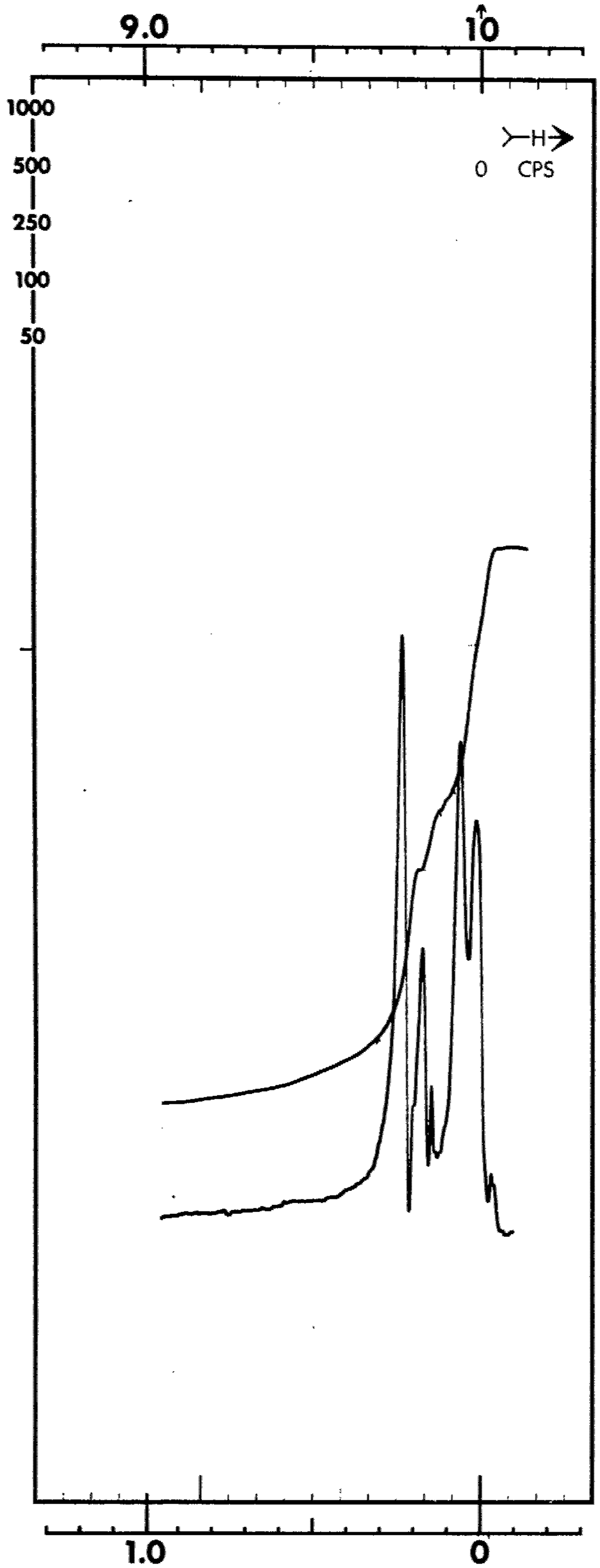

Figure 37 - N.m.r. Spectrum of the Oligomer from Hexamethylcyclotrisilazane and Ammonium Bromide (CCl_4)

