INTERNAL MOTION IN ORGANOSILICON-NITROGEN COMPOUNDS

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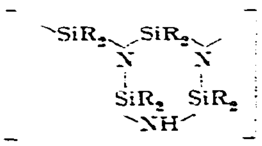
INTRODUCTION

It is well known that the unique physical properties of polymethylsiloxanes stem from internal motion of low energy barrier[1-4]. Since an N–H group is isoelectronic with an oxygen atom, one might expect that polymers analogous to the siloxanes in which N–H groups replace oxygen atoms would offer an interesting comparison. Such polymers can be made by allowing dimethyldichlorosilane to react with ammonia according to the equation:

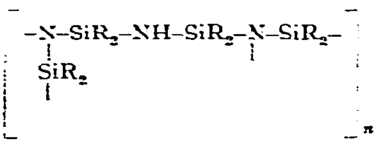
$$n(CH_3)_2SiCl_2 + 3nNH_3 \longrightarrow [(CH_3)_2SiNH]_n + 2nNH_4Cl$$

Because the nitrogen atoms have an "extra" hydrogen atom which is capable of further substitution by other dimethylsilyl groups to give a highly cross-linked polymer, and because the donor properties of nitrogen are quite different from those of oxygen, it is of immediate interest to compare the physical behavior of the polymers based on silicon–nitrogen bonds with that of the corresponding siloxanes in terms of the intramolecular motion.

At least three types of motion are possible in polymethylsilazanes and related silylamines. The first type of motion is a C_3 reorientation of the methyl group about the silicon–carbon bond. This type of motion is well known in the polysiloxanes[1-4]. A second mode is movement of the entire $(CH_3)_2Si$ group about the silicon–nitrogen bond, which is more likely to be a bending or rocking motion than a rotation. The third type of motion is translational motion of the chain segments. The silazane polymers recently prepared in this Laboratory were found to be highly cross-linked[5,6]. This high degree of cross-linking should have several effects on the internal motion of the polymer. First, the degree of translational motion of the chain segments should be lowered considerably, causing the polymer to lose its small-molecule properties at low temperatures. Second, the high degree of cross-linking makes the formation of small rings inevitable. Krüger[5] found that the ratio of secondary to tertiary nitrogen in the silazane polymers was approximately 2 to 3. This would indicate either of two structures,


(I)

or


(II)

$R = CH_3$,

the polymers probably being a mixture of (I) and (II). This formation of small rings should hinder free rotation of the $(CH_3)_2Si$ groups about silicon–nitrogen bonds. Third, with such a high proportion of tertiary nitrogen the effects of d_π–p_π bonding also should be apparent. Silazanes exhibit considerable d_π–p_π interaction between the silicon and the neighboring nitrogen atoms, arising from contributions of the "extra pair" of electrons on the nitrogen atoms to the empty *d* orbitals of the silicon atom, and this additional coupling serves to bond the silazane framework together more firmly than the looser silicon–oxygen framework of the siloxanes.

The specific purposes of the present investigation were (1) to compare the properties of the silazanes in general with those of the siloxanes by means of the techniques of broad-line nuclear magnetic resonance, determining (if possible) the types and degree of molecular motion present, (2) to study the effect of temperature on the internal motion, (3) to analyze the effect of cross-liking on the properties of the polymers at low temperatures, the silazanes usually being considerably more cross-linked than the siloxanes because of their trifunctional nitrogen atoms, and (4) to study the effects of the degree of crystallinity of the polymers on the internal motion at low temperature.

A polymer prepared by allowing dimethyldichlorosilane to react with ethylenediamine also was examined. For comparison, several pure compounds were examined, including the ring compounds hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, and some chain species of low molecular weight. In no case could a straight-chain polymer be obtained with little or no cross-linking, as is done in silicone rubber. This naturally limited the degree of comparison with the siloxanes, but the closest possible approximation was made.

EXPERIMENTAL

Measurements were taken on a fixed-field, variable frequency broad-line NMR spectrometer described in detail elsewhere[7,8]. The spectrometer is equipped with temperature control which allows measurements to be taken from —196°C to +300°C.

As the silazanes and silylamines are sensitive to moisture and decompose slowly in room air to form ammonia and the analogous siloxanes, all samples were sealed into 11 mm diameter sample tubing immediately after preparation. This necessitated placing the thermocouple alongside the sample tube instead of directly into the sample tube itself. Hence to insure that the sample tube and the gas were at equilibrium, the following procedure for cooling was followed:

Samples were placed in the probe assembly and were cooled at approximately 2°C per minute to the desired temperature, to eliminate hysteresis effects[3]. When the system reached the desired temperature, as shown by a constant reading on the potentiometer, the probe was kept at this temperature for approximately 10 minutes to allow the sample to come to equilibrium, and then two measurements, taking approximately 20 minutes each, were taken at each temperature; subsequent measurements were taken at 15° intervals.

