POLYMERIC METHYLSILAZANES

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There are only eight elements on earth which are present to the extent of 1 per cent or more, (viz. O, Si, Al, Fe, Na, K, Mg, and Ca) and of these eight silicon is the only one which has properties of both a metal and a non-metal. This circumstance leads to an unusually rich and diverse chemical behaviour, so that silicon spreads itself throughout ionic, covalent, organo-metallic, and colloidal chemistry. Our knowledge of its mineral and ceramic chemistry stretches back ten thousand years, but the covalent chemistry of silicon has come a long way since Berzelius made silicon tetrachloride in 1823 and Friedel and Crafts made the first organosilicon compounds in 1863. The known covalent compounds now exceed 14,000 in number, and they are no longer confined to the laboratory, as Alfred Stock claimed, but have earned a place in polymer chemistry, in industry, in space exploration, and even in cosmetics. To those who know silicon, it is not at all surprising that organosilicon materials should prove their value in all these ways; the only point that is surprising is that it should all happen so quickly. It is only twenty-eight years since an active interest in organosilicon compounds began to take form, and the position as it now exists, is that to describe even the purely scientific side of the subject a three-volume compendium (Dr Bazant's) is required.

In my talk this afternoon I shall touch upon a new and important aspect of organosilicon chemistry, the one that concerns the relation of silicon to nitrogen. Nitrogen is only 1/5000th as abundant as silicon, and even though there is so much of it in the atmosphere, it is not a natural partner in chemical combination with silicon. Just as Alfred Stock's hydrides and Frederick Stanley Kipping's phenyl chlorosilanes were in their time, silicon–nitrogen compounds are purely products of laboratory synthesis. This is a consequence of the greater bond formation energy of silicon–oxygen bonds, 89 kcal/mole, than silicon–nitrogen bonds, 77 kcal/mole, a circumstance which leads to the ready exchange of oxygen for nitrogen in most silicon–nitrogen compounds. Some exceptions arise when many silicon atoms are bound to one nitrogen atom, notably in silicon nitride itself, a stable and unreactive but quite useless by-product of the commercial manufacture of silicon. Multiple bonding between silicon and nitrogen atoms is responsible for this effect, and although it is always a factor in the chemical behaviour of silicon–nitrogen compounds, it reaches overriding proportions only through the cumulative effect of several silicon atoms bound to one nitrogen atom.

Passing by the methods for preparing silicon–nitrogen compounds, which will become apparent as the papers of the symposium proceed, I should like to direct your attention to the particular series of substances known as the "silazanes".

Simple silazanes contain alternate silicon and nitrogen atoms, as in $(CH_3)_3Si–NH–Si(CH_3)_3$, hexamethyldisilazane (analogous to $(CH_3)_3Si–O–Si(CH_3)_3$, hexamethyldisiloxane) and $[-(CH_3)_2Si–NH–]_4$, octamethylcyclotetrasilazane.

Silylamines, on the other hand, come within the customary meaning of amines, diamines, etc.

$$CH_3–NH–SiH_3$$
(methyl silyl amine)

and

$$\begin{array}{l} NH–CH_2–CH_2–NH \\ \quad | \qquad\qquad | \\ Si(CH_3)_3 \qquad Si(CH_3)_3 \end{array}$$
(bis-trimethylsilylethylenediamine)

The essential feature of a polysilazane is a structural framework or "backbone" made up entirely of alternate silicon and nitrogen atoms, with no carbon atoms or chains of carbon atoms in the "backbone" itself. The possible variations consist only in the number and type of alkyl or aryl groups attached to the silicon atoms, and the type and degree of cross-linking, if any, between polymer chains. This matter is very elementary, but it is pointed out because polymers in which the structural framework contains carbon as well as silicon and nitrogen (as in the condensation products of ethylene diamine and dimethyldichlorosilane) are properly called polysilylamines, and are distinctly different from polysilazanes in their properties. Although quite a bit is known about polysilylamines, and we have investigated them extensively in our own work, this particular discussion will be confined to polysilazanes.

The small cyclic methylsilazanes, hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, are easily made by ammonolysis of dimethyldichlorosilane, which in turn is obtained from silicon and methyl chloride. Since the corresponding hydrolysis of dimethyldichlorosilane produces about equal amounts of cyclic and linear polymeric methylsiloxanes, one of the first questions to be asked is whether the corresponding ammonolysis produces any linear methylsilazanes along with the cyclic compounds. If so, we should like to compare the analogous silazane and siloxane polymers.

Simple ammonolysis in liquid ammonia appears to give the cyclic trimer and tetramer as the only silazanes, with the trimer predominating[1]. However, when Brewer and Haber[1] carried out the ammonolysis by adding gaseous ammonia to a benzene solution of dimethyldichlorosilane, first at 30° and then at reflux temperature, about 5 per cent of the product was non-volatile silazane polymer:

$$\underset{\text{(in benzene)}}{(CH_3)_2SiCl_2} + NH_3 \xrightarrow[30°—80°]{6\text{ h}} \begin{array}{ll} \text{(i)} & [(CH_3)_2SiNH]_3 \text{ (185 g)} \\ \text{(ii)} & [(CH_3)_2SiNH]_3 \text{ (210 g)} \\ \text{(iii)} & \text{Non-volatile residue (20 g)} \end{array}$$