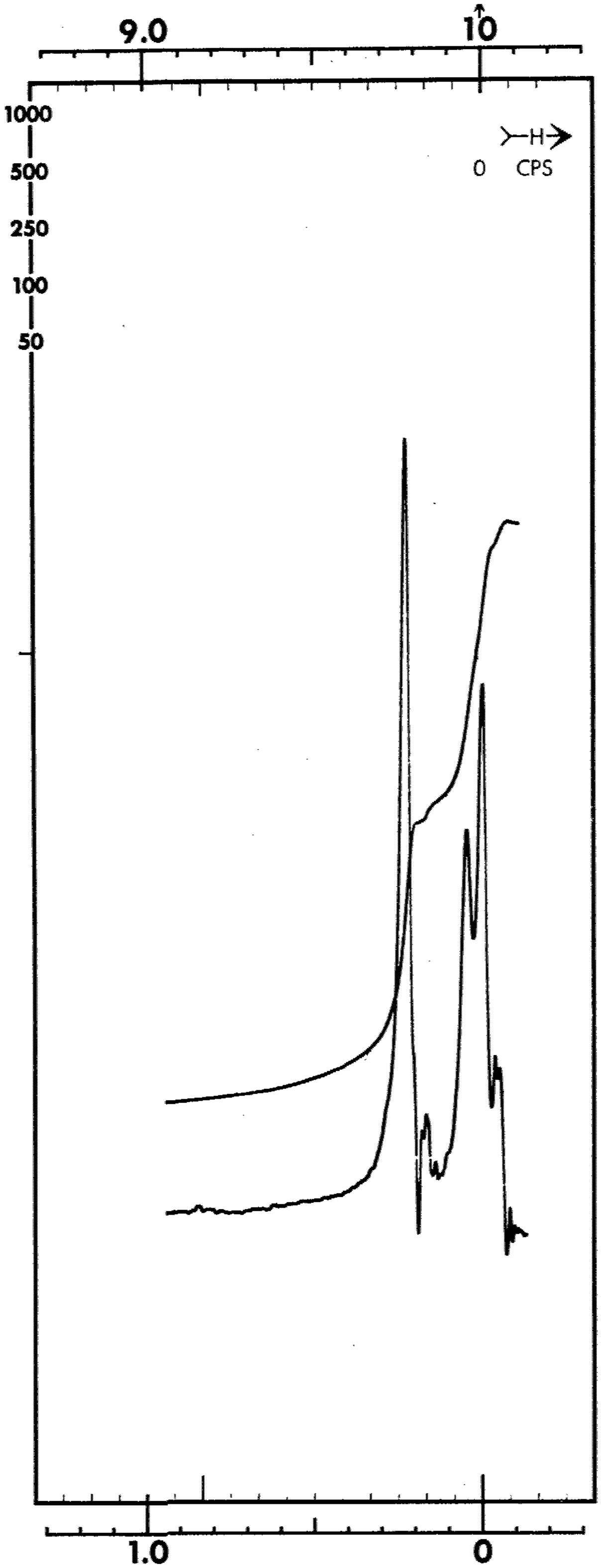

Figure 38 - N.m.r. Spectrum of the Oligomer from Hexamethylcyclotrisilazane and Dichlorodimethylsilane (CCl_4)