For very low temperature measurements a different procedure was followed. The sample tubes were allowed to cool in liquid nitrogen for approximately 24 hours. After this period of time the probe temperature control was set for —145° (the lowest temperature that could conveniently be obtained using the gas-flow method), and the samples were transferred immediately to the probe and allowed to warm from —196°C to —145°C. Finally, measurements at —196°C were taken in a liquid-nitrogen Dewar vessel made to fit the probe.

Most samples were modulated at amplitudes less than 1/3 their line width; however, in some cases this proved rather difficult because of small signal intensities. Room-temperature measurements were probably considerably broadened by modulation and by inhomogeneity of the magnetic field at the site of the sample.

RESULTS AND ANALYSIS

When dimethyldichlorosilane reacts with ammonia under conditions such as those used for forming a silicone, one obtains in high yields a mixture of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, plus a small amount of polymer[3]. If one wants to obtain a high polymer, one must either open the silazane rings and join the fragments to form a linear polymer, or connect together the rings themselves.

Recently in this Laboratory Krüger has been successful in polymerizing mixtures of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane by using ammonium halides as catalysts[6]. Several types of highly cross-linked polymers were obtained, and the behavior of these is summarized below:

1. Polymers cross-linked only through tertiary nitrogen atoms

Two polymers which were cross-linked only through tertiary nitrogen atoms were studied. The first, rubber No. 178, was prepared by Krüger[6] by heating freshly distilled hexamethylcyclotrisilazane with 1 % of ammonium bromide to 280°C for several hours under an atmosphere of dry nitrogen. A dark brown material resulted, having properties between those of a rubber and those of a wax. The other sample, rubber No. 211, was prepared by carrying out the reaction of dimethyldichlorosilane with ammonia to obtain a mixture of cyclic tetramer and trimer, and then heating this crude mixture with 5 % of ammonium bromide as a catalyst to 280°C for several hours. A white, waxy material resulted. Rubber No. 211 looked very much like polyethylene; both compounds were flexible, but not elastic.

Crystallinity measurements of No. 211 by X-ray diffraction techniques using CuK_α radiation indicate that the compound is approximately 50 % crystalline*. It was found that the crystallites in No. 211 are rather large and are probably not entirely polymeric.

Nuclear magnetic resonance measurements were taken from —196°C to +50°C. The temperature dependences of line width and second moment are shown in Figure 1. One should note the remarkable difference in the low-temperature properties of the silazanes as compared to those of siloxanes in Figures 2 and 3. One also will note that the two silazane compounds behave in essentially the same manner, as indicated by the second moment data. The difference in the line width (which after all is only a qualitative description of the motion) may not have as much significance.

At —196°C the second moment of No. 211 is found to be 8.5 ± 0.5 gauss^2. This value is slightly larger than the value of 8.0 ± 0.5 gauss^2 found in the current investigation of siloxanes at this same temperature, but is close to the value reported by Powles *et al.*[4] for siloxanes. The theoretical second moment for a rigid methyl group in

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* The authors are indebted to Dr. W. P. SLICHTER of the Bell Telephone Laboratories for making the crystallinity measurements needed for this investigation.

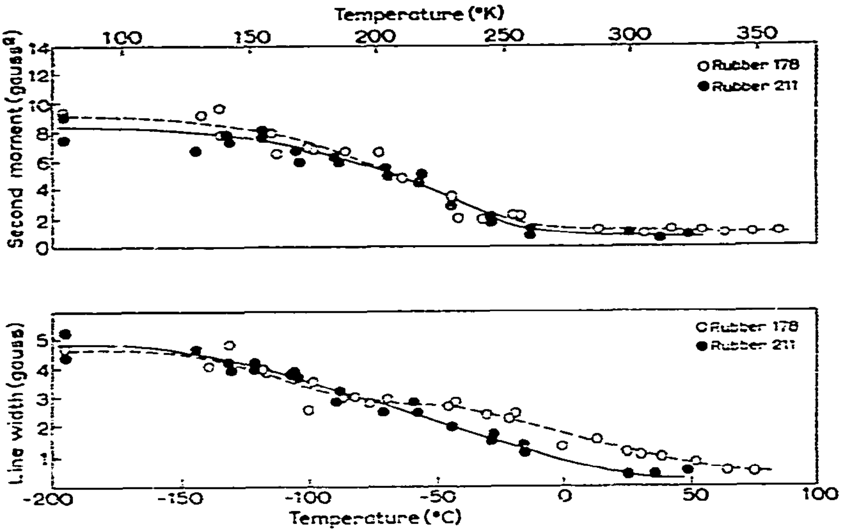
Temperature (°K)
100
150
200
250
300
350
Second moment (gauss²)
14
12
10
8
6
4
2
0
○ Rubber 178
● Rubber 211
Line width (gauss)
5
4
3
2
1
○ Rubber 178
● Rubber 211
-200
-150
-100
-50
0
50
100
Temperature (°C)

Fig. 1.

