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Technical report No. ARPA-19

SILAZANE POLYMERS

By

George Redl

October, 1965

MALLINCKRODT LABORATORY
DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY • CAMBRIDGE MASSACHUSETTS

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Mallinckrodt Laboratory
Department of Chemistry
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Cambridge, Massachusetts

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ABSTRACT

Although methods for making linear polymers of dimethylsiloxane (i e., silicone rubber) from the corresponding cyclic siloxanes have been known for 20 years, no method for preparing a corresponding linear polymer of dimethylsilazane from the cyclic silazanes had been found when this work began. The only available process for obtaining solid polymeric dimethylsilazane of any kind was that discovered by Carl Krüger, ARPA Research Fellow in 1962-64; the product of this method was crosslinked through tertiary nitrogen atoms through an unavoidable side reaction.

A study of the kinetics and mechanisms of the Krüger condensation revealed that the evolution of ammonia which brings about the crosslinking could be suppressed by conducting the reaction under a pressure of ammonia. In fact, polymerization of cyclic dimethylsilazane could be accomplished by heating the silazane under ammonia pressure alone, without any Krüger catalyst. An equilibrium mixture resulted, from which a low yield of linear polymer was isolated. Elemental analysis, NMR sprectra, and infrared absorption spectra all prove that this product is indeed linear polymer composed of a multiplicity of $(CH_3)_2Si$-NH- units. The process is described, and variations of it are reported. Methods for improving the yield and for increasing the molecular weight now are being sought.

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SILAZANE POLYMERS

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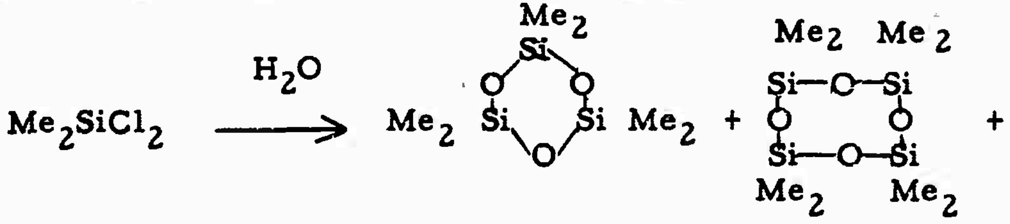
INTRODUCTION

The work to be reported here forms a part of a long-term project of the investigation of nitrogen-containing organosilicon polymers at Harvard University.

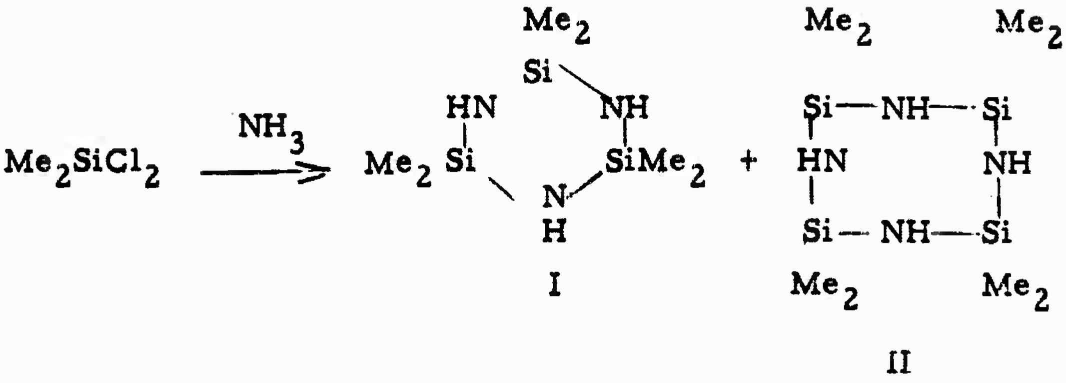
The interest in this field has been stimulated by the very rapid progress in the chemistry and industrial application of oxygen-containing organosilicon polymers (the silicones). A further incentive has been to learn more about the fundamental chemistry of the silicon-nitrogen bond. One of the reasons why progress with silazane polymers has been so much slower than that with the silicones is the strong tendency for silicon-nitrogen systems to form small ring compounds where, by analogy with siloxanes, polymers would be expected.

For example, while the hydrolysis of dimethyldichlorosilane yields, besides cyclic siloxanes, about 50% of linear siloxane polymer



$$HO\text{-}(Me_2\text{-}Si\text{-}O)_nH \qquad (1)$$

The ammonolysis of the same compound results almost exclusively in the formation of the cyclic products hexamethylcyclotrisilazane (I) and octamethylcyclotetrasilazane (II).



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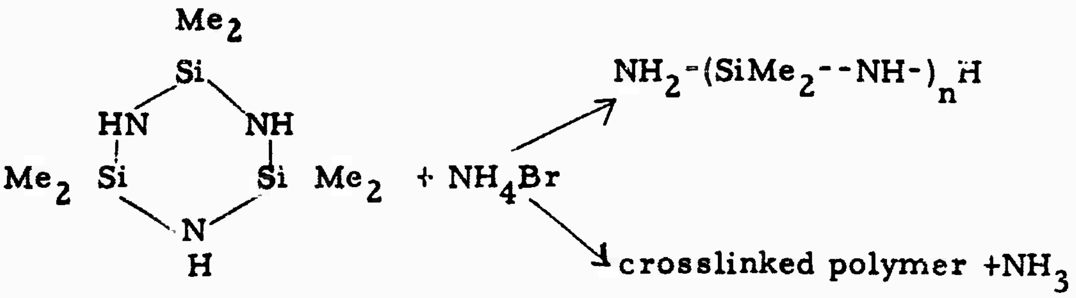
Furthermore, the cyclic siloxanes can be converted into linear polymers by equilibration with catalysts such as sulphuric acid or potassium hydroxide. Sulphuric acid and other oxygen-containing strong acids destroy the silicon-nitrogen bond, while potassium hydroxide is either completely ineffective, or, at sufficiently high temperatures (above 100°C), it attacks the carbon-silicon bonds of organosilazanes. So neither type of reagent can be used as equilibration catalyst.

Ammonium salts have been used as catalysts for a number of reactions of silicon-nitrogen compounds, and their role can be considered as that of a mild acid catalyst in the ammonia system, incapable of converting silazanes to siloxanes the way acids in the water system do.

Ammonium halides (and especially ammonium bromide) have been successfully applied by Krüger in these laboratories as catalysts for converting cyclic silazanes into polymers [1 cf.]. However, instead of the expected simple conversion into linear silazane



(3)

ammonia evolution was observed and the polymer obtained was crosslinked via trisilyl-substituted nitrogen atoms. In fact, for every molecule of ammonia eliminated, two $\equiv Si\text{-}NH\text{-}Si\equiv$ groupings have to be converted into $\equiv Si\text{-}\underset{\underset{Si\equiv}{|}}{N}\text{-}Si\equiv$ groupings. The stoichiometry of this process can be represented as follows:

$$n(\text{-}NH\text{-}SiMe_2\text{-})_3 \longrightarrow [\text{-}\overset{|}{N}\text{-}(SiMe_2\text{-})_{3/2}]_{2n} + nNH_3 \qquad (4)$$

This would describe the polymerization reaction if the ammonia elimination were carried out to completion. However, the analytical results on the isolated polymer clearly indicated that the ammonia elimination was incomplete; i.e., secondary as well as tertiary nitrogen atoms were present in the polymer.

It seemed worthwhile to find out some details of the mechanism of this ammonium halide catalyzed polymerization reaction of cyclic silazanes.

ARPA-19 DISCUSSION OF EXPERIMENTAL RESULTS

Cyclic and linear polysilazanes

As a first approach to the mechanism of the polymerization reaction [3], it was decided to measure the rate of ammonia evolution. If the rate of crosslinking is defined as the rate of formation of trisilyl-substituted nitrogen groupings, then it is exactly double the rate of ammonia evolution. The reaction was originally described by Krüger [1] as being carried out in a stream of nitrogen. In a preliminary series of kinetic measurements by Krüger the ammonia was absorbed by hydrochloric acid and the acid back-titrated at intervals. In order to get continuous readings and also to eliminate the time-consuming titrations, it was decided to follow the rate of ammonia evolution directly by volume expansion. Therefore, a gas burette (with liquid seal) was connected directly to the polymerization vessel, so that the reaction was carried out in an effectively closed system at constant pressure (1 atm.). Surprisingly, only a few percent of the expected volume expansion was observed. It had to be assumed that in the closed system the initially eliminated ammonia suppressed further elimination of ammonia. Indeed, examination of the isolated polymer showed that it was somewhat less crosslinked than the polymer obtained by open system (nitrogen stream) polymerization.*

This observation made it clear that no kinetic study could be carried out this way, but on the other hand, it suggested a method by which

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* The degree of crosslinking can easily be estimated from the analytical results, since the calculated values for the two extreme cases (purely linear and completely crosslinked structures) are sufficiently different. However, it was found that the estimation can also be based on the high resolution NMR spectra of the polymers, and in fact, this method proved to be faster and more convenient. The NMR spectra will be discussed in detail in a separate chapter.

linear silazanes (similar to the linear siloxanes) might be prepared. It was this approach that was pursued further.

Since the closed-system polymerization was seen to retard the evolution of ammonia, it was reasonable to assume that the ammonia evolution might be suppressed completely by applying a sufficient pressure of ammonia at the beginning. It was hoped that if the ammonia elimination, and thereby the crosslinking, could be suppressed, ring-chain equilibrium (similar to that of the analogous siloxane system) would be reached. This expectation was borne out by the subsequent experiments. Carefully purified samples of hexamethylcyclotrisilazane (I) were heated for several days in the presence of a few percent of ammonium bromide and under different pressures of ammonia. The reaction product invariably contained at least 50% of unchanged (I) and some octamethylcyclotetrasilazane (II). After removing all the volatile products by distillation, a viscous, oily polymer was obtained. Under 1.5 atm. of ammonia pressure the degree of crosslinking of the isolated polymer was greatly diminished, and under 4 atm. of ammonia pressure crosslinking was undetectable in the NMR spectrum of the polymer. The analytical results (see experimental section) also were in good agreement with the values calculated for a purely linear polymer.

While the linear dimethylsiloxane polymers, $HO\text{-}(SiMe_2\text{-}O\text{-})_nH$, have molecular weights of several hundred thousand (which value can further be increased by the condensation of the terminal hydroxyl groups), the average molecular weight of the linear dimethylsilazane polymer samples obtained herein varied between one and two thousand. This low molecular weight is understandable, since the ammonia pressure which has to be applied in order to suppress crosslinking by mid-chain elimination of ammonia also opposes the condensation of the terminal NH_2 groups which would be necessary for the formation of longer chains. More precisely, the observed average molecular weight must correspond to the equilibrium state of the following reaction:

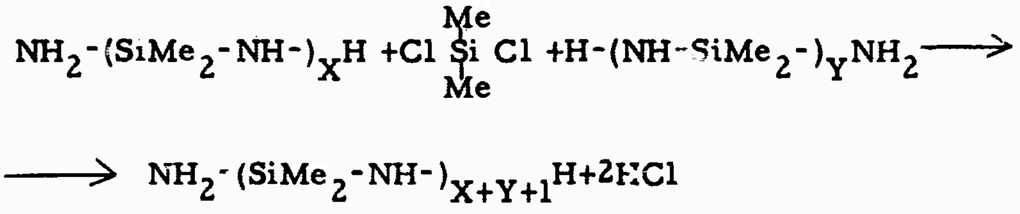
$$NH_2\text{-}(SiMe_2\text{-}NH\text{-})_xH + NH_2\text{-}(SiMe_2\text{-}NH\text{-})_yH \rightleftharpoons$$

$$NH_2\text{-}(SiMe_2\text{-}NH\text{-})_{x+y}H + NH_3 \qquad (5)$$

A number of attempts were made to increase the molecular weight of the polymer after its separation from the equilibrium mixture.

The molecular weight of linear siloxanes can be increased simply by heating, which causes condensation of the terminal hydroxyl groups. When the linear dimethylsilazane polymer was heated at 170° C in vacuum, a slow depolymerization appeared to take place. An oligomeric oil was collected in the cold trap, but the molecular weight of the residual polysilazane did not increase. The oligomeric oil did not contain I or II.