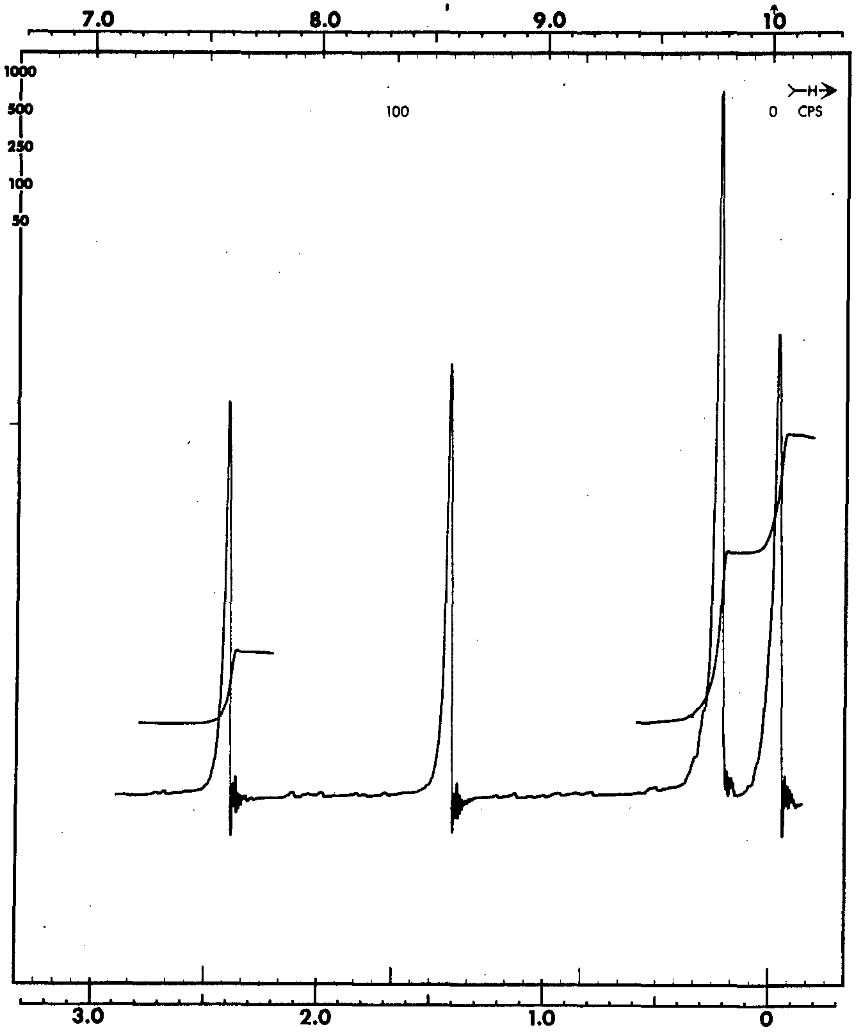

Figure 39 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_2SiMe_2NMe_2$ (CCl_4) - Cyclohexane Internal Standard

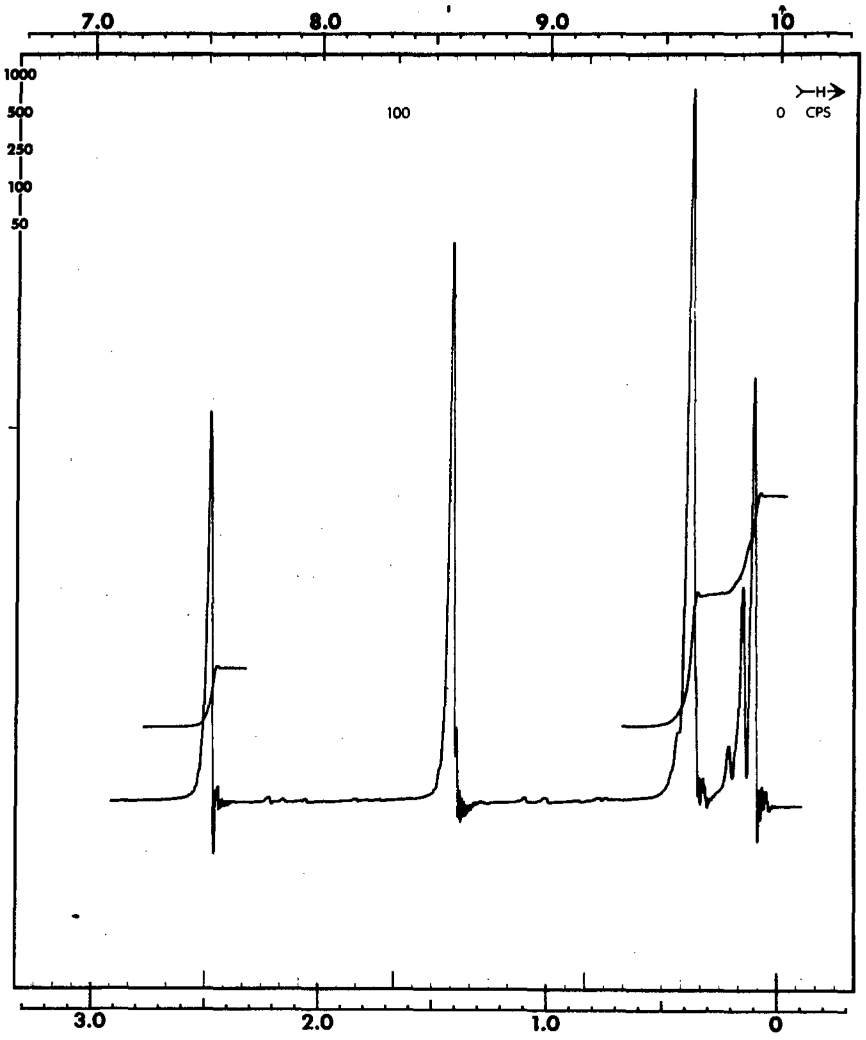

Figure 40 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_2SiMe_2NMe_2$ (C_6H_6) - Cyclohexane Internal Standard