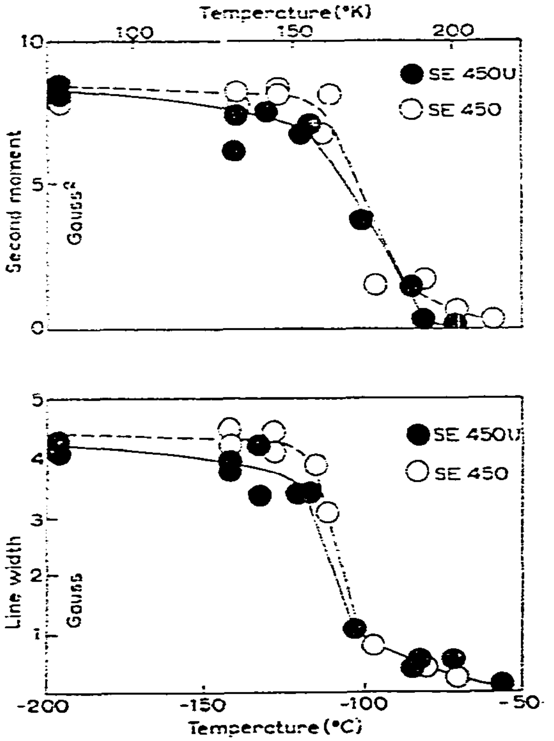
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Fig. 2.

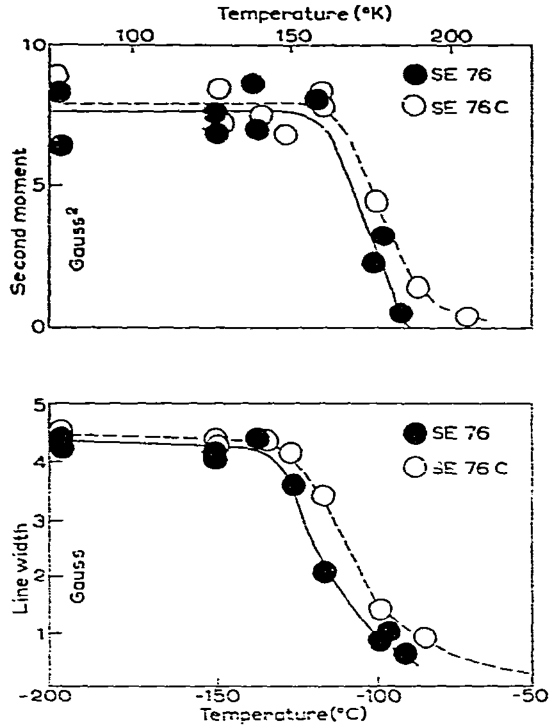


Fig. 3.

a polycrystalline solid is 22.5 gauss². To this must be added a contribution by neighboring methyl groups. Powles *et al.*[4] have estimated the intermolecular contribution to be 1.3 gauss². Kusumoto *et al.*[2] suggest a value which is closer to 2 gauss². In the present silazanes there are also protons bonded to nitrogen atoms, and hence a contribution must be added for them. The second moment for an isolated N–H group is found to be 1.9 gauss², using the equation of Van Vleck[10,8]. Assuming that in a repeating unit there are eight methyl groups to one N–H group (*i.e.*, a total of 25 protons), the second moment should then be:

$$[\Delta H_2]^2 = 24/25\,(24.5) + 1/25\,(1.9) = 23.6\ \text{gauss}^2$$

Thus one sees that the contribution due to the NH group is negligible. It is known that a C_3 reorientation of the methyl group reduces the intramolecular contribution to the second moment by a factor of 1/4[1], but probably does not effect the intermolecular contribution. This gives a second moment of:

$$[\Delta H_2]^2 = 1/4\,(22.5) + 2 = 7.6\ \text{gauss}^2$$

which agrees quite well with the observed value. Thus at —196°C it is reasonable to assume that the only motion is reorientation of the methyl groups about the carbon–silicon bond.