An alternative attempt was made to react the polymer with calculated amounts of dimethyldichlorosilane. It was hoped that chain lengthening would take place according to the following condensation reaction.



$$NH_2\text{-}(SiMe_2\text{-}NH\text{-})_XH + Cl\overset{Me}{\underset{Me}{Si}}Cl + H\text{-}(NH\text{-}SiMe_2\text{-})_YNH_2 \longrightarrow$$

$$\longrightarrow NH_2\text{-}(SiMe_2\text{-}NH\text{-})_{X+Y+1}H + 2HCl \qquad (6)$$

Pyridine was used as HCl acceptor, but in spite of that, extensive degradation took place and no pure linear silazane polymer could be recovered from the reaction product. An attempt also was made to use dimethyldiethoxysilane instead of dimethyldichlorosilane, since the condensation would produce ethanol instead of hydrochloric acid. However, this proved to be too mild an agent and, after the reaction, the silazane polymer was recovered unchanged.

Ring-chain equilibrium of the dimethylsilazane system

As mentioned earlier, the straight reaction products from which the polymer samples were isolated invariably contained considerable amounts of the cyclic silazanes I and II.

In the equilibration of dimethylsiloxanes the linear polymer prevails strongly over the cyclic siloxanes. In the silazane system it is seen that the equilibrium is rather on the side of the cyclic silazanes. The equilibrium mixture was analyzed by vapor phase chromatography and by distillation. The equilibrium composition reached at 140°C reaction temperature was found to contain 50% I, 20% II, 20% linear polymer and 5% distillable oligomeric oil. The same composition was reached irrespective of whether the starting material was I or II or a previously isolated sample of the linear polymer. This shows that a true equilibrium has indeed been achieved.

In the gas-chromatograms only two major peaks, corresponding to I and II, were observed although there were some hardly observable small peaks which may have been due to trace amounts of larger rings or, less likely, to low molecular weight linear silazanes. Again, this result should be compared with the equilibrium situation in the siloxane system where cyclic tri-, tetra-, penta-, hexa-, hepta-, octa- and even higher siloxanes are present in significant amounts at equilibrium. Thermodynamic calculations have recently been published about the ring-chain equilibrium state of the dimethyl siloxane system [2]. The results were at least in qualitative agreement with the observed equilibrium composition.

It would be interesting to carry out similar calculations for the silazane system in order to see whether the two characteristic features of the equilibrium state (the prevalence of rings over chains and the very strong preference for the 6 and 8 membered rings) could be predicted.

The temperature dependence of the equilibrium composition was not determined accurately, for almost all the equilibration experiments were carried out at 140° ± 5°C reaction temperatures. At lower temperatures, the equilibrium was reached very slowly, if at all, and at higher temperatures some crosslinking did take place in spite of the applied ammonia pressure. However, from a few trial experiments the conclusion seems to be that at lower temperatures the ring-chain equilibrium is even more strongly on the side of the cyclic products and the ratio I to II changes in favor of II. At higher temperatures, the opposite is true; I prevails even more strongly over II and there seems to be a small increase in the proportion of the polymer present at equilibrium.

In view of the fact that the equilibrium mixture obtained at 140°C contained 20% of linear polymer it seemed surprising that no linear polymer would be formed in the ammonolysis of Me_2SiCl_2. In a published account of this reaction, mention is made of a residue (10-20%) which is obtained after the distillation of cyclic silazanes I and II [3].

We found that if care was taken to avoid contact with the atmosphere during all stages of the preparation, then the involatile residue was less than 5%. The nitrogen content of this residue was 3.97% as opposed to the calculated value of 19.15% for a silazane polymer $(\text{-SiMe}_2\text{-NH-})_n$. The conclusion seems to be that in spite of the attempts to avoid contact with the atmosphere some hydrolysis did occur which resulted in the small amount of predominantly siloxane residue.

The explanation for the absence of linear silazane polymer among the ammonolysis products of Me_2SiCl_2 is probably that the reaction is kinetically controlled and that the product composition does not correspond to the thermodynamic equilibrium (compare discussion of similar effect to the N-butyl system).

Catalysts for the equilibration reaction

For the open system (nitrogen stream) polymerization, Krüger [4] found that the ammonium halide catalyst which seemed to give the best result was ammonium bromide. When ammonium bromide is added to hexamethylcyclotrisilazane (I), no apparent dissolution takes place, and the ammonium bromide crystals settle to the bottom of the reaction vessel. When this mixture is heated to the reaction temperature of around 140° C no obvious change is observed, but when the mixture is cooled to room temperature the clear liquid becomes turbid from reprecipitated ammonium bromide. Thus, ammonium bromide is very slightly soluble in the hot reaction mixture. The catalysis probably takes place both in the solution and on the surface of the undissolved ammonium bromide crystals. The heterogeneous catalysis has to be assumed to explain Krüger's observation [1] that increasing the amount of ammonium bromide speeded up the polymerization.

When the polymerization (equilibration) was carried out under 4 atm. ammonia pressure in the presence of ammonium bromide, it was noted that no turbidity developed when the mixture was cooled to room temperature at the end of the reaction.

This could be explained if we assume that the dissolution of ammonium bromide in the hot reaction mixture takes place solely or chiefly by reversible thermal dissociation.

$$NH_4Br \rightleftharpoons NH_3 + HBr \qquad (7)$$

Then the applied ammonia pressure would shift the equilibrium to the left so that only traces of ammonium bromide would go into solution. The reduced solubility under ammonia pressure raised the question as to how effective a catalyst ammonium bromide really is for the equilibration reaction. To test this, ammonium bromide was omitted from the reaction mixture and it was found that the same equilibrium was reached, although much slower than in the presence of ammonium bromide. In fact, it was necessary to increase the ammonia pressure to 15-20 atm. in order to achieve equilibrium in a reasonable time. The fact that increasing ammonia pressure speeded up the equilibration shows that its role goes beyond that of just suppressing the crosslinking reaction. To test this, an experiment was carried out in which a sample of I was heated under nitrogen pressure in the absence of ammonium bromide. No reaction took place at all, proving that the presence of ammonia is essential for the equilibration.

We can now summarize the role of ammonium bromide as follows. For the formation of the silazane polymer crosslinked via trisilyl-substituted nitrogen, ammonium bromide catalyst (or some other ammonium salt) is necessary. For the establishment of the ring-chain equilibrium, ammonium bromide is a good catalyst but its presence is not essential. The fact that equilibration takes place only under ammonia pressure is very important because it permits the isolation of the linear polymer from the equilibrium mixture by distilling off the volatile silazanes. If it is important to obtain a linear polymer completely free from crosslinking, it is better not to use ammonium bromide catalyst, for if traces of the catalyst are left in the mixture, then in the distillation process, when ammonia pressure is no longer present, crosslinking could take place

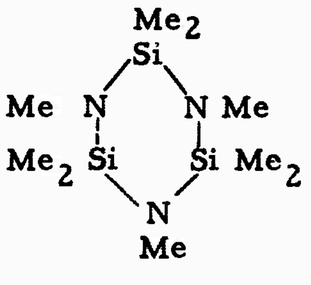
When a slightly colored sample of I was treated for a long time with active charcoal, it was noticed that crystals of II appeared in the flask. This observation suggested that charcoal may be a good catalyst for the equilibration. This proved to be true, and the catalytic effect of charcoal was thought to be due to its absorbing of ammonia, and thereby increasing the effective ammonia pressure in the reaction mixture. However, it turned out that in the absence of ammonia charcoal also catalyzed the crosslinking reaction, and so the suspicion arose that its catalytic effect may be due to some impurity such as an ammonium halide. So a sample of the charcoal was extracted with hot water and the solution tested for halide ions. The test was negative, and thus the question of how the catalytic effect of the charcoal should be explained was left open.

Equilibration of N-alkylated silazanes

After it proved possible to establish a ring-chain equilibrium in the $-SiMe_2-NH-$ system under ammonia pressure, and from the equilibrium mixture a linear polymer could be isolated, it was almost inevitable to try to extend this method to N-alkylated silazanes. It was hoped that equilibration under the pressure, or in the presence of the appropriate primary amine would lead to equilibria from which N-alkylated linear silazane polymers could be isolated.

The first system to be tried was the N-methyl one, and for starting material the cyclic trimer nonamethylcyclotrisilazane (III) was chosen.

Now, as discussed earlier, hexamethylcyclotrisilazane (I) eliminates ammonia and forms a crosslinked polymer if it is heated with ammonium bromide catalyst. In contrast to this III is completely unreactive under the same conditions [4].

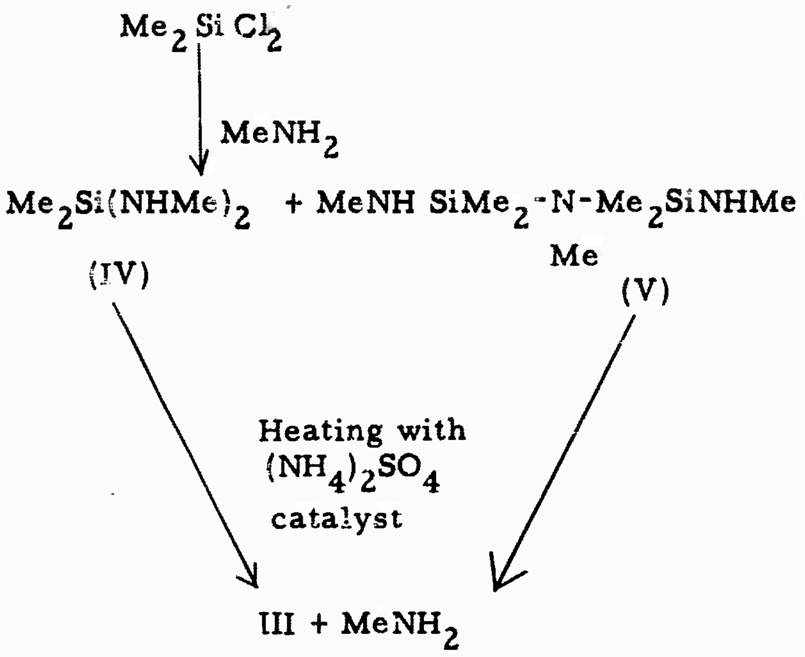


$\xrightarrow[160^\circ]{NH_4Br}$ No reaction (8)

III

This was interpreted in the following way. In the N-methyl system, the route to a crosslinked polymer (via trisilyl-substituted nitrogen) is apparently blocked. For the ring-chain equilibrium there are two alternatives: either the equilibrium is completely on the side of the cyclic trimer, or for the attainment of equilibrium the presence of methylamine is also essential. That ammonia was essential for the establishment of ring-chain equilibrium in the $-SiMe_2-NH-$ system was discussed earlier (although in that system the situation is less clear-cut, for in the absence of ammonia but in the presence of NH_4Br the crosslinking reaction takes place). It, therefore, cannot be said with certainty that, if the crosslinking reaction could be blocked by some means other than a pressure of ammonia, the ring-chain equilibrium could be reached with NH_4Br catalyst alone without the agency of ammonia.

In the N-methyl system, the situation is complicated by the fact that the linear monomer (IV) and the linear dimer (V) are also stable.



(9)

The compounds corresponding to IV and V in the $-SiMe_2-NH-$ system are so unstable toward condensation (which produces the cyclic trimer and cyclic tetramer) that they do not appear in the ring-chain equilibrium of that system.

The equilibration of III under methylamine pressure was carried out both with and without the addition of $(NH_4)_2SO_4$. The reactions were carried out in an autoclave at $140 \pm 5^\circ$ C, at reaction times from 1 to 5 days. The products were distilled, but from none of the products could any nonvolatile polymeric residue be isolated. The equilibrium in this system seems to be completely on the side of the cyclic compound III.

Polymerization of III was also attempted by the use of a basic catalyst $NaNH_2$. The use of this reagent as a catalyst in the $-SiMe_2-NH-$

system was not attempted because $NaNH_2$ is reported to metalate the NH- group. It was hoped that the N-Me bond would resist metalation. However, when III was heated in the presence of $NaNH_2$ at 140° C, and all volatile products were removed, the remaining material contained sodium and was insoluble in organic solvents, although it dissolved easily in dilute hydrochloric acid. The analytical results indicated virtually total loss of the N-methyl groups.