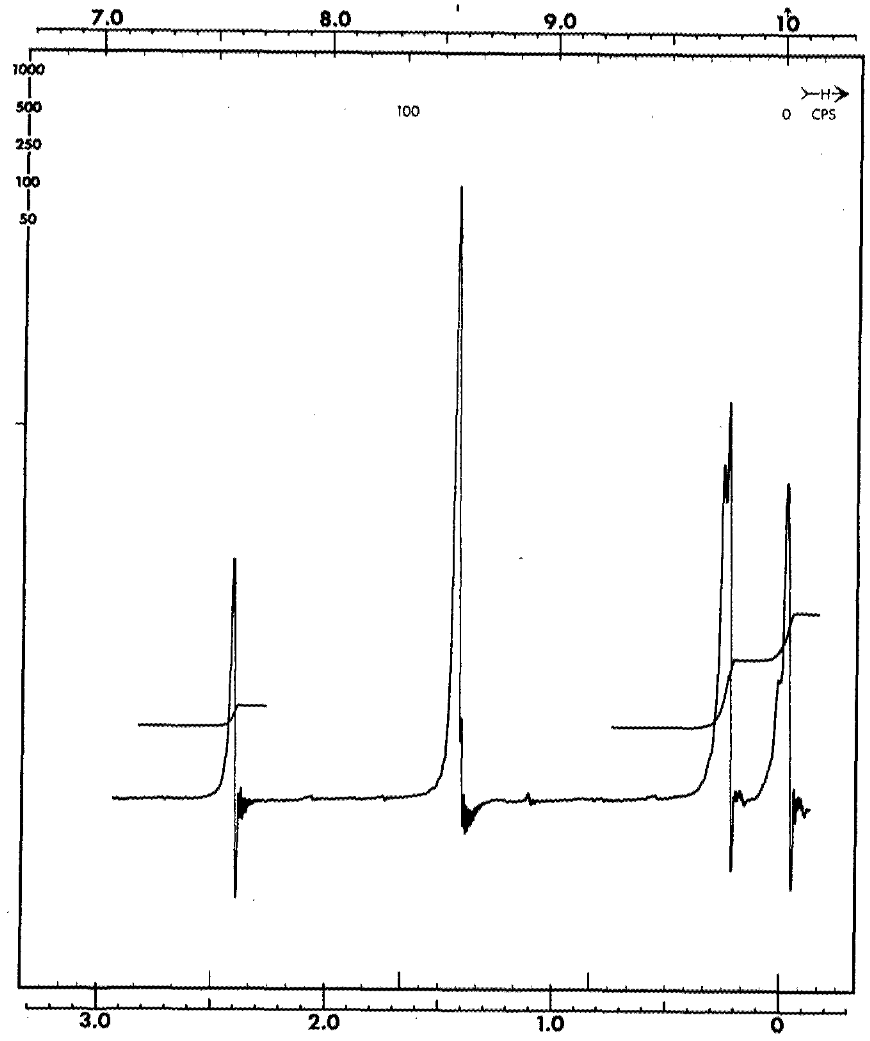

Figure 41 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_3SiMe_2NMe_2$ (CCl_4) - Cyclohexane Internal Standard