As the silazane samples 178 and 211 are warmed to room temperature, the secor moment decreases, which indicates the onset of motion of the $(CH_3)_2Si$ groups abo the silicon–nitrogen bonds and also some translational motion of the chain segment It is necessary to assume translational motion of the chains because the second momer decreases to a value less than the intermolecular broadening contribution. This sma value can only be explained by assuming some movement of the chains past each other

Figure 4 shows a spectrum of No. 211 at —87°C in which the lines for th crystalline and amorphous components can be seen. The line for the amorphous com ponent is considerably broader than that for a siloxane at the same temperatur indicating that there is rotational restiction of the $(CH_3)_2Si$ groups due to the hig

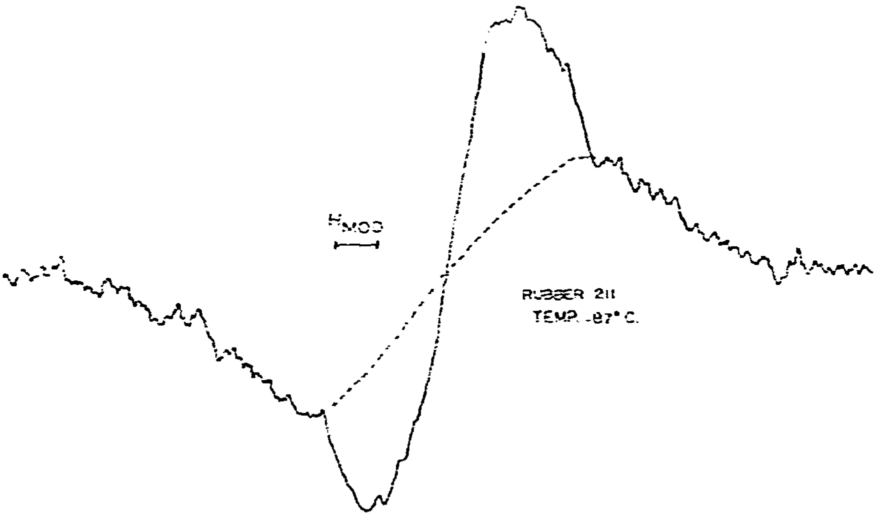


Fig. 4.

degree of cross-linking. Hence we see that as the polymers become more highly cross-linked, they tend to lose their low-temperature, small-molecule properties. This is a further indication that the uniqueness of silicones is due to separation of the siloxane chains, probably because of the large volume swept out by rotating methyl groups. Only by a high degree of cross-linking are the siloxane chains forced to interact.

2. *Polymers cross-linked through tertiary silicon and tertiary nitrogen atoms*

Rubber No. 237 was prepared by Krüger[6] by mixing 55 g of hexamethylcyclotrisilazane and 3 g of methyltrichlorosilane with 5 % ammonium bromide and heating the mixture in the same manner as in the preparation of No. 178. Ammonia was then bubbled through the mixture to effect cross-linking with methyltrichlorosilane. An elastic, waxy polymer resulted which melts at 178–190°C. Crystallinity measurements show that No. 237 also is approximately 50 % crystalline; however, the crystal grains are very fine rather than coarse, as was found in No. 211.

The temperature dependence of the line width and second moment for No. 237 is shown in Figure 5. The curves are almost identical with those for No. 211, which signifies that no further hindrance to the motion is brought about by the addition of methyltrichlorosilane. Since most of the protons are found on the $(CH_3)_2Si$ groups,

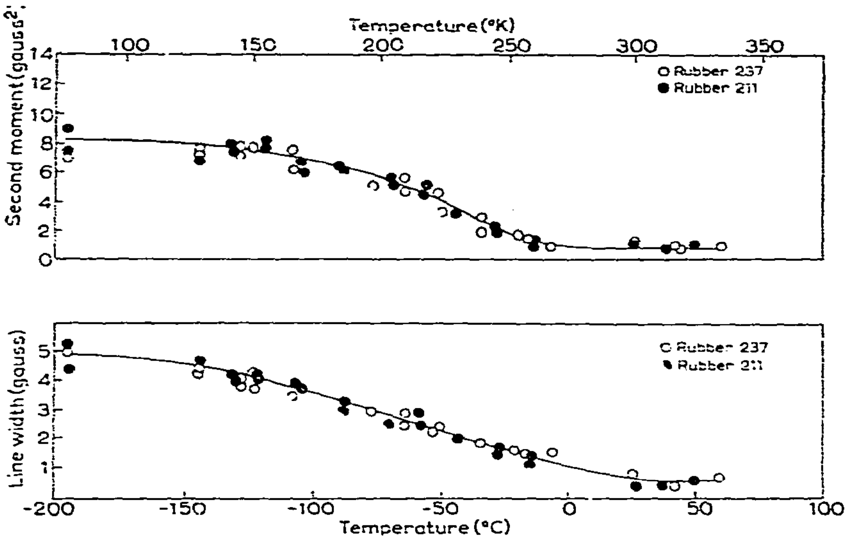


Fig. 5.

rather than on the CH_3–Si groups, the absorption will depend mostly on the behavior of the $(CH_3)_2Si$ groups. Cross-linking with methyltrichlorosilane should not affect the local motion of the $(CH_3)_2Si$ groups, but should affect the translational motion of the chains. This is further evidence that localized motion of the $(CH_3)_2Si$ group rather than translational motion of the chains is the main cause of the line narrowing. If the degree of cross-linking by methyltrichlorosilane were to be made very high, then the $(CH_3)_2Si$ motion undoubtedly will be affected because of the further formation of small rings.