After failing to isolate an N-methyl linear silazane polymer, the N-n-butyl system was tried. In this system steric hindrance was cited [5] to explain the failure to obtain the cyclic trimer by heating bis (n-butylamino) dimethylsilane (VI) with $(NH_4)_2SO_4$. This method gives good yields with the cyclic trimers in the N-methyl and N-ethyl systems. Since cyclization appeared to be an unfavorable process, it was hoped that the ring-chain equilibrium would be strongly on the side of the linear products.

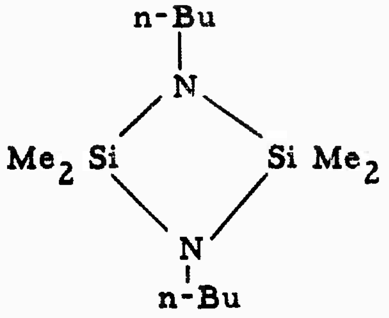
The study of the N-butyl system is far from being completed, but the preliminary results suggest that this system has some very interesting features. Equilibration of VI was first attempted by pyrolysis alone, without the addition of any catalyst. Condensation of n-butylamine started above 180° C and the reaction was carried out at 200° C. When the n-butylamine condensation ceased, the weight loss corresponded to 43% of the calculated amount of n-butylamine according to the scheme

$$\underset{\text{(VI)}}{Me_2Si(NH\text{-}n\text{-}Bu)_2} \longrightarrow -Me_2Si\text{-}N\text{-}n\text{-}Bu- + n\text{-}BuNH_2 \qquad (10)$$

Gas-chromatographic analysis of the product showed only one major component, the retention time of which was smaller than that of VI. Only a very small amount of unchanged VI was found to be present. Distillation of the product left no appreciable amount of polymeric residue.

The distillate was then further pyrolyzed at 200° C but with the addition of $(NH_4)_2SO_4$ catalyst. No more n-butylamine condensed but nevertheless extensive changes took place. However, no appreciable amount of polymeric residue was obtained after distillation of the product. Gas-chromatographic analysis showed that most of the primary pyrolysis product (without catalyst) disappeared, and products with much longer retention times were formed. There were 3 new major peaks, of which the one with the longest retention time was the largest. A very small quantity of the compound corresponding to the largest peak was collected from the analytical gas-chromatograph and its analysis was in reasonably good agreement with the calculated figures for a cyclic silazane, $(\text{-}Me_2Si\text{-}N\text{-}n\text{-}Bu\text{-})_X$. It was probably the cyclic trimer, but larger quantities will have to be collected and the molecular weight determined. Isolation and identification of the other two major products also remains to be done.

Since the primary pyrolysis product of VI was further pyrolyzed with $(NH_4)_2SO_4$ catalyst, no pure compound was isolated from the primary pyrolysis product. However, by analogy of some closely related pyrolysis reactions reported by Fink [6], it is probable that the major component of the primary pyrolysis was the cyclic dimer VII.



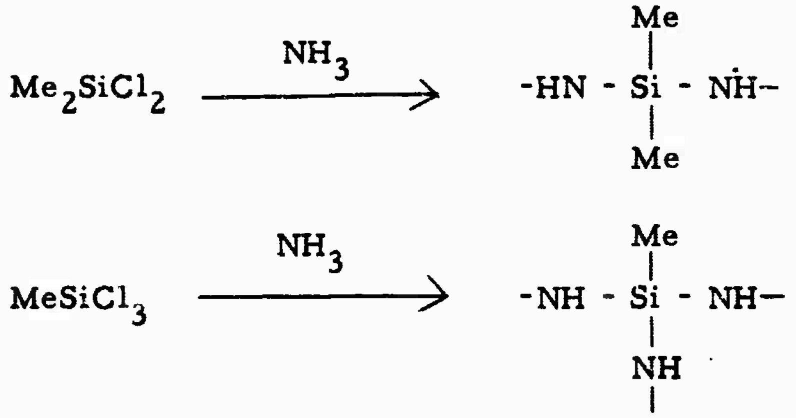
(VII)

This compound was also prepared by Fink [6] via a different route. The results of this preliminary study of equilibration of the n-butyl system indicate that steric hindrance does not prevent the formation of the cyclic compounds as was suggested in reference 5. Further, the very different products of the pyrolysis with and without catalyst suggest that there are at least two different mechanisms operating. The pyrolysis without catalyst appears to be a kinetically controlled reaction leading to the cyclic dimer by way of some specially favorable mechanism, while the presence of a catalyst seems to be necessary for a free redistribution of the $-SiMe_2-N-n-Bu-$ units leading to a thermodynamic equilibrium. This interpretation, if extended to the $-SiMe_2-NH-$ system, helps to understand the observation that although 20% linear polymer is present at equilibrium only cyclic trimer and tetramer are formed in the ammonolysis of Me_2SiCl_2.

Crosslinking via trifunctional silicon in silazane polymers

In previous sections, linear and crosslinked (via trisilyl-substituted nitrogen) dimethylsilazane polymers were discussed. It is surprising that the silazane analogues of the crosslinked (via silicon) siloxanes had not been studied before.*

The crosslinked methylsiloxane polymers are obtained by the hydrolysis of mixtures of methylchlorosilanes. It could be expected the ammonolysis of methylchlorosilane mixtures would yield the corresponding crosslinked silazanes. In order to have as simple a system as possible, only binary mixtures of dimethyldichlorosilane and methyltrichlorosilane were used. The former was the source of difunctional and the latter the source of trifunctional building units.



$$Me_2SiCl_2 \xrightarrow{NH_3} -HN-\overset{Me}{\underset{Me}{Si}}-NH- \qquad (11)$$

$$MeSiCl_3 \xrightarrow{NH_3} -NH-\overset{Me}{\underset{NH}{Si}}-NH-$$

From a 1:1 molar mixture of the starting materials a colorless reaction product was obtained which was separated by distillation into volatile materials and polymeric residue. Among the volatile products the cyclic silazanes I and II were found, as expected. Other volatile products, probably incorporating some trifunctional silazane units (see above), also were present, but as attention was focused on the polymer, these were not identified.

The polymeric residue was a viscous oil with an average mo-

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*In methyl-siloxy polymers the oxygen atoms, of course, cannot be the center of crosslinking, and the specification 'via silicon' is used only to distinguish from the possible case of crosslinking via methylene bridges. This latter type of crosslinking is found in some silicone rubbers after vulcanization.

lecular weight of about 1000. The analysis figures (see experimental section) showed that the di- and tri-functional units were present in about equal proportions.

Although ammonium chloride is formed in the ammonolysis, which could conceivably catalyze a reaction leading to crosslinking via nitrogen, the reaction temperature of 80° was well below the temperature (above 140° C) at which this type of crosslinking reaction could take place with appreciable rate. The NMR spectra also indicated the absence of crosslinking via nitrogen.

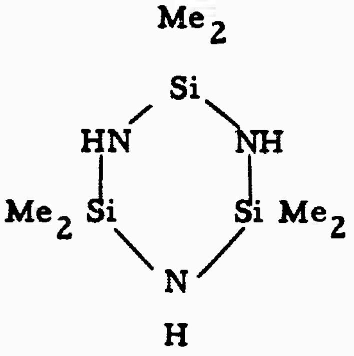
When the molar ratio of methyltrichlorosilane to dimethyldichlorosilane was increased to 7:4 the polymer obtained was a brittle (not sticky) resin which could be crushed into a fine powder. This indicated an increased amount of crosslinking, i.e., an increased ratio of trifunctional to difunctional building units. However, the analytical results did not show a significant difference between the two polymer samples. A further increase in the proportion of methyltrichlorosilane in the starting material did not result in any change in the isolated polymer. It appears that beyond a certain degree of crosslinking the polymer becomes insoluble in the solvent (ligroin) and is precipitated together with ammonium chloride. From the analysis figures, this limit of crosslinking seems to be around 65%, which is equivalent to a C:Si ratio of 1.35.

An attempt was made to isolate a polysilazane with C:Si ratio of 1.00 which in the above sense corresponds to 100% crosslinking. The starting material was pure methyltrichlorosilane, and after ammonolysis the filtrate was worked up in the usual way but it contained no silazanes. The product was clearly insoluble in the solvent and it precipitated together with the ammonium chloride. The separation of this solid mixture was attempted by vacuum sublimation. It was hoped that the ammonium chloride would sublime and the polysilazane would be isolated as the residue. However, depolymerization of the polysilazane must have taken place. for after the sublimation no appreciable amount of residue remained. An alternative method that should be tried would be the extraction of the solid mixture by liquid ammonia.

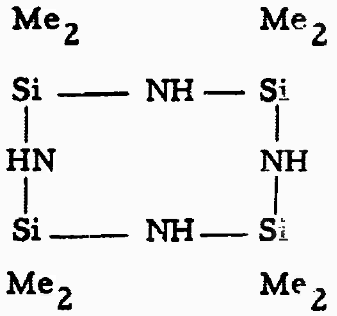
DISCUSSION OF THE NMR SPECTRA

Cyclic and linear polysilazanes

The high resolution NMR spectra of both hexamethylcyclotrisilazane (I) and of octamethylcyclotetrasilazane (II) consist of a single sharp peak together with ^{29}Si satellites (in carbon tetrachloride solution $\delta = 0.055$ ppm with respect to TMS as internal standard). This means that the methyl protons are all equivalent in both I and II.



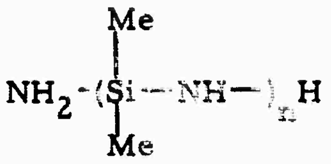
I



II

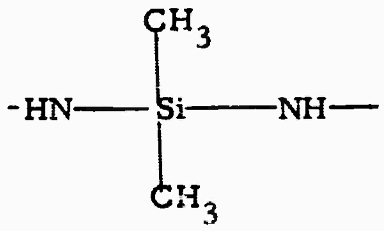
Both I and II are believed to have puckered ring structures [7] and the single methyl proton peak must be interpreted as a result of rapid interchange between the various possible puckered conformations. Moreover, the spectrum of a solution containing both I and II consists also of a single methyl proton peak, that is, the methyl proton environment must be virtually identical in both cyclic silazanes. The azo proton peak could not be found in the spectra, probably because it is broadened to such an extent that it disappears in the noise as the recording gain is increased.

Neglecting the effect of distance from the terminal group, the methyl protons in a linear polymer of the structure are expected to be



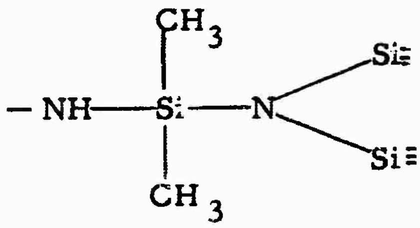
$$NH_2\text{-}(\overset{Me}{\underset{Me}{Si}}\text{—}NH\text{—})_nH$$

all equivalent and their environment must be very similar to the environment in the cyclic silazanes I and II. Thus the spectrum of the linear polymer should consist also of a single peak, either coinciding with, or very close to, the methyl proton peak of the cyclic silazanes. On the other hand, in a polydimethylsilazane, partially crosslinked via trisilyl-substituted nitrogen atoms (such as obtained by polymerization in an open system), a number of different methyl proton environments must be possible. Again, considering only nearest neighbor effects, three distinct methyl proton environments can be discussed.

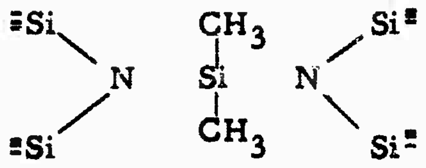


$$\text{-}HN\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}NH\text{—}$$

(A)



(B)



(C)

If crosslinking were complete, only type C methyl proton environment would be present.

For various degrees of partial crosslinking, the ratio of the number of protons in the three possible environments can be calculated, assuming random distribution. See Table I.

TABLE I

	100% crosslinking	80% crosslinking	50% crosslinking	20% crosslinking
% A	0	4	25	64
% B	0	32	50	32
% C	100	64	25	4

S. 1. is the NMR spectrum of the equilibrium mixture obtained in the closed system polymerization of I with ammonium bromide catalyst. Besides the peak at $\delta = 0.055$ ppm (which is due to the cyclic silazanes I and II present in the equilibrium) there are four other peaks at δ values of 0.093, 0.17, 0.19 and 0.25. In view of the considerations discussed at the beginning of this section, the peak ($\delta = 0.093$) nearest to the peak of the cyclic

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Percent crosslinking means the percent of trisilyl-substituted nitrogen atoms with respect to the total nitrogen content.