A similar story was told by Osthoff and Kantor[2], who gave directions for preparing the two cyclic dimethylsilazanes by ammonolysis in benzene at 30° over a period of 9 h, followed by refluxing for 3 h to remove the ammonia. Removal of benzene gives a crude product corresponding to a 93 per cent yield of dimethylsilazanes, but fractional distillation gives 36 to 50 per cent of cyclic trimer and 26 to 42 per cent of cyclic tetramer, plus a variable amount of non-distillable liquid†:

$$(CH_3)_2SiCl_2 + NH_3 \xrightarrow[\text{(ii) 3 h reflux temp.}]{\text{(i) 9 h at 30°}} \begin{matrix}\text{(i) } [(CH_3)_2SiNH]_3 \text{ (103–141 g)} \\ \text{(ii) } [(CH_3)_2SiNH]_4 \text{ (73–120 g)} \\ \text{(iii) Non-volatile residue (9–94 g)}\end{matrix}$$

(500 g, in benzene)

It has generally been assumed that the non-volatile residues from such ammonolyses are linear polymeric dimethylsilazanes of composition $[(CH_3)_2SiNH]_x$ (with terminal NH_2 groups), corresponding to the relatively large amount of linear polymeric dimethylsiloxanes of composition $[(CH_3)_2SiO]_x$ (with terminal OH groups) formed during hydrolysis. Since we now know much more about the catalytic effects of ammonium halides, as a result of the work done by Dr C. R. Krüger in our laboratory, we feel certain that the non-volatile residue is not linear silazane polymer but cross-linked material of high molecular weight formed by the catalytic condensation of —NH— groups, evolving ammonia and cross-linking the residue tertiary nitrogen atoms as shown in equation (1):

$$(R_2SiNH)_3 \xrightarrow[NH_4Cl]{80°} [2(R_2Si)_{3/2}N]_x + NH_3 \qquad (1)$$

Contemporary evidence, considered in retrospect, provides the following details about the reaction given in equation (1).

(i) Ammonolysis at −35° produces little or no residue; (ii) Must reflux to remove excess ammonia; (iii) The slower the distillation (NH_4Cl present), the more the residue; (iv) NH_4Cl opens trimer ring (Brewer and Haber "equilibration", 1948).

Even on the basis of purely contemporary evidence, our conclusion is strengthened by the finding of Brewer and Haber that octamethyltrisilazane could be made by heating hexamethylcyclotrisilazane and hexamethyldisilazane with ammonium chloride catalyst in a bomb at 300° or even at 400°C (equation 2):

$$\left.\begin{matrix}81 \text{ g } (CH_3)_3SiNHSi(CH_3)_3 \text{ (0·5 mole)} \\ + \\ 37 \text{ g } [(CH_3)_2SiNH]_3 \text{ (0·17 mole)} \\ + \\ 0{\cdot}5 \text{ g } NH_4Cl\end{matrix}\right\} \xrightarrow[\text{(in bomb)}]{312° \text{ for } 26 \text{ h}} (CH_3)_3SiNH(CH_3)_2SiNHSi(CH_3)_3 \text{ (19 g)} \qquad (2)$$

The same results as given in equation (2) were obtained by Brewer and Haber[1] on heating for 14 h at 410°, or for 72 h at 350°.

† Zeitler and Brown, checking the work of Osthoff and Cantor, *Inorg. Synth.* Vol. V, p. 61, found 60 g of "dark brown liquid which could not be distilled under reduced pressure, probably a mixture of higher molecular weight silazanes".

It can be seen from the reaction (equation 2) that ammonia was confined, leading to equilibrium. I should like to refer to this conclusion later. Before going on, however, let me point out that Brewer and Haber discovered that the ammonolysis product of methyldichlorosilane lost ammonia during distillation and set to a gel or even changed to a brittle resin (equation 3):

$$\underset{(230\ \text{g})}{CH_3SiHCl_2} + NH_3 \xrightarrow{\text{ether}} (CH_3SiH\text{–}NH\text{–})_3, \text{ etc.} \qquad (3)$$

Removal of ether left "viscous oil", not volatile at 195°; destructive distillation gave a brittle resin + some NH_3, and 28 g of a moble liquid. Fractional distillation of this liquid gave more ammonia, 5·2 g of trimer, and a residual gel[2]. The conclusion drawn from the above observations can be presented as in equation (4)

$$3x(CH_3SiHNH)_n \rightarrow [(CH_3SiH)_3N_2]_{nx} + nxNH_3 \qquad (4)$$

This reaction takes place without a catalyst, or in the presence of traces of dissolved ammonium chloride, but such behaviour is consistent with the same authors' conclusion that "the greater the bulk of the substituents, the more stable is the aminosilane".

Our own experience in the preparation of the cyclic methylsilazanes is that substantially no linear polymer of dimethylsilazane is formed during ammonolysis. If care is exercised to separate the ammonium chloride afterwards, and the temperature of preparation and purification are kept low, the condensation product formed during subsequent operations is less cross-linked. We have never obtained any distillable linear polymers, and whenever any non-distillable material remained, it always was cross-linked.