3. Polymers cross-linked through vinyl groups and tertiary nitrogen atoms

Rubber No. 241 was prepared by Krüger[6] by mixing 40 g of hexamethylcyclotrisilazane, 10 g of trimethyltrivinylcyclotrisilazane and 5 % ammonium bromide, and then heating the mixture as was done in the preparation of No. 178. A rubber which swelled in carbon tetrachloride was obtained. The temperature dependence of the line width and second moment is shown in Figure 6. The large increase in second moment is due to the presence of wings which persist even up to —40° C. This indicates a much greater hindrance to motion in No. 241 than in the polymers previously examined. This restriction in motion can be explained by the fact that the cross-links derived from vinyl groups are fixed and cannot reorient about any bond. In effect, a vinyl group can be thought of as a methyl group attached to a silicon atom of one chain and also bonded to a methyl group on a silicon atom of another chain. This makes rotation of the methyl groups about the silicon–nitrogen bond impossible. The ratio of methyl groups to vinyl groups is still large enough, however, so as not to affect the low-temperature second moment; the majority of protons are still capable of a C_3 reorientation about the silicon–carbon bond.

4. Polymers cross-linked by air oxidation and tertiary nitrogen atoms.

Rubber No. 236B was prepared by Krüger[6] by mixing hexamethylcyclotrisilazane with an equal weight of ammonium bromide and heating the mixture as in the previous preparations. A polymer melting at 90–100° C was obtained. Dry air was bubbled through the molten polymer for 3 hours at 250–270°C resulting in a tough rubber. Crystallinity measurements show that the degree of crystallinity in No. 236B is low, probably less than 25%. The temperature dependence curves, shown in Figure 7, are identical with those for No. 211 and No. 237, both of which have high crystallinities of 50% or more. This would seem to indicate that the degree of crystallinity does not effect the molecular motion in the polymers as much as the degree of cross-linking does.

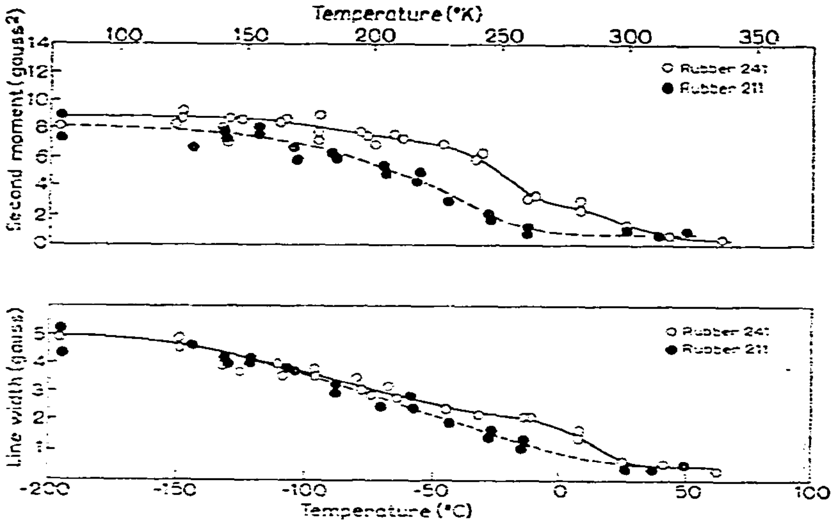


Fig. 6.

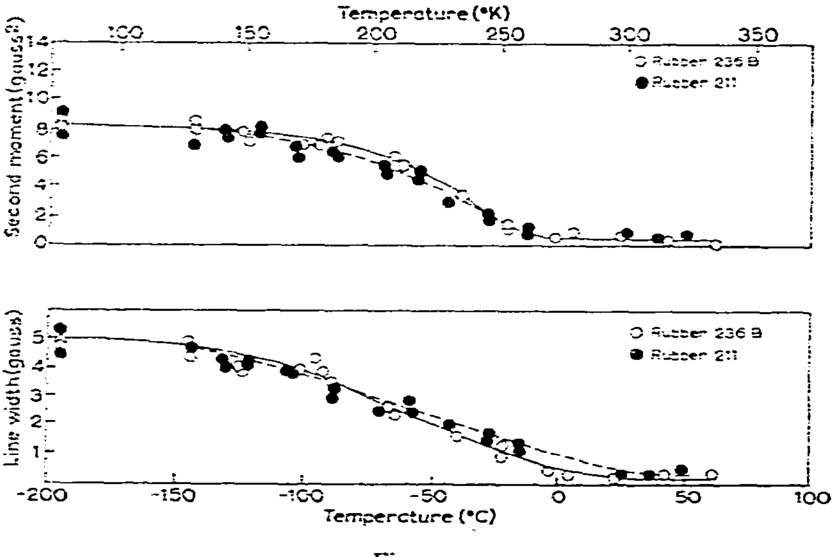
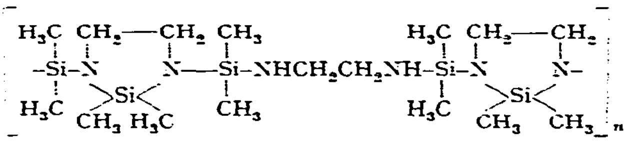


Fig. 7.