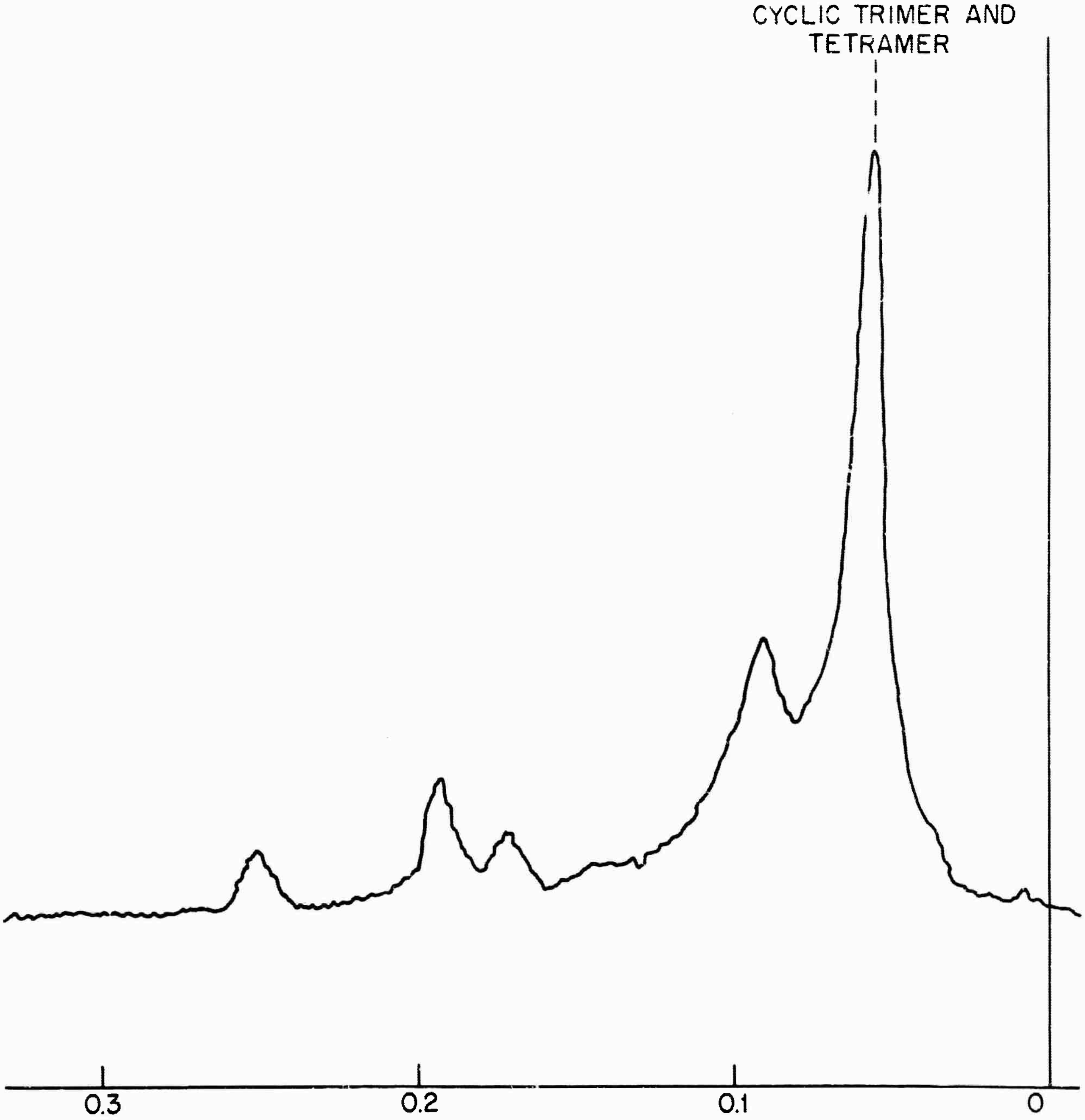

FIG. S.1 POLYMERIZATION PRODUCT-CLOSED SYSTEM REACTION

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silazanes is assigned to those methyl protons of the partially crosslinked polymer which are in (A) type of environment. The correctness of this assignment was confirmed by the spectra of polymer samples in which crosslinking was gradually suppressed.

S. 2. shows the NMR spectrum of a sample obtained from the equilibration product of I under 1. 5 atm. of ammonia pressure by partially removing the cyclic silazanes present at equilibrium. The greatly increased relative intensity of the peak at δ = 0. 093 ppm was attributed to the diminished degree of crosslinking. A further important feature of this spectrum is that in comparison with S. 1. the relative intensity of the peak at δ = 0. 25 ppm is much more strongly diminished that that of the peaks at δ values of 0. 17 and 0. 19 ppm. This allows the assignment (by considering Table 1) of the peak at δ = 0. 25 ppm to methyl protons in C type of environments in the polymer. The peaks at δ values 0. 17 and 0. 19 ppm should then be assigned to methyl protons in (B) type environment. This assignment is reasonable since the B type environment is intermediate between the A and C type of environments and the position of the peaks assigned to methyl protons in B type environments is in-between the peaks assigned to protons in A and C type environments. The reason why there should be two peaks resulting from protons in B type of environment is not understood.

The NMR spectrum of the equilibration product of I obtained under 4 atm. of ammonia pressure is shown on S. 3. and that of the polymer isolated from the equilibrium mixture, on S. 4.

In S. 4. the peaks assigned to protons in B and C type environments have disappeared completely and only the peak assigned to protons in A type environment remained.

To confirm the total absence of crosslinking in the linear polymer a spectrum was recorded first at normal spectrum amplitude and then at 20 times increased gain (S. 5.). The total absence of the "crosslinked" peaks is obvious but the broad azo proton peak was unexpectedly found this way. The sharp peak superimposed on the azo proton peak was shown to be a spinning side band of the methyl proton peak. The integration ratio of methyl and azo proton peaks was in agreement with the expected value of 6:1 (within experimental error due to overlap). It should be emphasized that an increase of the recording gain failed to bring out the azo proton peak in the spectrum of I. This observation means that the azo proton peak is much broader in the cyclic silazanes than in the linear polymer, but the reason for this is not understood.

When a sample of the linear polymer was exposed to the atmosphere, the polysilazane was slowly hydrolyzed, as was indicated by the gradual decrease of the nitrogen content and by the appearance of a new peak at $\delta \approx 0.50$ ppm in the NMR spectrum. The relative intensity of this peak increased parallel with the progress of the hydrolysis. Comparing the case of the partially hydrolyzed polymer with that of the partially cross-linked (via trisilyl—substituted nitrogens) polymer, one would expect at least three different methyl proton peaks in the NMR spectrum of the partially hydrolyzed polymer. In such a polymer, besides the originally prevailing A type of proton environment, there should be the following new methyl proton environments present.