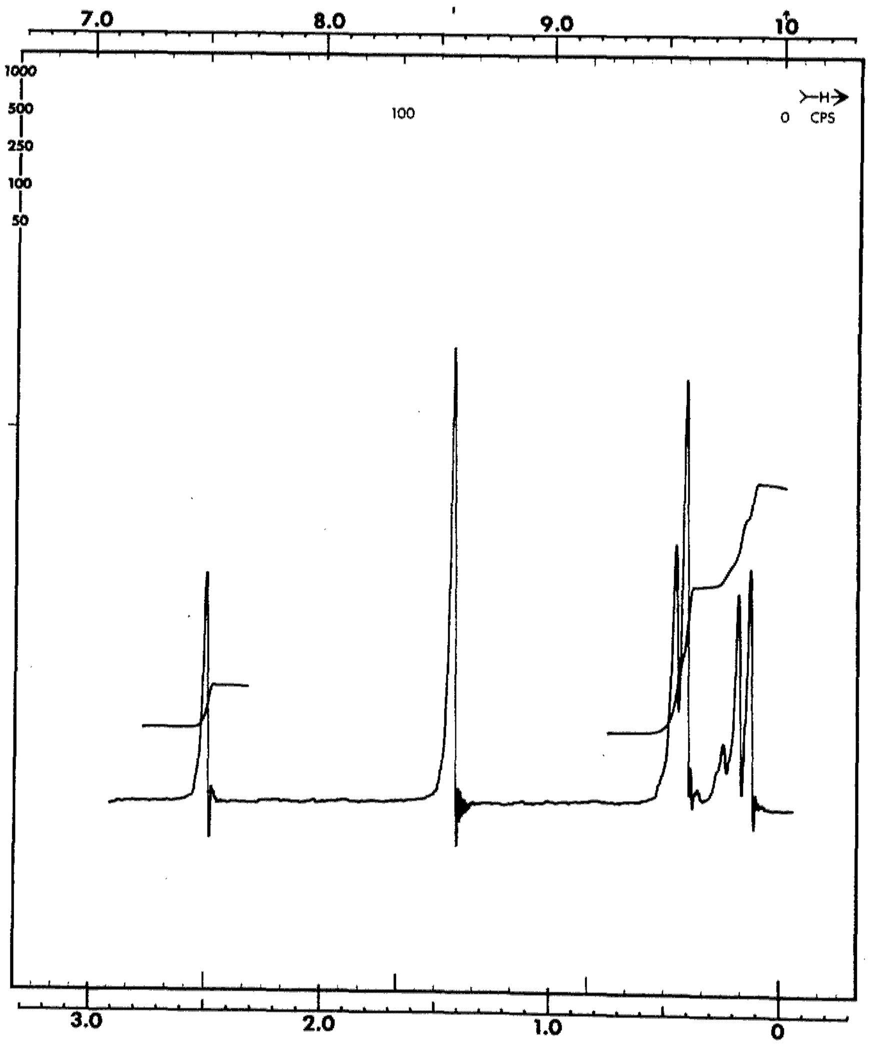

Figure 42 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_3SiMe_2NMe_2$ (C_6H_6) - Cyclohexane Internal Standard

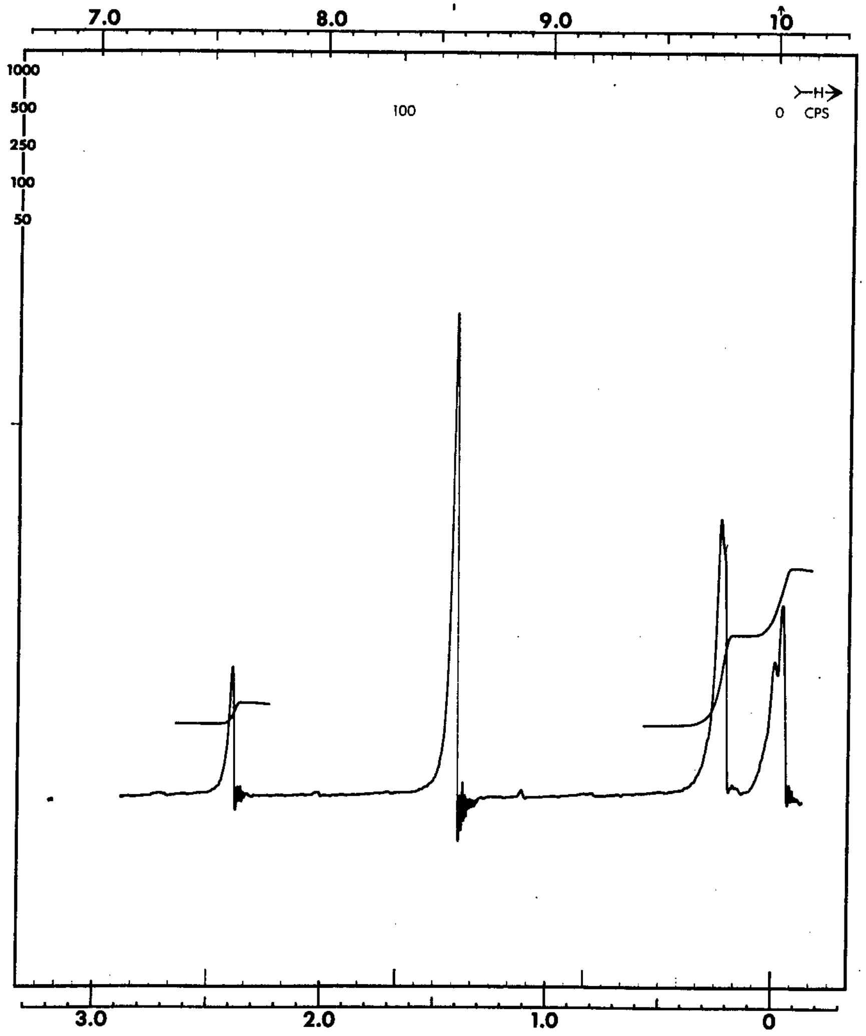

Figure 43 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_4SiMe_2NMe_2$ (CCl_4) - Cyclohexane Internal Standard