As cross-linking by air oxidation is the same as cross-linking by methyltrichlorosilane (since methyl groups are cleaved from silicon by the process, evolving formaldehyde and water), one would expect the compounds to behave in the same way. They do.

5. *Minné Polymer*

It was found by Minné[11], and independently by Lienhard[12], that a polymeric material could be obtained from the reaction of ethylenediamine and dimethyldichlorosilane. Subsequent research in this area by Kummer[13,14] led to two more polymers: polymer (I) in xylene and polymer (II) in benzene. From analytical data on polymer (I) and polymer (II) it was found that both had the average structure:



The presence of the five-membered rings in the polymer is supported by IR measurements[14] and by double-resonance high resolution NMR[15]. In no case could a pure linear compound, similar to that prepared by Minné, be obtained, even with an excess of ethylenediamine.

The polymer investigated by broad-line NMR was prepared by Kummer[14] by mixing 0.15 moles of dimethyldichlorosilane (which had been diluted with an equal volume of xylene) with 0.3 moles of anhydrous ethylenediamine, also diluted with 80 ml of xylene, under an atmosphere of dry nitrogen. After the chlorosilane had been added, the mixture was refluxed and then the solid material which had formed was filtered off by suction filtration using a medium glass frit. Most of the xylene solvent was removed at room temperature by reducing the pressure to 1 mm, and then the product was heated to 70–100°C for 2 hours at 1 mm to complete the removal. The product, polymer (III), was a viscous oil. High resolution NMR, IR, and analytical data indicated that the compound had the structure shown above[13], containing both rings and chains. Broad-line spectra were taken from room temperature down to —196°C. The temperature dependence of the line width and second moment is shown in Figure 8. The second moment at —196°C is found to be 13.4 ± 0.5 gauss^2. One should note the remarkable difference between polymer (III) and rubber No. 211. The dependence of polymer (III) is very similar to that of natural rubber[16]; however, methyl rotation does not cease at —196°C. The large difference between polymer (III) and No. 211 is not unexpected, since polymer (III) is considerably more organic in nature. A behavior more like natural rubber, rather than like silicone rubber, would be expected because of the backbone of ethylene groups alternating with silicon atoms. In any case, one would not expect the chains to remain separated to the same degree because of the smaller content of $(CH_3)_2Si$ groups.

One can obtain a theoretical second moment at —196°C by adding up contributions to the second moment from various groups in the molecule. In this case the total number of protons is 44, and assuming that the methyl groups are freely rotating about the silicon–carbon bond, their contribution to the second moment would be 5.4 gauss^2 plus a 2 gauss^2 contribution for internal broadening.

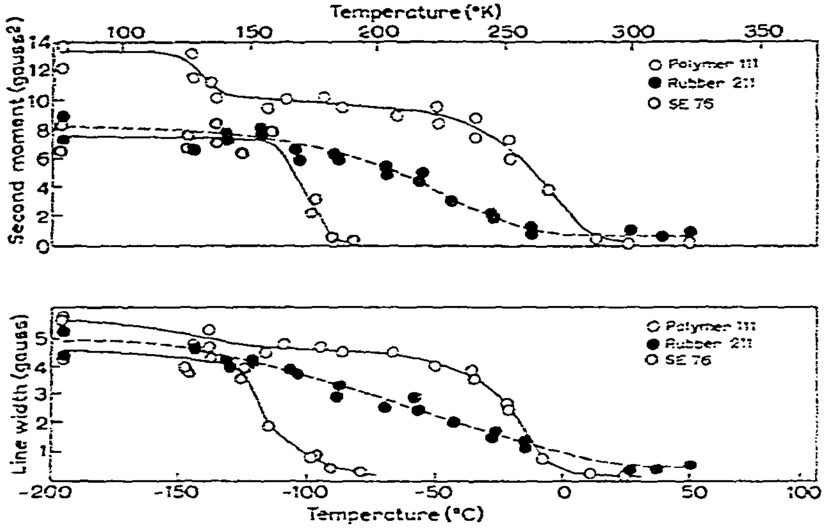


Fig. 8.

The contribution due to the N–CH$_2$CH$_2$–N group is hard to determine, but can be estimated from the value of 24.2 gauss^2 found in solid ethylenediamine. Hence:

$$[\Delta H_2]^2 = 30/44\ (7.4) + 14/44\ (24.2) = 12.7\ \text{gauss}^2$$

which agrees quite well with the observed value.