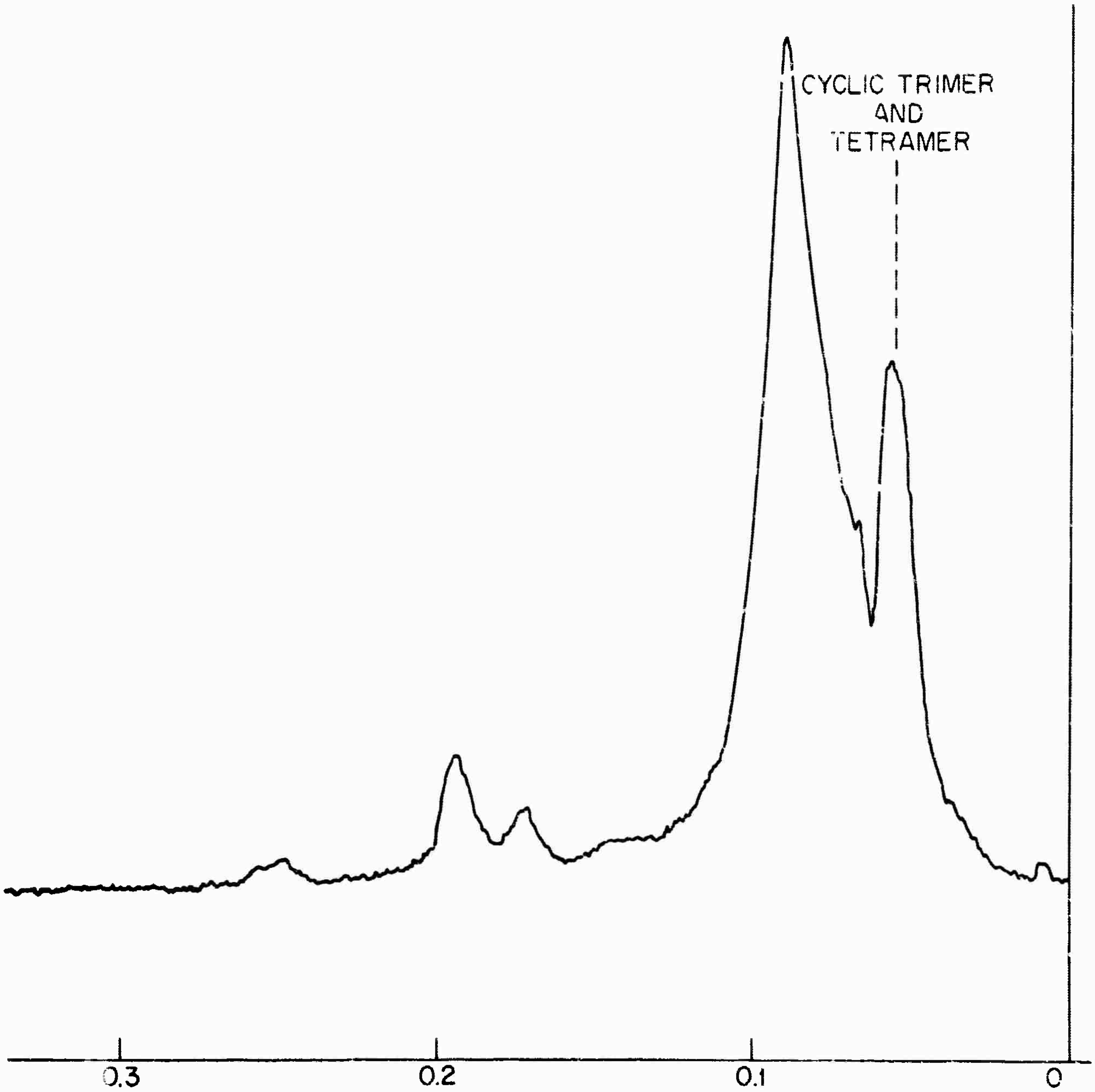


FIG. S.2 POLYMERIZATION UNDER 1.5 ATM. NH_3 PRESSURE

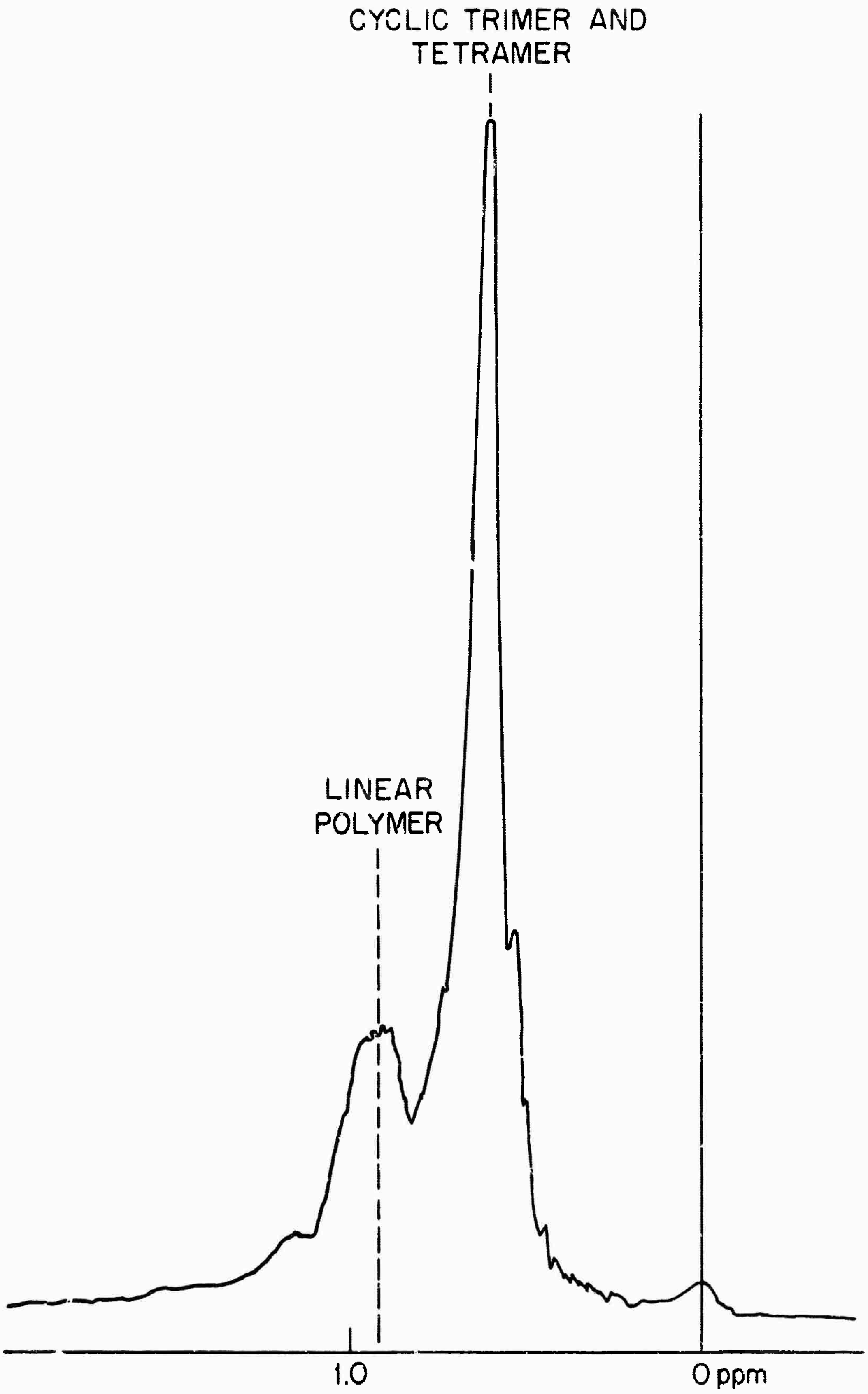


FIG. S.3 NMR SPECTRUM OF EQUILIBRIUM MIXTURE (140°C/4 ATM. NH_3)

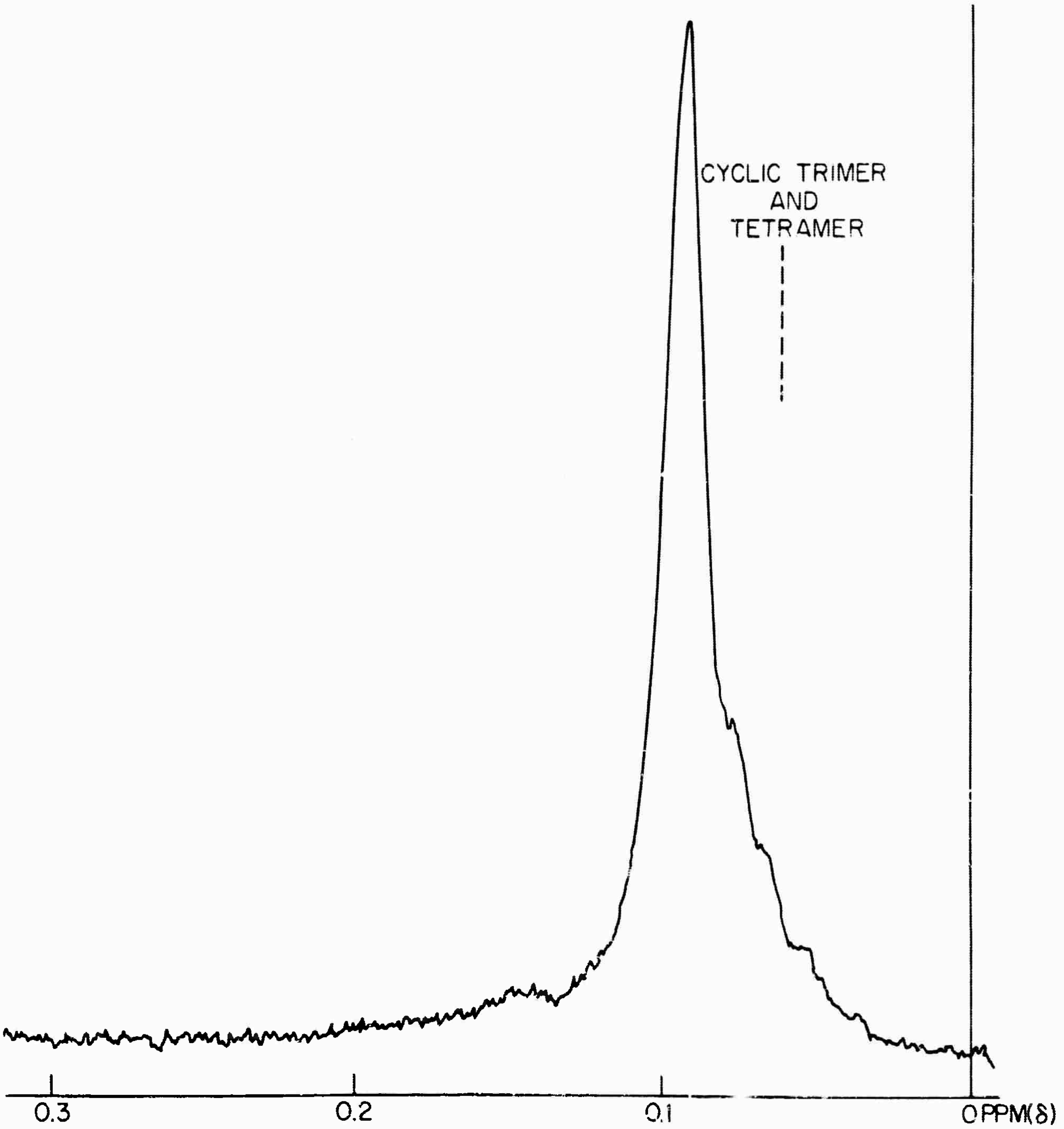


FIG. S.4 LINEAR SILAZANE POLYMER

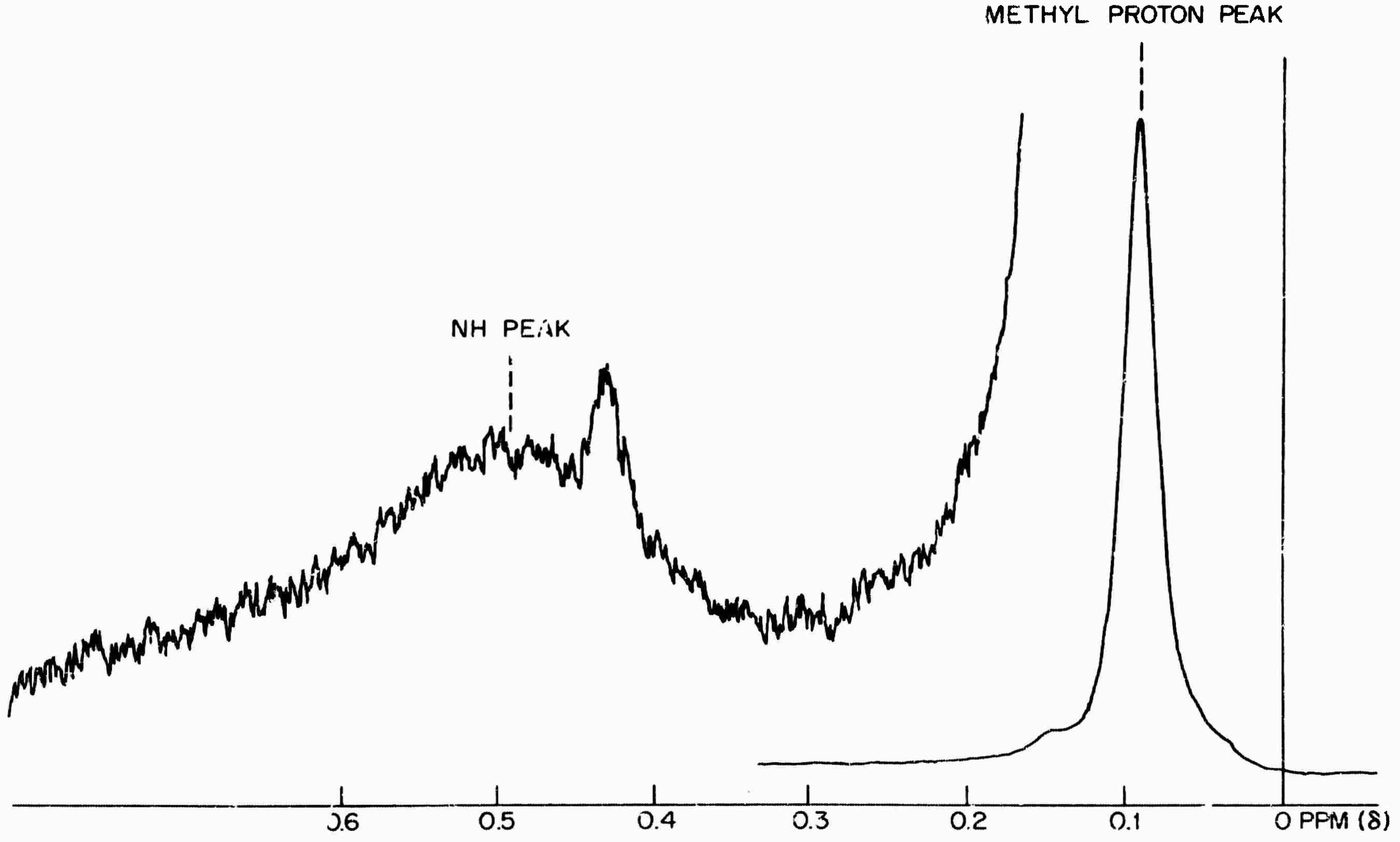
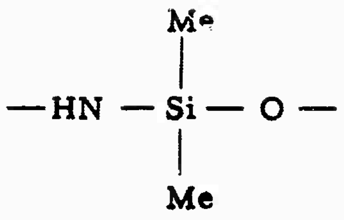
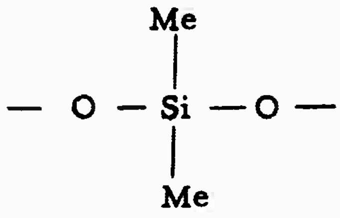


FIG. S.5 LINEAR SILAZANE POLYMER



$$-\text{HN}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}-\text{O}-$$

(D)



$$-\text{O}-\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}-\text{O}-$$

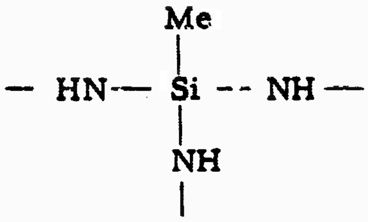
(E)

In view of this it is surprising that only one new peak can be seen on S. 6 and S. 7 which show the NMR spectrum of a linear polymer sample exposed to the atmosphere for 4 and 9 days, respectively.

The NMR spectrum of the oligomeric oil collected by distillation in the process of isolating the linear polymer is recorded on S. 8. The main peak has a chemical shift of $\delta=0.082$ ppm which is certainly due to protons of methyl groups attached to silicon and its position is very close to the methyl proton peak of the linear polymer ($\delta=0.093$ ppm). There is definitely no trace of peaks which were assigned to B and C type environments in the spectrum of the partially crosslinked polymer. In view of these it could be inferred that the oligomeric oil consists mainly of low molecular weight linear polysilazanes. However, the analysis results (see experimental section) and especially the low nitrogen content (16.69%) do not agree with this inference.

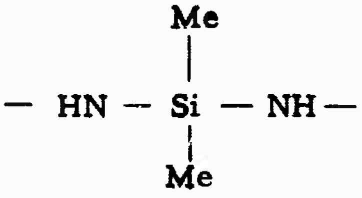
Silazane polymers crosslinked via trifunctional silicon atoms

These polymers are built up of F and G type of units.



$$-\mathrm{HN}-\underset{\substack{|\\ \mathrm{NH}\\ |}}{\overset{\substack{\mathrm{Me}\\ |}}{\mathrm{Si}}}-\mathrm{NH}-$$

(F)



$$-\mathrm{HN}-\underset{\substack{|\\ \mathrm{Me}}}{\overset{\substack{\mathrm{Me}\\ |}}{\mathrm{Si}}}-\mathrm{NH}-$$

(G)

Considering only nearest neighbor effects, there should be only two kinds of methyl protons in the polymer. It should be noted that unit G is identical with unit A which was discussed in connection with the spectra of the linear polymer.