These matters have not always been so clear to us. We had begun a general investigation of silicon–nitrogen polymers a decade ago by studying the reactions of diamines with dialkyldichlorosilanes, but the products always seemed to re-arrange themselves to form silicon–nitrogen–silicon sequences, so that it seemed better to start with a silazane structure at the very beginning than to develop it later. Since the high molecular weight silicon elastomers were made by catalytic rearrangement of cyclic siloxanes, and since the corresponding cyclic silazanes were readily obtainable by the ammonolyses just described, we began a long search for appropriate catalysts which would open silazane rings. The conclusions drawn can be stated very simply as follows:

(i) Potassium hydroxide remains the most satisfactory catalyst for opening siloxane rings (equations 5 and 6).

$$Si\text{–}O\text{–}Si + OH^- \xrightarrow{150°} Si\text{–}OH + SiO^- \qquad (5)$$

$$SiO^- + Si^*\text{–}O\text{–}Si^{**} \rightarrow Si\text{–}O\text{–}Si^{**} + Si^*\text{–}O^- \qquad (6)$$

(and so on, to very high molecular weights)

However, silazanes react differently with potassium hydroxide, splitting out methane and forming products cross-linked through trifunctional silicon (Andrianov and Rumba, 1962).

(ii) Acid catalysts, such as sulphuric acid and ferric chloride, also open siloxane rings and produce elastomers (equations 7 and 8):

$$\text{Si–O–Si} + \text{H}_2\text{SO}_4 \xrightarrow{25^\circ} \text{SiOH} + \text{SiOSO}_3\text{H} \qquad (7)$$

$$\text{Si*OH} + \text{SiOSO}_3\text{H} \rightarrow \text{Si*–O–Si} + \text{H}_2\text{SO}_4, \text{ etc.} \qquad (8)$$

However, silazanes are hydrolysed rapidly by water-system acids like sulphuric acid, producing siloxanes and ammonium salts, so such acids cannot be used as rearrangement catalysts.

(iii) Bases in the ammonia system, such as potassium amide or sodamide, are inviting possibilities as catalysts for rearranging silazanes. However, experiments showed that they metalate the NH groups instead (equation 9):

$$\text{–SiNH–} + \text{KNH}_2 \xrightarrow{160^\circ} \text{–SiNK} + \text{NH}_3 \qquad (9)$$

(iv) Acids in the ammonia system, such as ammonium bromide and iodide, turned out to be very effective catalysts for opening silazane rings (equations 10 and 11):

$$\begin{array}{l}\text{–Si—N–} \\ \quad\uparrow \quad\uparrow \\ \text{Br}^- \ \text{NH}_4^+\end{array} \rightarrow \text{Br–Si–NH}_2 + \text{NH}_3 \qquad (10)$$

and so

$$n(\text{R}_2\text{SiNH})_3 \xrightarrow[190^\circ,\ 4\text{ h}]{\text{NH}_4\text{Br}} 2[(\text{R}_2\text{Si})_{3/2}\text{N}]_n + n\,\text{NH}_3 \qquad (11)$$

(Krüger, 1962)

The products are cross-linked through tertiary nitrogen, of course, so that no linear silazanes corresponding to silicone elastomers are obtained. The products instead are oils and resinous or rubbery waxes, with molecular weights of a few thousand. If the reaction just shown is carried out in a stream of nitrogen, the evolution of ammonia can be followed by absorbing the ammonia in acid; when this is done, the reaction is found to be 70 per cent complete in 4 h, but not entirely complete in 24 h. Increasing the amount of catalyst increases the rate of ammonia evolution but does not change the character of the product; a considerable amount of liquid oligomer is produced, plus three to eight times as much waxy and somewhat rubbery polymer which is not volatile at 200° and 1 mm. *Figure 1* shows how the condensation reaction proceeds with 5 per cent by weight of ammonium chloride, bromide or iodide; *Table 1* shows the composition of the products. It is interesting to note that even though pure trimer (hexamethylcyclotrisilazane) was used as the starting material, considerable tetramer was recovered at the end of the reaction, proving that ammonium halide is indeed a rearrangement catalyst. Unfortunately for the pursuit of purely linear polymer, it also acts as a condensation catalyst by the mechanism shown in equation (10) resulting in cross-linked condensation products. It should also be noted that ammonium iodide, the strongest acid, produces the most polymer. As for the rate, *Figure 2* shows its dependence upon weight per cent of ammonium bromide used in the reaction.

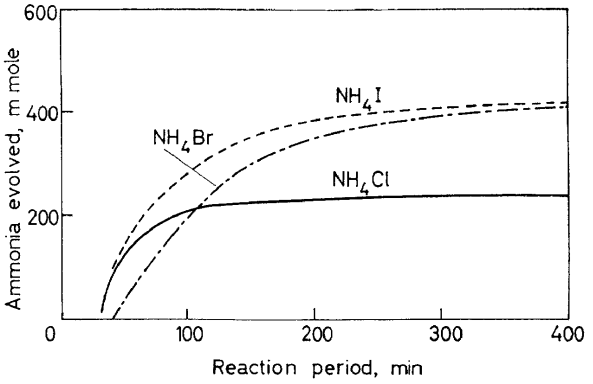


Figure 1. Effect of addition of 5 per cent (by wt) of ammonium chloride, bromide, iodide on the progress of the reaction

Table 1. Polymer and oligomer in relation to catalyst

Catalyst	*Weight* (%)	*Oligomer*	*Polymer* (%)
NH_4Cl	5	31% Trimer 19% Tetramer 33% Oligomer	11
NH_4Br	5	25% Oligomer	57
NH_4I	5	8% Oligomer	69
NH_4Br	1	17% Oligomer	73
NH_4Br	10	17% Oligomer	61
NH_4Br	45	28% Oligomer	49