At —145°C there is a slight narrowing of the absorption curve and a decrease of second moment from approximately 13 gauss^2 to 10 gauss^2. There is no direct evidence from NMR as to what causes this narrowing. At —40°C a transition occurs which is similar to that found in the polysiloxanes at —110°C. At this temperature motion of the (CH$_3$)$_2$Si groups as well as translational motion of the chains must be present, as is evidenced by the fact that the line narrows to a value much smaller than that estimated for the intermolecular broadening contribution.

6. *Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane*

The two simplest organosilazane ring compounds, hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, were prepared by the reaction of dimethyldichlorosilane with ammonia according to the procedure given in *Inorg. Syn.*[9]. Nuclear resonance measurements were taken from —196°C to room temperature, and the results are shown in Figure 9. The values are seen to be slightly higher than those for silazane polymers. Because of the lack of sufficient crystallographic data, the broadening correction for the second moment is difficult to determine; however, Rochow and LeClair[1] have found that the correction in cyclic siloxanes can be as large as 3 gauss^2. This increase could account for the larger second moments.

One will note that the second moments for both species are essentially constant from —196°C to room temperature. This indicates that any motion other than C_3 reorientation of the methyl groups is "frozen out" in the crystal. As in the polymers, the spectra were simple bell-shaped curves with no appreciable structure.

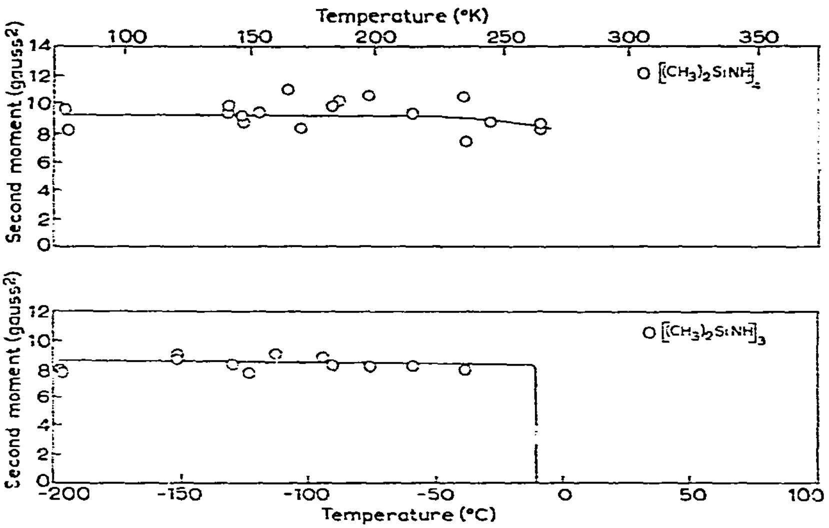


Fig. 9.

7. *Effects of methyl substitution on the nitrogen atoms*

Attempts have been made to polymerize nonamethylcyclotrisilazane[17]. So far little success has been achieved, for it seems that the cyclic compounds are far too stable[17]. The advantage in obtaining an *N*-methyl silazane is that cross-linking through the nitrogen atoms will be prohibited, and a linear polymer should result. Two methyl-substituted compounds were studied: the six-membered ring and a three-membered chain. The study concentrated upon the reorientation of the methyl groups bonded to the nitrogen atoms. We shall consider the three-membered chain, bis (methylamino)-dimethylsilane, first.

The compound contains four methyl groups, one bonded to each of the nitrogen atoms and two bonded to the central silicon atom. There are two amino hydrogen atoms, giving a total of 14 protons. It has been shown that the dipole–dipole contribution of the nitrogen atoms to the protons in the methyl groups is negligible. Hence if the methyl groups which are bonded to the nitrogen atoms are rigid, and the methyl groups bonded to the silicon are reorienting about the carbon–silicon bond, the second moment should be:

$$[\Delta H_2]^2 = 3/7\ (8.4) + 3/7\ (25.5) + 1/7\ (1.9) = 14.8\ \text{gauss}^2$$

using a 3.0 gauss² intermolecular broadening contribution. However, if all methyl groups are reorienting, the second moment should be:

$$[\Delta H_2]^2 = 6/7\ (8.4) + 1/7\ (1.9) = 7.5\ \text{gauss}^2$$

The experimental second moment at —196°C was found to be 9.0 ± 0.5 gauss². This is shown in Figure 10. This result tends to indicate that all the methyl groups are reorienting, for the broadening correction is probably underestimated rather than overestimated. At —140°C a rapid decrease in the second moment indicates melting of the compound.