The actual spectra (S.9 and S. 10) show that the methyl proton region cannot be clearly separated into two sets of peaks which could be assigned to protons in (F) and (G) type of environment, respectively. Nevertheless, two tentative assignments can be made on the basis of the changes in the relative intensities of the peaks corresponding to changes in the ratio of $MeSiCl_3$ to Me_2SiCl_2 in the starting mixture. The relatively broad peak (at $\delta=0.10$ and 0.12 ppm in S. 9 and S. 10, respectively) is probably associated with methyl protons in (G) type environment, since the relative intensity of this peak is increased as the proportion of Me_2SiCl_2 is increased in the starting material. The chemical shift of the single methyl proton peak ($\delta=0.93$ ppm) in the spectrum of the linear polymer can be considered as the limiting position for $MeSiCl_3:Me_2SiCl_2=0$ in a series of crosslinked polymers

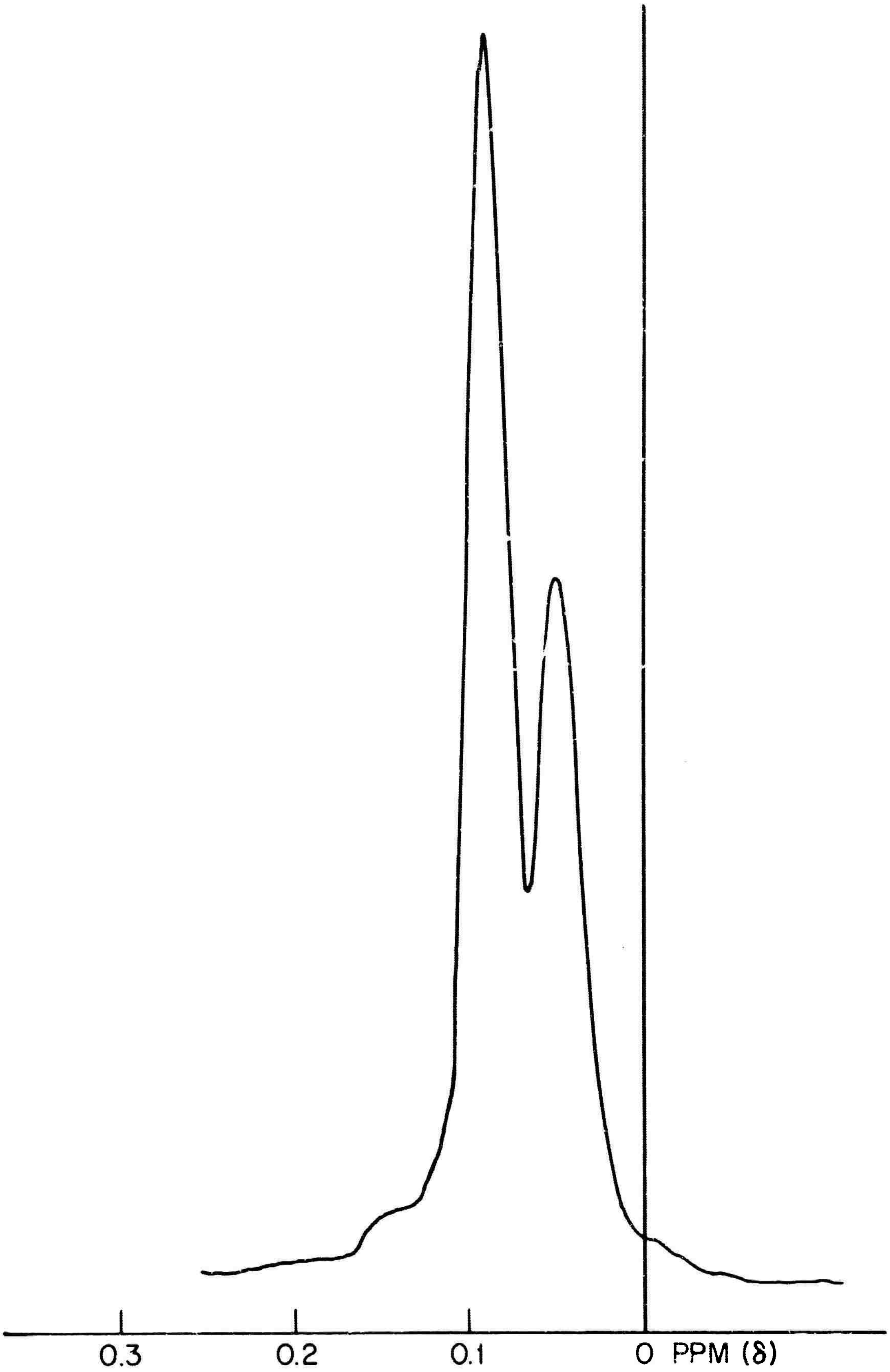


FIG. S.6 PARTIALLY HYDROLIZED LINEAR POLYMER

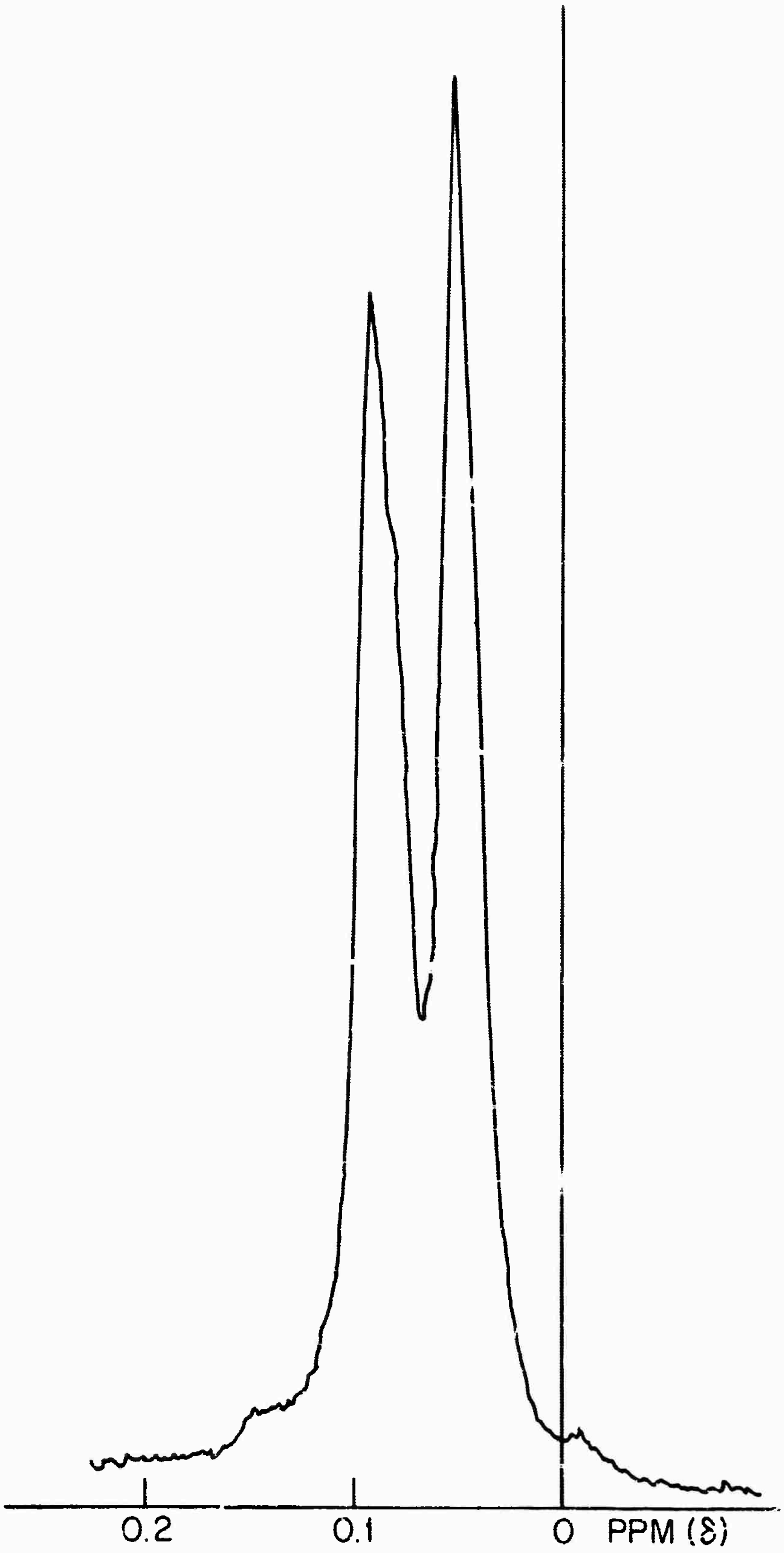


FIG. S.7 PARTIALLY HYDROLIZED LINEAR POLYMER

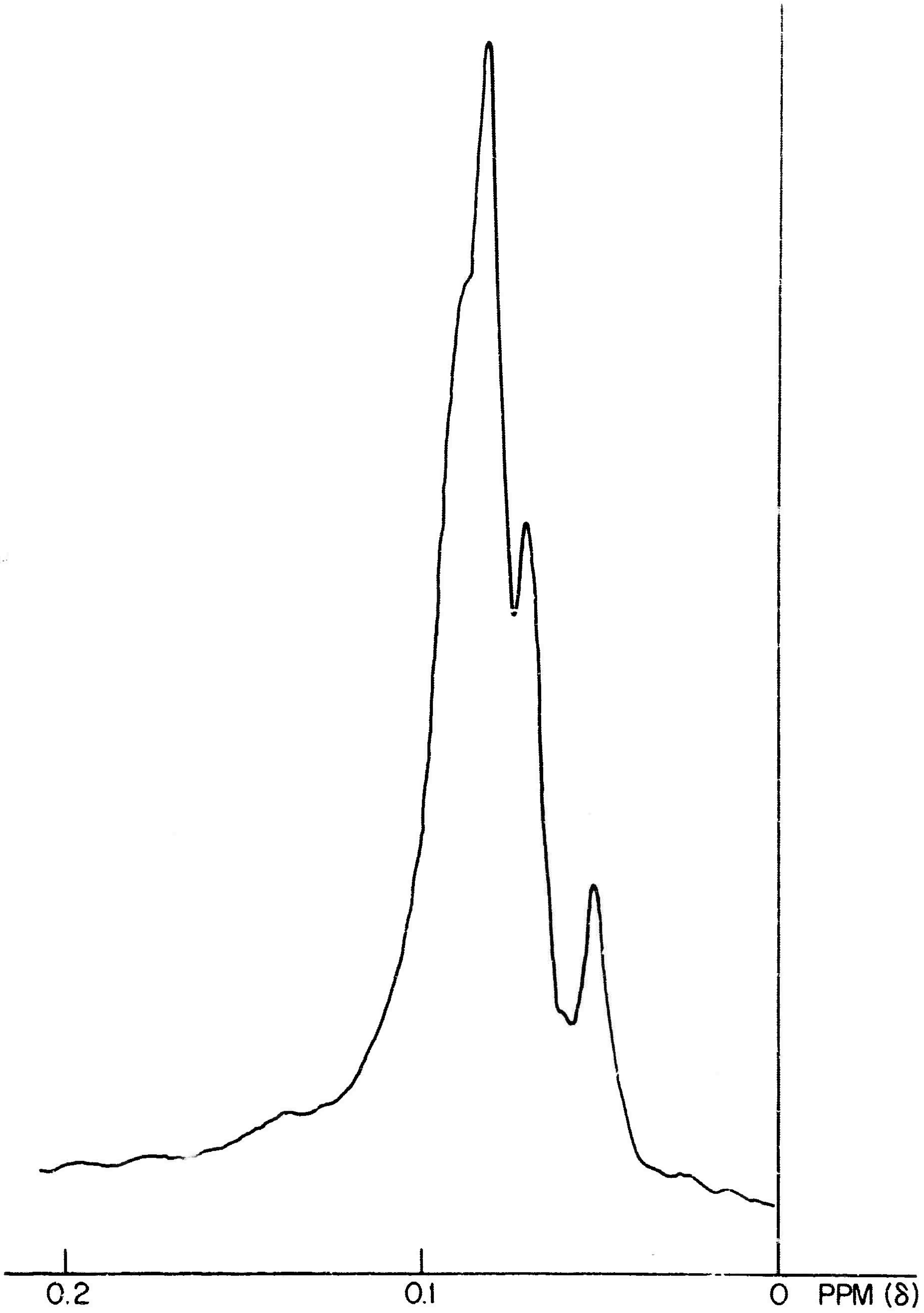


FIG. S.8 OLIGOMERIC OIL

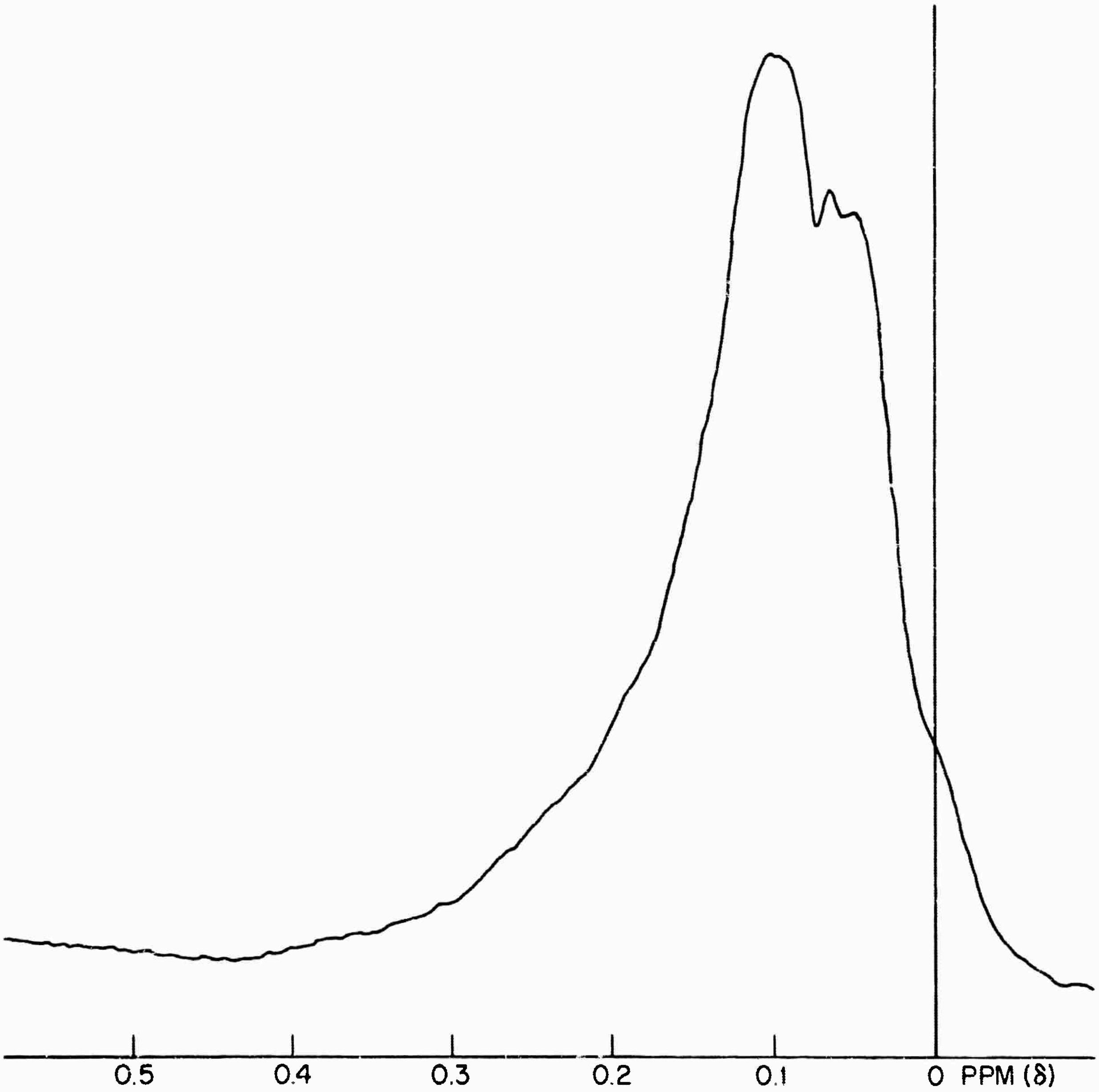


FIG. S.9 POLYSILAZANE FROM $MeSiCl_3$: Me_2SiCl_2 = 1:1

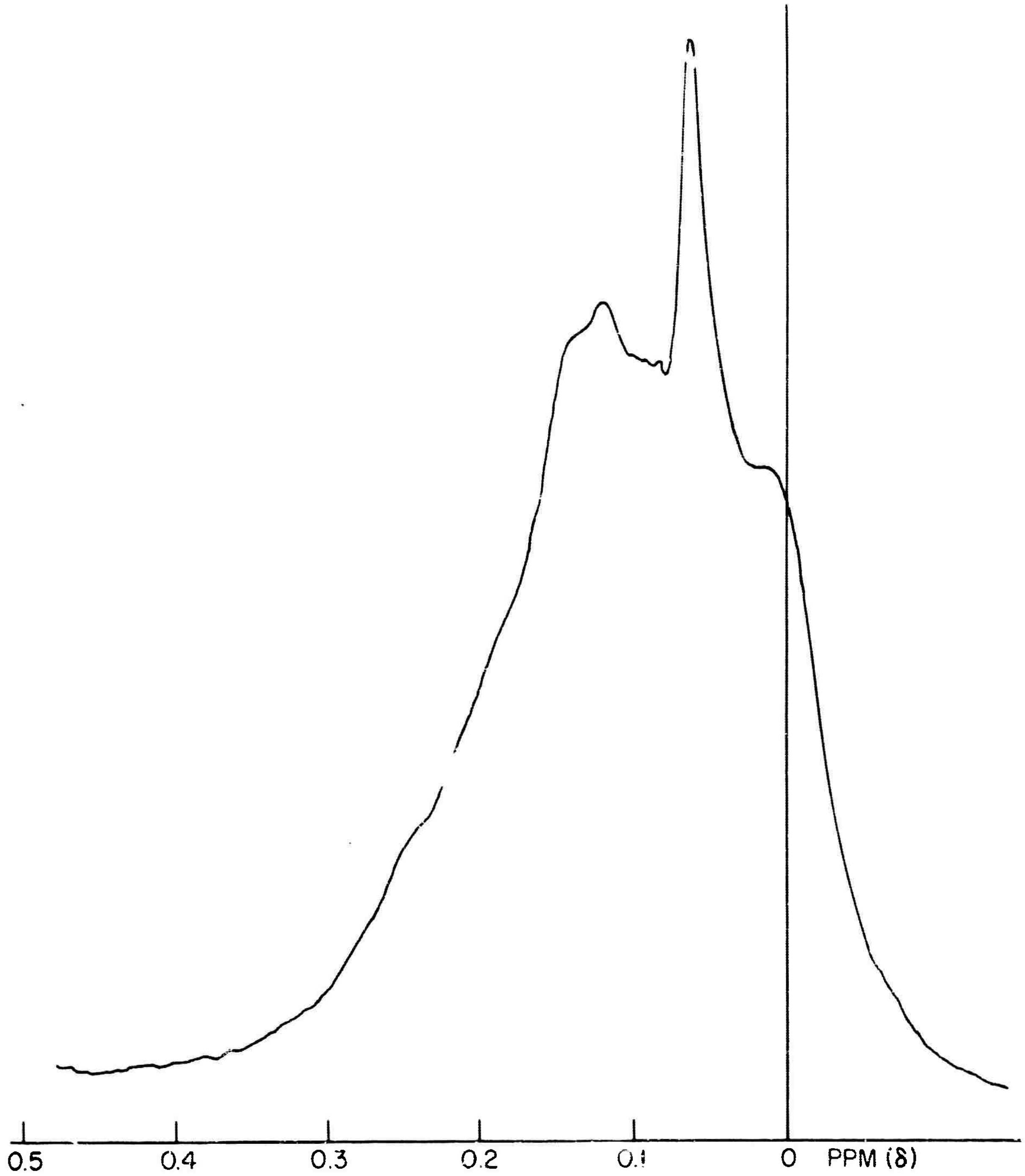


FIG. S.10 POLYSILAZANE FROM MeSiCl : Me_2SiCl_2 = 3:1

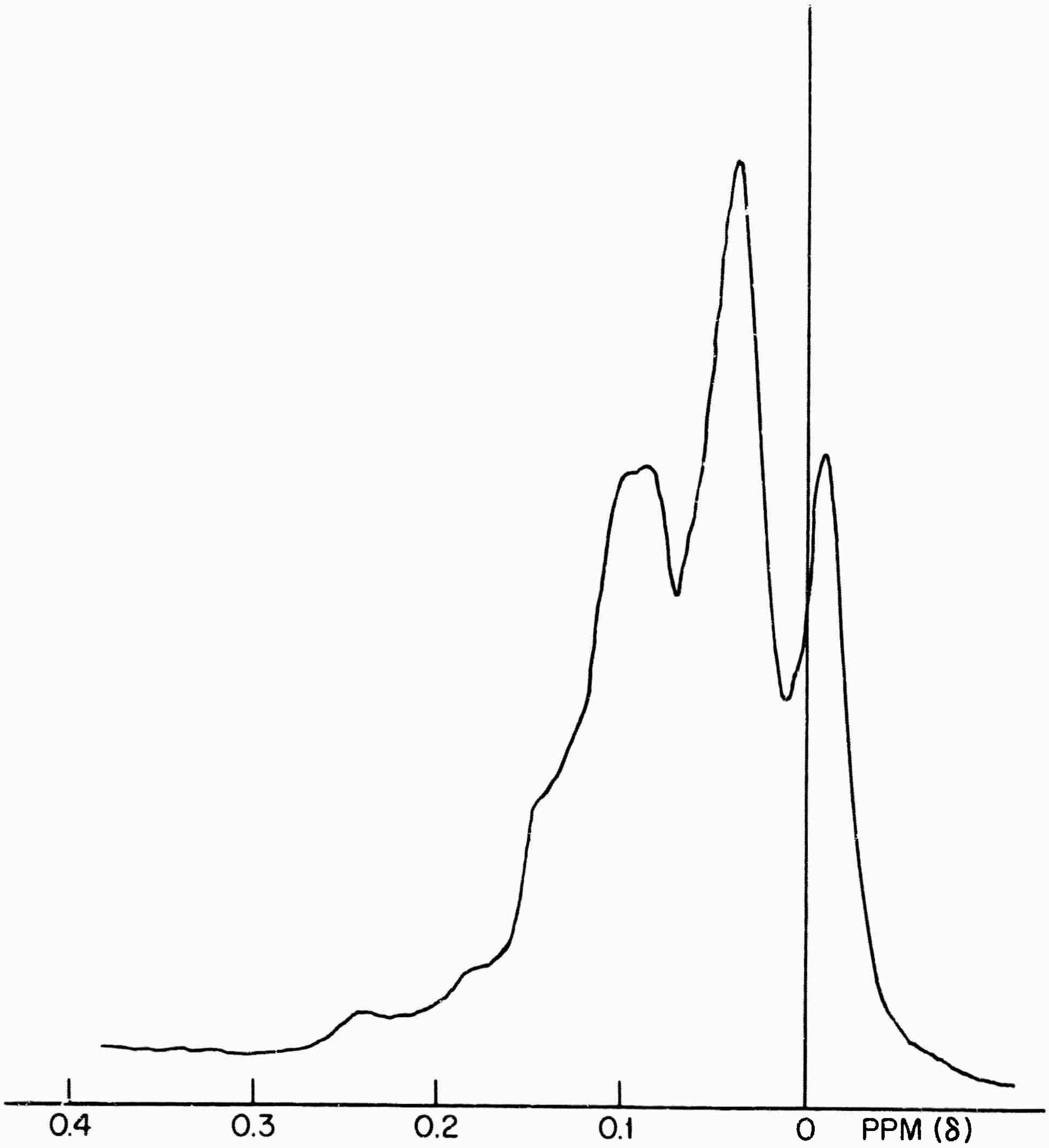


FIG. S.11 OLIGOMERIC OIL FROM $MeSiCl_3$: Me_2SiCl_2 = 1:1

obtained from varying mixtures of Me_2SiCl_2 and $MeSiCl_3$. The other tentative assignment is for the peak at $\delta=0.063$ ppm. This peak must be associated with methyl protons in F type environment, for it is clearly this peak whose relative intensity increases when the proportion of $MeSiCl_3$ is increased in the starting mixture.