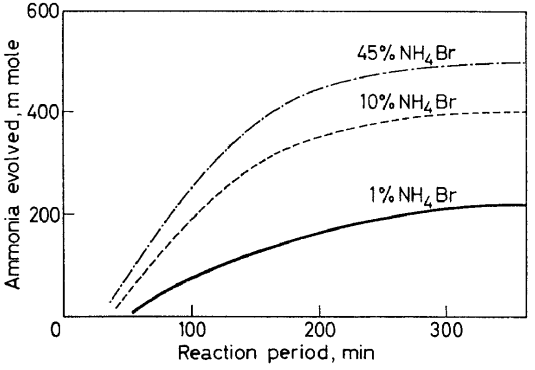


Figure 2. Effect of addition of ammonium bromide on the rate of polymerization of hexamethylcyclotrisilazane

In keeping with the simultaneous rearrangement function of the catalyst, *Figure 3* shows that the trimer, tetramer, and the crude ammonolysis product react equally well; the crude material being slightly slower in its reaction because it already contains (due to the method used in its preparation) a small amount of cross-linked silazane polymer.

Many other versions of condensed polymer have been made by the use of ammonium bromide: methyl vinyl silazane, methyl silazane containing trifunctional silicon atoms, silazanes containing metallated nitrogen atoms (which react with trimethylchlorosilane to yield resinous substances) and so

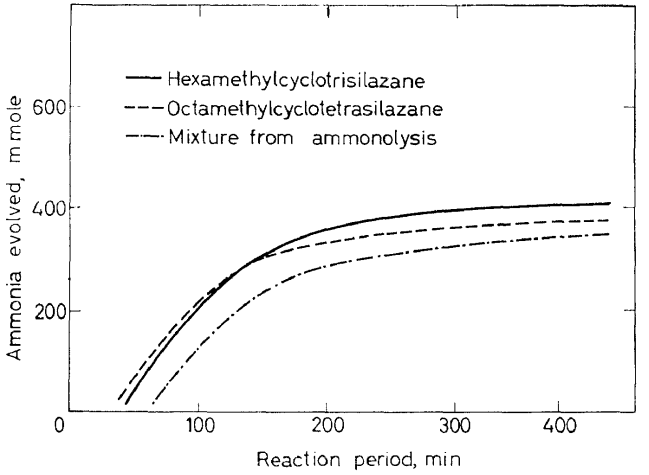


Figure 3. Comparative reactivities of the trimer, the tetramer, and the crude ammonolysis product towards the polymerization of silazanes

on. These are described in a number of publications[3]. I shall briefly discuss here the rates of hydrolysis (*Figure 4*) of silazane polymers which may be of interest.

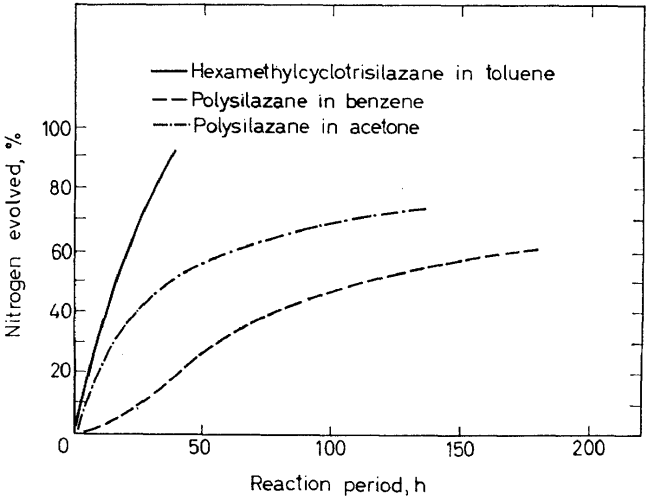


Figure 4. Rates of hydrolysis of silazane polymers

Since the rearrangement of cyclic silazanes with ammonium halides always leads to cross-linked condensation products, we had to turn elsewhere in our search for linear dimethylsilazane. It occurred to us that since the

ammonolysis of dichlorosilanes can be carried out in such a way as to prevent simultaneous cross-linking, if the conditions are mild enough, it should be possible to preserve bifunctional units and make linear polymers from them if only they are of such character that they could not form rings readily. To test this hypothesis, α,ω-dichlorosiloxanes were prepared (equations 12 and 13) by the partial hydrolysis of dimethyldichlorosilane and after separation by distillation, the pure compounds were treated with ammonia in ether solution[4]; the polymers obtained were with both Si–N and Si–O links.

$$(CH_3)_2SiCl_2 + H_2O \rightarrow \underset{(A)}{Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl}$$

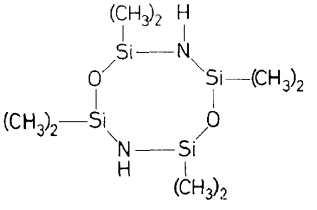
where $n = 1,2$, and 3 (12)

$$(A) + NH_3 \xrightarrow[35°]{\text{ether}} \text{Corresponding } \alpha,\omega\text{-diaminosiloxanes, which upon distillation evolved } NH_3 \text{ and formed siloxane–silazanes.} \quad (13)$$

To our surprise, both ring and chain compounds were formed. The ring products formed from the separate dichlorosilanes of equation (12) are shown in equations (13), (14) and (15).