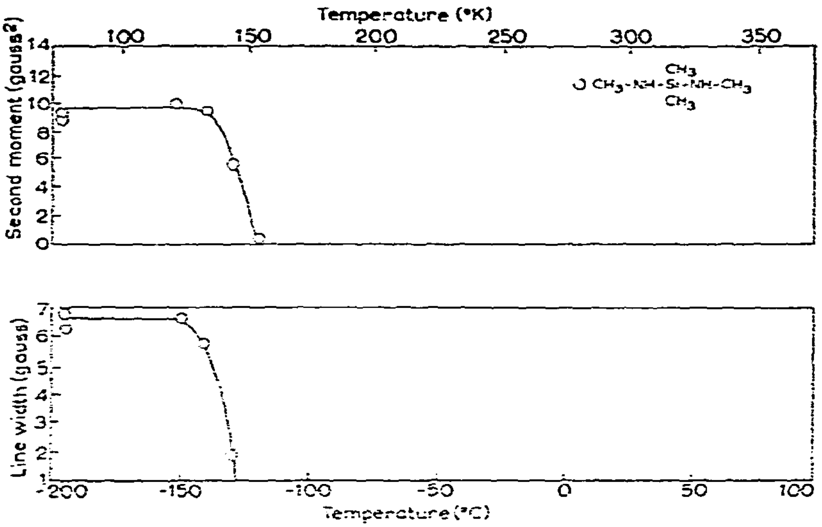


Fig. 10.

Spectra of nonamethylcyclotrisilazane were taken at —196° C. The second moment was found to be 9.6 ± 0.5 gauss². Again this is closer to the value calculated for reorientation of all methyl groups, 8.4 gauss², assuming a 3 gauss² broadening correction. The second moment for rigid nitrogen-linked methyl groups is calculated to be

$$\langle \Delta H_2 \rangle^2 = 2/3\ (8.4) + 1/3\ (25.5) = 14.1 \text{ gauss}^2$$

which is significantly higher than the experimental value.

CONCLUSION

The results of this work indicate that the degree of molecular motion in highly cross-linked organosilicon–nitrogen polymers is considerably less than that found in organosiloxane polymers. Two explanations can be given for this lack of internal motion. The first is that silicon–nitrogen compounds exhibit considerable $d\pi$–$p\pi$ interaction and that this results in a more rigid framework than in the analogous siloxanes. Just how large this "back-bonding" effect is will not be known until a linear silazane polymer is prepared. Second, the silazane polymers which were studied were considerably more cross-linked than the siloxanes. This high degree of cross-linking inevitably causes the formation of small rings which, in turn, inhibit the motion of the $(CH_3)_2Si$ groups about the silicon–nitrogen bond. In siloxane materials such as silicone rubber, where the degree of cross-linking is small (*i.e.*, approximately one link every 50 siloxane units) the configurational rings which may form are very large and would not hinder motion any more than in a linear siloxane. Recent work on highly cross-linked siloxanes by Huggins *et al.*[13] has shown that siloxane polymers which are highly cross-linked (*i.e.*, approximately one cross-link every 6 siloxane units) show a much more gradual "freezing out", similar to that found in the silazanes.

The results further indicate that the degree of crystallinity of the polymers has little or no effect on the low-temperature molecular motion. As in the siloxanes, it is found that the silazanes also have unusually free rotation of the methyl groups which persists down to the temperature of liquid nitrogen. Methyl rotation in organic polymers "freezes out" long before this temperature is reached. Freely rotating methyl groups have been related to the unusual properties of the silicones[1]. If it is true that rotating methyl groups take up more space than rigid methyl groups, the large volume swept out by the methyl groups will prohibit the chains from coming close together. This situation allows the chains to move rather independently from each other, whereas they would normally tangle. That this reorientation of the methyl groups also is found in polyorganosilazanes signifies that they too might exhibit only slightly poorer low-temperature properties, provided cross-linking could be eliminated. This situation is not changed by the presence of methyl groups attached to the nitrogen atoms, and this point is important because it appears that *N*-methyl substitution may be the solution to the preparation of linear polysilazanes.

ACKNOWLEDGEMENT

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SUMMARY

Intramolecular motion in some pure solid organosilazanes and in a number of solid dimethylsilazane and dimethylsilylamine polymers cross-linked by various methods was studied by the technique of broad-line nuclear magnetic resonance. Second moments and line widths are reported as a function of temperature from —196° to 50° and comparisons with corresponding polydimethylsiloxanes are made. The degree of internal motion in the silazane polymers is found to be considerably less than that in siloxanes between the temperatures of —120° to 0°; above and below that there is little difference. The low-temperature mobility is related to C_3 reorientation of methyl groups attached to silicon atoms, and the differences between silazanes and siloxanes are explained by increased $d\pi$–$p\pi$ interaction between silicon and nitrogen atoms in the former. The degree of crystallinity of the silazane polymers had little effect on the low-temperature intramolecular motion, but the kind and degree of cross-linking within the polymers had a marked effect.

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