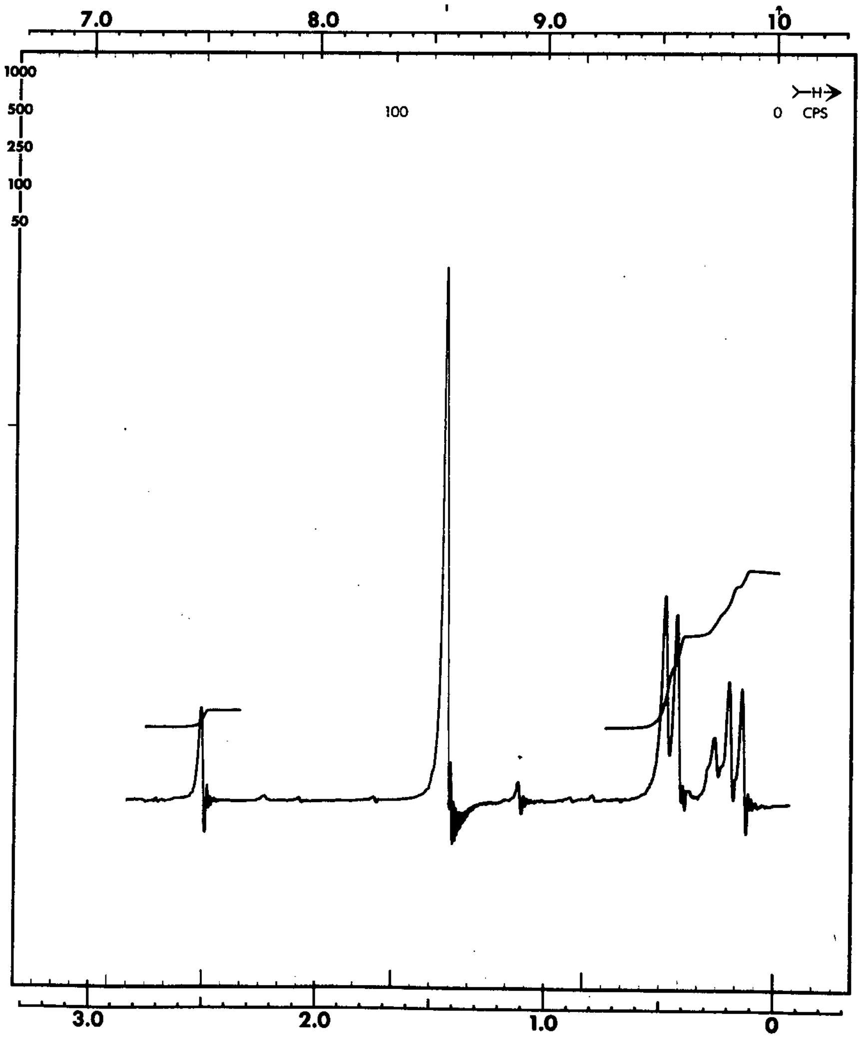

Figure 44 - N.m.r. Spectrum of a Fraction Containing Mostly $Me_2N[SiMe_2(NSiMe_2)_2]_4SiMe_2NMe_2$ (C_6H_6) - Cyclohexane Internal Standard

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13. ABSTRACT

Condensation polymers of N,N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane and bis(p-dimethylhydroxysilylphenyl) ether and p-phenylenebis(dimethylsilanol) were prepared and characterized. Under various conditions of preparation, the polymers lost solubility in nonpolar solvents before high molecular weights could be achieved. The condensation of the same arylene disilanols with N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane in the presence of sodium hydride gave polymers with less tendency to lose solubility, but high molecular weight materials were not obtained. Condensation reactions of arylene disilanols with the amino-, methylamino-, and diethylaminosilyl derivatives of the cyclodisilazane monomers are also reported. Evidence is offered for the structure of the oligomers obtained by equilibrating dichlorodimethylsilane with hexamethylcyclotrisilazane under various conditions and the structure compared with that of other similarly prepared materilas that have been reported by others. Additional details are offered on the synthesis of monomers and intermediates.

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