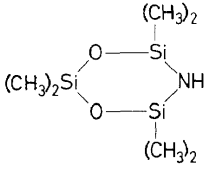
Product obtained when

$n = 1$



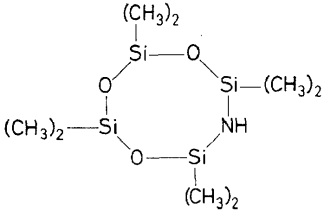
---(13)

$n = 2$



---(14)

$n = 3$



---(15)

Resinous and viscous oily chain polymers were also produced in the reactions, and were recovered. The material from the reaction (equation 15), for example, contained 22·3 g. of polymer as against 19·5 g. of the cyclic siloxane–silazane shown, indicating that the idea was sound and that polymers can indeed be produced in this way. Of course the more dimethylsiloxy

units the original dichlorosilane starting material contains, the more the product resembles a pure siloxane in its properties, so the method works best for those polymers which are farthest away from a pure linear dimethylsilazane. For this reason the method was not pursued further.

The search for a linear polysilazane seemed halted, but then further progress came to be attained in an entirely unexpected way. During an attempt to study the kinetics and mechanism of the ammonium bromide condensation further, Dr George Redl set up a closed system in which he expected to follow the evolution of ammonia by a rise in pressure. To his surprise, a very small pressure developed early and then stayed constant, indicating equilibrium. The equilibrium mixture yielded a small amount of polymer with an n.m.r. spectrum which contained a pronounced peak near the trimer starting material (*Figure 5*).

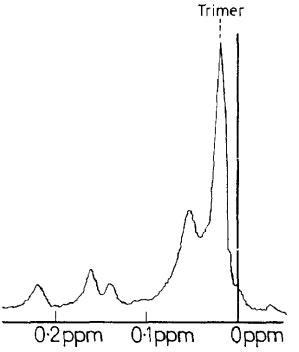


Figure 5. Methyl proton resonance spectra of polymerization in a closed system

The i.r. spectrum and the chemical analysis both supported the view that here was a polymer containing a major proportion of $(CH_3)_2SiNH$ units, *i.e.* containing more secondary nitrogen than tertiary nitrogen, and consequently less cross-linking through condensation. Pushing the reversibility further, Dr Redl dissolved 5 per cent of ammonium bromide in hexamethylcyclotrisilazane and started refluxing under 1·5 atm. pressure of ammonia. This time the ammonium bromide precipitated out, but the polymer formed anyway. Its spectrum (*Figure 6*) showed much more linear silazane and correspondingly less cross-linked material.

The procedure was repeated in a bomb under 4 atm pressure of ammonia, and here at last there was obtained a linear dimethylsilazane. *Figure 7* shows that substantially all the dimethylsilyl groups in it are the same, and that the proton environment is very nearly that of the pure hexamethylcyclotrisilazane starting material.

The i.r. spectrum and analytical data also show clearly that at last we are dealing with a linear polysilazane. Although it is present in only a small proportion in the equilibrium mixture, the polymer can be isolated in the form of a very viscous liquid containing a wide range of molecular weights. It hydrolyses very little in moist air, but of course rapidly as dilute solution in a homogeneous medium. We would like to find a way to raise the molecular

weight to that of an elastomer. Meanwhile some tests are in progress to determine its suitability as a practical polymer in dry atmospheres.

We believe that the Redl rearrangement of cyclic trimer to linear polymer is actually catalysed by ammonia, and that ammonium bromide has nothing

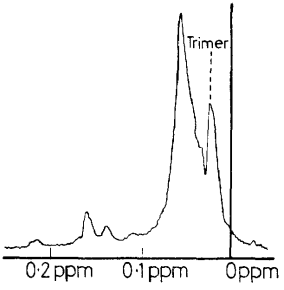


Figure 6. Methyl proton resonance spectra of polymerization under 1·5 atm ammonia pressure

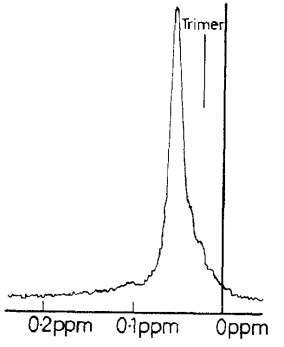


Figure 7. Methyl proton resonance spectra of polymerization under 4 atm ammonia pressure

to do with it[5]. In fact, the reaction runs just as well without ever having added any ammonium bromide. The course of the reaction as we see it at present can be presented as follows:

(i) Much ammonia dissolves in dimethylsilazane trimer or tetramer under 4 atm pressure; (ii) In the nitrogenous solvent the solute dissociates into ammonium and amide ions; (iii) the ammonium ions suppress the solubility of ammonium bromide, if present; (iv) The amide ions act catalytically to open Si–N bonds the way OH^- ions open the Si–O bonds of siloxanes. This is what was sought from the use of potassium amide, but the purpose was defeated by the metallation reaction.

A variation of the linear dimethylsilazane consists in incorporating a small and well-regulated amount of cross-linking through trifunctional silicon atoms, using the ammonia-pressure polymerization. This procedure increases the molecular weight of the polymer and makes it more viscous, but of course it

is not elastic. We would much prefer to have an entirely linear dimethylsilazane of very high molecular weight, made up only of bifunctional units. Until such time as we can get such a material in quantity, we must do what we can with the materials we have, testing them in the form of small samples as intensively as possible.