EXPERIMENTAL SECTION

Ammonolysis of Me_2SiCl_2

In order to have sufficient quantitites of hexamethylcyclotrisilazane, I (cyclic trimer), this reaction was carried out many times (with minor variations in the method) by Mr. Robert L. Lambert, to whom we are grateful for this assistance. The yield and the ratio of cyclic trimer to cyclic tetramer varied from preparation to preparation, but no systematic study was carried out to determine the effect of factors such as concentration and temperature on this ratio. A small-scale preparation is described below which was designed to determine whether any linear polysilazane is formed besides the cyclic silazanes. Ammonia gas was passed above the surface of a solution of Me_2SiCl_2 (50 g) in ligroin (500 ml). The mixture was stirred vigorously and the rate of ammonia passage was adjusted so that a temperature of 40-50° was maintained by the exothermic reaction. After 7 hours the exothermic reaction had ceased, but to make sure that the reaction was complete, ammonia was passed in for another hour while the solvent was refluxed. Then the bulky NH_4Cl precipitate was filtered on fritted glass under nitrogen. The solvent was removed from the filtrate in vacuum. The crude product was 25 g of colorless oil, which was distilled up to 140°C/0.05 mm Hg. The residue (1.04g) was a slightly yellow greasy oil with a nitrogen content of only 3.97%.

The same procedure was applied for the larger scale (8 fold) reactions where the primary aim was synthesis of I. However, the filtration of the NH_4Cl was carried out in the atmosphere, and consequently there was more extensive hydrolysis resulting in a greater proportion of non-volatile residue. The condensates from the first distillation of several runs were collected and then fractionated on a 4' Vigreaux column. The fractions were analyzed by gas chromatography and the fraction collected at 58-59°C/4 mm Hg was virtually pure I. After fractionation the residue solidified was recrystallized from cyclohexane to give octamethylcyclotetrasilazane.

Equilibration of hexamethylcyclotrisilazane (I) under ammonia pressure

The analytical runs which were designed to establish the equilibrium conditions were carried out in an Autoclave Engineers 8" micro reactor. For the various runs 1-5 g I was placed into a glass vial, a few crystals of NH_4Br were added and the vial placed inside the autoclave. This was first evacuated and then filled with ammonia gas up to 4 atm. at room temperature. (The ammonia gas was used from a lecture bottle and all fittings and valves were made of stainless steel.) The sealed autoclave was then immersed in an oil bath, the temperature of which was kept at 140± 5° C. The reaction time was varied from 6 hours to 14 days, after which the autoclave was cooled to room temperature. The ammonia pressure dropped normally to about 2 atm., which was then released and the vial removed from the autoclave. The product was a colorless liquid looking no different from the starting material. This product contained a large amount of dissolved ammonia which was given off rather abruptly if the vial was shaken. The release of ammonia was normally accompanied by frothing and the crystallization of octamethylcyclotetrasilazane (II) from the liquid. (The frothing often resulted in loss of some product which made the run useless for analytical determination of product composition.) For the purpose of analysis, the content of the vial was washed quantitatively into a volumetric flask with cyclohexane and the concentration of I and II was determined by gas chromatography. The polymer content of the reaction product was determined by distilling a weighed amount of product and then weighing the residue. The distillation was carried out at 0.05 mm Hg pressure and the temperature was slowly raised to 140° C. In the final stage of the distillation the tube containing the residue was held in a horizontal position in order to prevent refluxing and to ensure the complete removal of volatile products without the necessity of overheating the residue (see Figure I).

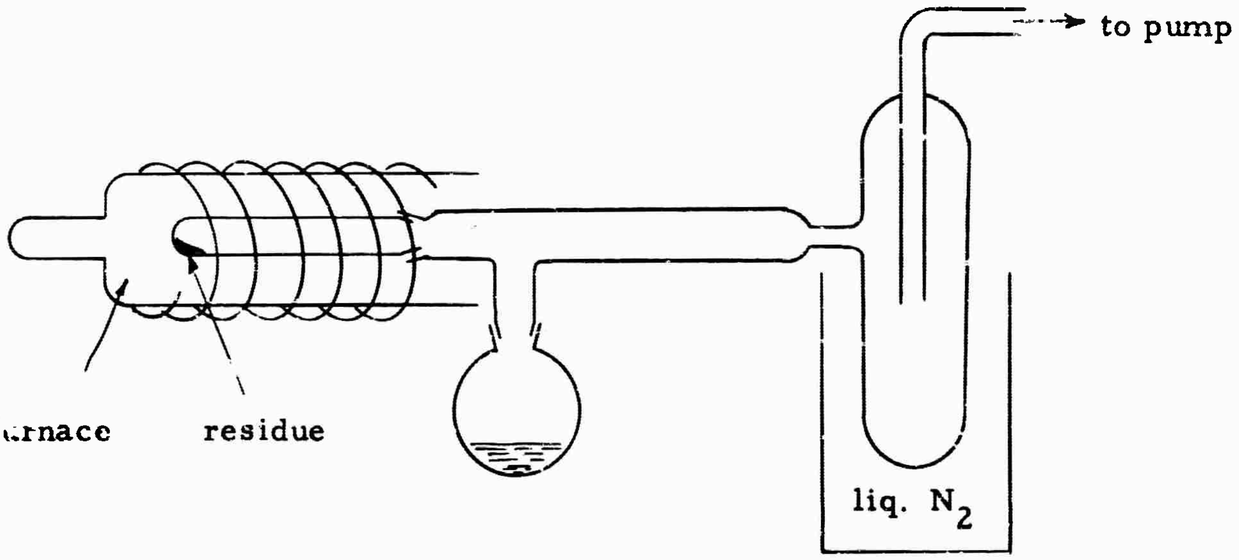


Figure I

The results of both determinations (gas chromatography and distillation) varied within a 10% spread from run to run and the figures quoted in the text are average figures from a large number of runs.

The preparative runs which were designed to isolate larger quantities of linear polymer were carried out by a slightly modified procedure, an example of which is described below.

The starting material I (180 g) was placed in a 250 ml round bottom flask and stoppered with a fritted glass stopper. (This was found to be the most effective way to prevent frothing out of the product when the dissolved ammonia is given off after the ammonia pressure is released.) No NH_4Br catalyst was added, in order to avoid possible crosslinking side reaction during the distillation stage.

The flask was placed inside an autoclave. Following evacuation, the autoclave was filled with ammonia up to 10 atm. pressure, and then kept in a 140±5°C bath for 10 days. After cooling to room temperature, 6 atm. of pressure was recorded in the autoclave which was now released and the flask removed from the autoclave. The product was completely colorless and after some time considerable amounts of II crystallized out. The mixture was subjected to vacuum distillation in several stages. In the first stage, great care had to be taken to avoid bumping and frothing caused by dissolved ammonia; then the bulk of I was collected followed by the sublimation of II. After the sublimation of II the temperature was raised to 140° C and the pressure was 0.05 mm Hg.

This condition was maintained for 3 hours during which 4.2 g of oligomeric oil was collected. The residue (33.2. g), the linear polymer, was a colorless viscous oil.

Analysis results:	C%	H%	N%	Si%
Calculated for $(-SiMe_2-NH-_x)$	32.81	9.65	19.15	38.37
Found for linear polymer	32.22	9.16	19.78	38.28
Found for oligomeric oil	32.42	9.25	16.69	41.41

Preparation of silazane polymers crosslinked via trifunctional silicon atoms

These polymers were prepared by the ammonolysis of mixtures of $MeSiCl_3$ and Me_2SiCl_2 containing different ratios of the two chlorosilazanes.

A typical reaction starting with a 3:1 ratio of $MeSiCl_3$:Me_2SiCl_2 is described in detail.

Ammonia gas was passed into a mixture of $MeSiCl_3$ (0.3 mole) and Me_2SiCl_2 (0.1 mole) in 800 ml ligroin. The reaction mixture was stirred vigorously, and the rate of gas flow was adjusted so that the exothermic reaction should maintain a temperature between 30-50° C. After 16 hours the heat evolution had ceased and the ammonolysis was regarded as virtually complete. However, ammonia was passed in for one hour with refluxing of the solvent. After cooling the mixture to room temperature the voluminous precipitate was filtered on fritted glass under nitrogen. The solvent was then removed in vacuum and the residue, a colorless oil, was subjected to further vacuum distillation at 0.03 mm Hg pressure. In the final stage of this distillation, a temperature of 160° C was maintained for 2 hours in order to remove the last traces of the volatile products. The residue (6.3 g) solidified into a brittle resin when it cooled to room temperature.

Analytical results: 23.54% C, 7.42% H, 26.58% N, 41.93% Si.

Starting from a mixture with a $MeSiCl_3$:Me_2SiCl_2 ratio of 7:4 the polymeric product was also a brittle resin at room temperature.

Analysis results: 24.67% C, 7.64% H, 24.62% N, 41.80% Si.

The product from an equimolecular mixture of $MeSiCl_3$ and Me_2SiCl_2 was a viscous colorless oil.

Analytical results: 23.52% C, 7.00% H, 24.26% N, 41.92% Si.

Preparation of nonamethylcyclotrisilazane

From a lecture bottle 47 g (1. 5 mole) of monomethylamine was frozen into an autoclave containing 100 ml ligroin. Then at -70° C 49 g (0. 38 mole) Me_2SiCl_2 was added and the autoclave was allowed to warm gradually to room temperature over 12 hours. After thorough shaking, the autoclave was heated to 50° C then cooled to room temperature again. There was very little residual pressure of methylamine which was released, and the product filtered from the precipitated aminehydrochloride. The solvent was removed in the aspirator and a colorless liquid residue was obtained which was presumably a mixture of $Me_2Si(NHMe)_2$ and $(MeNH-Me_2Si)_2NMe$. To bring about cyclization [5] the mixture was refluxed overnight in the presence of a few rystals of $(NH_4)_2SO_4$. The product was fractionated and the fraction (7. 3 g) collected at 70-73°C/1. 5 mm Hg crystallized in the receiver and was virtually pure nonamethylcyclotrisilazane.

Preparation of Bis(n-butylamino)dimethylsilane (VI)

n-Butylamine (8 moles) was added gradually to a 100°/o (w/v) solution of Me_2SiCl_2 (2 moles) in ligroin at room temperature, with vigorous stirring. The precipitated aminehydrochloride was filtered and the filtrate concentrated until all the solvent was removed The crude product (VIII) was fractionated at 12 mm Hg. The main fraction was collected at 90-92° C/12 mm Hg, n_D^{28} = 1. 428 (lit. [5] 1. 4270). When a sample of this product was left open to the atmosphere an unidentified white crystalline solid (probably a hydrolysis product) was deposited within a short time and the whole sample solidified after 3 hours.

Pyrolysis of Bis(n-butylamino) dimethylsilane (VI)

In a slow stream of dry nitrogen gas, $Me_2Si(NHn\text{-}Bu)_2$ (34 g) was heated overnight at 200° C. The weight loss was 5.8 g, and 3.7 g n-$BuNH_2$ was trapped from the gas stream. The rest apparently was carried away by the gas stream. Further, 2 hours heating did not result in any more loss of weight. The product was distilled in vacuum and there was no appreciable residue. Gas-chromatographic analysis showed that only a very small percentage (less than 5%) of the starting material remained unchanged. There was only one major peak in the gas-chromatogram with a retention time shorter than that of VI.

The same peak was also observed in the analysis of the fractions collected before the main fraction in the fractional distillation of the crude product VIII. The bulk of the primary pyrolysis product was then heated for another 12 hours in a stream on N_2 at 200° C in the presence of a few crystals of $(NH_4)_2SO_4$. No butylamine was trapped from the gas stream, but the gas-chromatographic analysis indicated extensive changes. Three new peaks appeared and a few milligrams of the compound corresponding to the largest of these peaks was collected.

Analytical results:	C%	H%	N%
Found	56.73	12.09	10.71
Calculated for $(\text{-}SiMe_2\text{-}NBu\text{-})_x$	55.75	11.69	10.84

Vacuum distillation of the product left no appreciable amount of polymeric residue.

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