One very revealing test that can be applied to small samples of the preparations I have described is to study internal mobility as a function of temperature by means of broad-line n.m.r. In this case we can study proton resonance, not in the usual manner of analysing proton environment by high-resolution n.m.r. of liquids, but by observing the broad-line spectra of the solid polymers over a wide range of temperatures. This cannot be done with the usual high-resolution equipment which is in general use; instead, one must have a well-controlled means of varying frequency or field strength over wide ranges, and of course the temperature must be held constant at any required value, from the boiling point of helium to 200°C or more. We have developed our own equipment for doing this, over a period of 14 years, and although it would take a long time to explain its features in detail, the block diagram (*Figure 8*) will show the principal parts. A large permanent

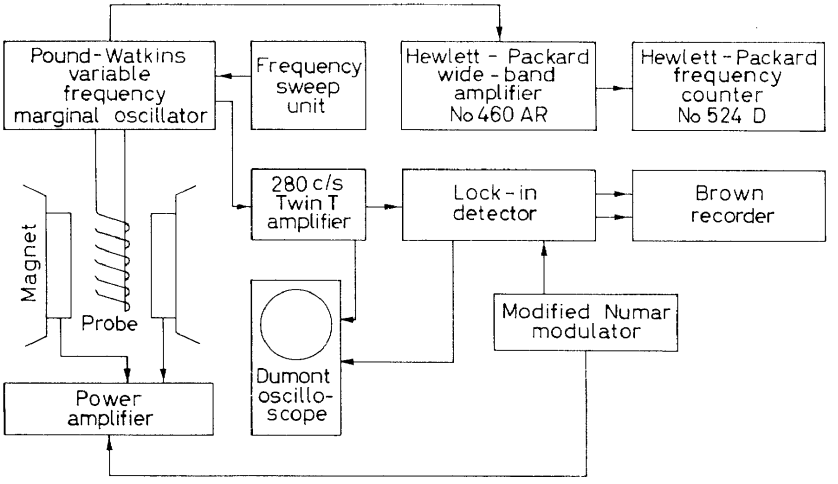


Figure 8. Diagram showing the equipment used for studying the broad-line spectra

magnet is used, and the sample is contained in a special cryostatic probe placed between the pole pieces of the magnet. A radio-frequency oscillator feeds an extremely weak signal at appropriate frequency to the sample, the frequency being varied ("swept") by means of a motor-controlled potential applied to a silicon-diode capacitor. At the same time the magnetic field is modulated at 280 c/s. Absorption of RF energy by the sample produces a 280-cycle frequency-modulation of the RF, which is registered as the first derivative of the absorption spectrum by means of a phase-sensitive detector and a linear recorder. If the internal molecular motions of the solid are of large amplitude and variety, the spectra of the derivatives will be narrow, even approaching those of liquid samples. On the other hand, if the lattice

is rigid and the molecular structural components are frozen in place, they contribute local magnetic effects and the derivative lines will be broad. By starting at a very low temperature and warming the sample very slowly while scanning the line over and over, some knowledge of the internal mobility can be obtained. This can be related to the individual motions of the various components of molecular structure, and this we have done in order to compare silicon–nitrogen bonding in polymers with silicon–oxygen bonding. As you will see, we can also compare the effects of cross-linking and of polymer reinforcement in the two series of materials.

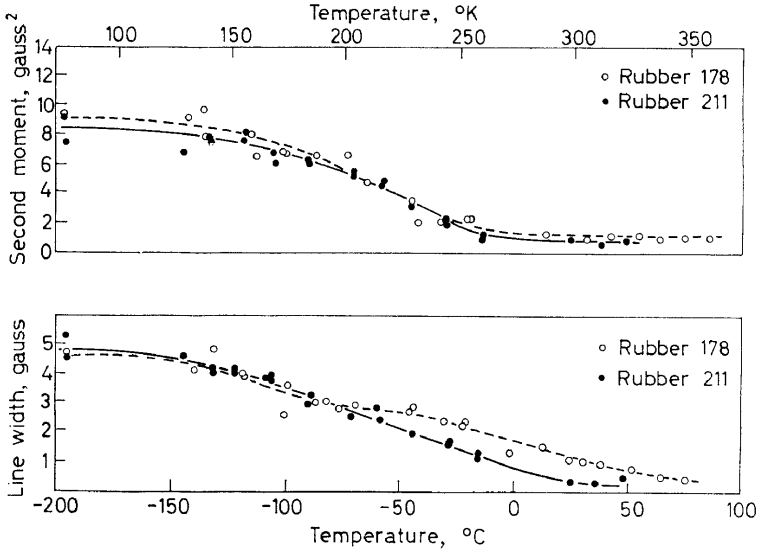


Figure 9. A comparison of the line width and second moment data in the case of two Krüger polymers—Rubber 178 and Rubber 211

Figure 9 shows the results of two preparations of cross-linked polysilazane prepared by ammonium bromide catalysis (No. 178 with 1 per cent ammonium bromide at 280°; No. 211 with 5 per cent ammonium bromide acting on crude ammonolysis product). Both line width and second moment show that internal motions commence at −150°C and increase gradually in intensity up to + 50°C. There is no sharp curtailment of internal motion; the materials commence to stiffen at 0°C and gradually become brittle. On the other hand, the behaviour of a commercial methyl silicone elastomer (shown in *Figure 10*) shows a sharp curtailment of molecular motion below −125°C and an astonishing freedom of motion above −100°C. This behaviour is much the same for the elastomer itself (dark circles) and the reinforced or filled rubber (light circles); the only differences are in the direction of more restriction of motion in the filled material because of a cross-linking action of the silica filler. It is the behaviour so well shown in *Figure 9* which makes silicone rubber useful at low temperatures, for the polymer itself remains elastic down to −100°C and even the filled and vulcanized "compounds" are elastic to −80° and flexible down to −120°. The polysilazanes

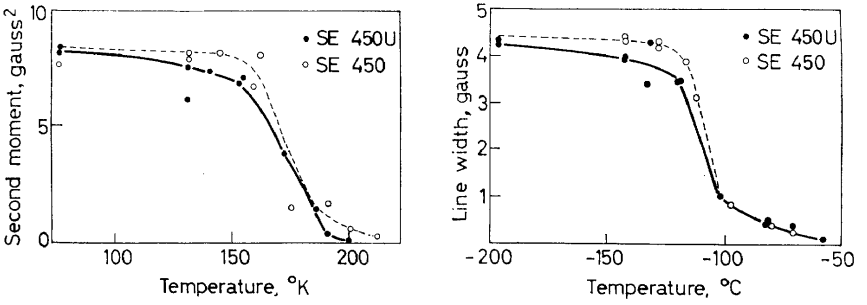


Figure 10. A comparison of the line width and second moment data in the case of two commercial methyl silicone elastomers—SE 450 U and SE 450

made by ammonium bromide catalysis do not come remotely near this performance.

The introduction of trifunctional silicon atoms into the ammonium bromide-catalysed polymers still further increases the cross-linking, of course, but the internal motions already are so inhibited by the tertiary nitrogen atoms that the trifunctional silicon atoms make no discernible difference. *Figure 11* compares such a doubly cross-linked polymer (No. 237) with the

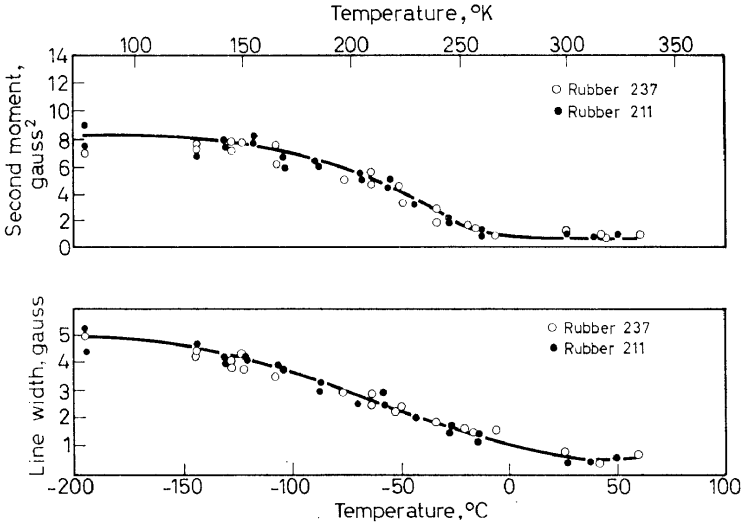


Figure 11. Comparative line width and second moment data, showing the effect of addition of more silicon on cross-linking, in respect of a doubly cross-linked polymer (No. 237) and a sample (No. 211) described earlier (cf. *Figure 9*)

previously displayed sample (No. 211), and the curves for line width and second moment are seen to be identical for the two samples.

To be sure, the polysilazanes made by ammonium bromide catalysis are not molecularly homogeneous. Among other considerations, there is a wide range of molecular weights. When cooled to −80° or −100°C, some of the constituents freeze in a more orderly way than others. We found that polymer No. 211 was approximately 50 per cent crystalline, as determined by

X-ray diffraction, and that it contained rather large crystallites which were responsible for much of the molecular rigidity. Since such crystallites appear progressively at various temperatures as the sample is cooled, they are responsible in large part for the gradual change of line-width and second moment with falling temperature. The amorphous portions of the polymer gives a sharper, narrower line (at moderately low temperatures) than the crystalline portion. *Figure 12* shows the spectrum for No. 211 at —87°, and this is seen to be a combination of a narrower line due to the amorphous component and a much wider absorption line due to the crystalline components:

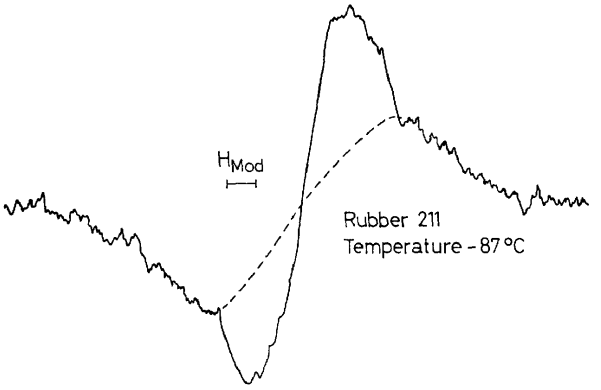


Figure 12. Amorphous and crystalline components of the silazane polymer, Rubber 211

Since the silazane polymers made by ammonium bromide catalysis are all highly cross-linked, they do not provide a fair comparison with the linear polysiloxanes in low temperature behaviour. As soon as linear dimethylsilazane became available by the ammonia-pressure catalysis (the Redl technique), we were anxious to compare it with the linear siloxanes in the n.m.r. equipment. *Figures 13* and *14* show the dependence of line-width on temperature for a sample of the new linear polymer *vs.* a linear siloxane.

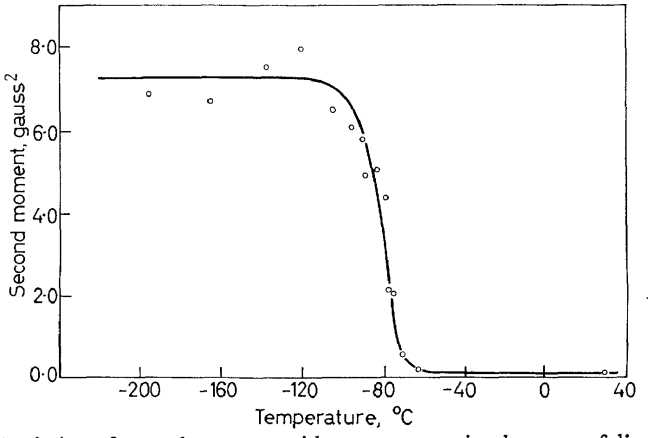


Figure 13. Variation of second moment with temperature in the case of linear silazane polymer

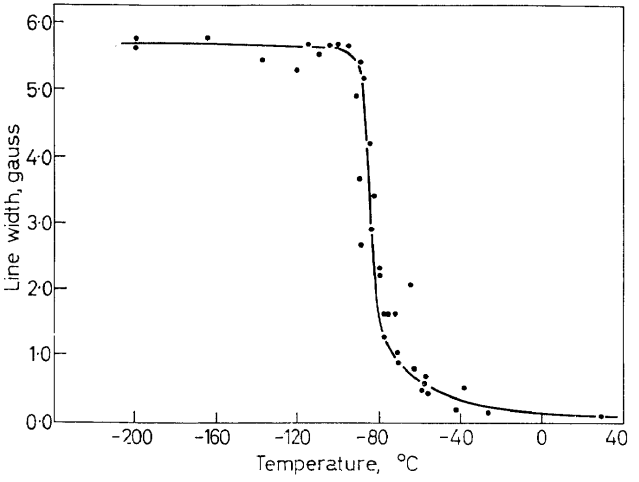


Figure 14. Variation of line width with temperature in the case of linear siloxane polymer

The result is surprisingly similar to that of a linear siloxane: the same sharp change of mobility in the range $-100°$ to $-150°C$, and about the same slope for the transition itself. We conclude that there is nothing inherent in the silicon–nitrogen bond that restricts molecular motion of the proton-bearing groups, or indeed of motion around the bonds to silicon. This leads to the further conclusion that about the same degree of π-bonding occurs in silazanes as in siloxanes. In a practical way, linear polysilazanes offer about as much promise for low-temperature utility as siloxane polymers, but are not any better in this respect.

A final point to be investigated is the effect of limited cross-linking through trifunctional silicon atoms in an otherwise linear silazane polymer, with no tertiary nitrogen present. The ammonia-pressure technique offers a method for preparing such polymers, and the broad-line spectra have just been obtained; the result is shown in *Figure 15.*

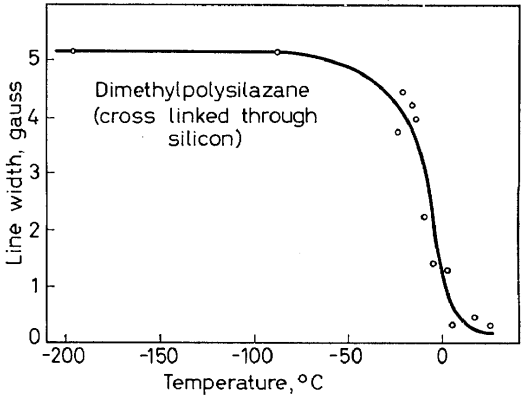


Figure 15. Variation of line width with temperature in the case of a silazane with trifunctional silicon

In conclusion, I may add that we have found ways to make polymethylsilazanes, both linear and with cross-linking through nitrogen, through silicon, and through vinyl groups, or by oxidative coupling. The materials containing much tertiary nitrogen show severe curtailment of molecular motion at low temperatures, and contain both crystalline and amorphous components. Linear silazanes exhibit about the same high degree of internal mobility as linear siloxanes, and have about the same degree of π-bonding to silicon.

At present there seems no reason to believe that silazane polymers will displace silicones from the market. It may well be that silazanes show greater adhesion to metals, as has been claimed, but there is always the danger of hydrolysis—at least in an earthbound application. The only conclusion possible at this time is that polysilazanes have no use. We should be careful about such conclusions, however, because F. S. Kipping said the same thing about his silicones in 1937.

I should like to express my appreciation to the young men who have laboured so long and hard to accomplish the results I have reported here, in particular to Dr Carl R. Krüger, Dr George Redl, Mr Robert Lambert, Dr James R. Barrante, Mr. Frank Model, Dr Peter Geymayer, Dr Dieter Kummer, Dr Klaus Lienhard, Dr Ronn N. Minné, Dr Hans Pfleger, Dr Joachim Pump, and Dr Richard Weiss.

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