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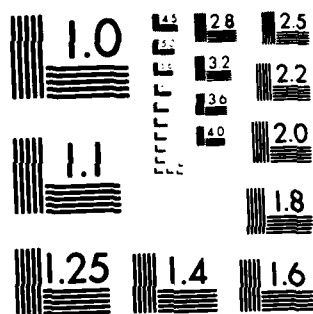
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by

Dietmar Seyferth and Gary H. Wiseman

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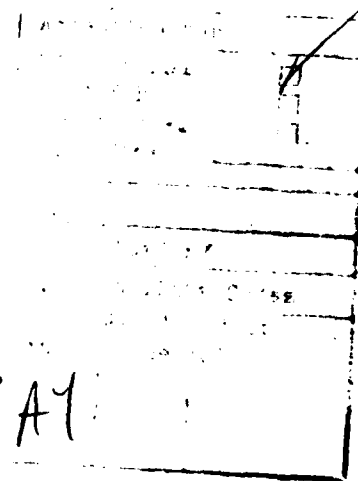
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CHAPTER 22

Silazane Precursors to Silicon Nitride

DIETMAR SEYFERTH AND GARY H. WISEMAN

Recently, we reported that the liquid silazane polymer* formed in the ammonolysis of dichlorosilane is an effective precursor to silicon nitride.⁽¹⁾ We anticipated that such a liquid precursor could have diverse uses, for example, for the production of oxidation-resistant fibers, to serve as a matrix material for other ceramic powders or fibers, or as an infiltration/coating agent for ceramic bodies. Coblenz, Wiseman, Davis, and Rice demonstrated that when carbon-carbon composites are coated with this polymer and pyrolyzed in an inert atmosphere, the resulting Si_3N_4 -coated bodies have noticeably improved oxidation resistance.⁽²⁾ The purpose of this chapter is to further detail our structural characterization of the polymer and to expand our earlier report⁽³⁾ concerning the development of other silazane precursors to Si_3N_4 or $\text{Si}_3\text{N}_4/\text{SiC}$.

The first report of the reaction of dichlorosilane with ammonia was that of Stock and Somieski some 60 years ago.⁽⁴⁾ They found that in benzene solution, ammonia and dichlorosilane reacted to yield a soluble silazane product which could be separated from the insoluble ammonium chloride by-product by filtration. Removal of the solvent at reduced pressure left a viscous oil which changed to a clear, hard glass after standing for one day at room temperature in the absence of air. Freezing point depression measurements of benzene solutions indicated that a polymer with a molecular weight of

* We use the term "polymer" in its broadest sense, that is, as a group of molecules whose structure can be generated through "repetition of one or a few elementary units" (P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 29), even though the polysilazanes under discussion are not high molecular weight materials as initially prepared.

Table 22.1 Characterization of H_2SiCl_2 Ammonolysis Products as a Function of Reaction Solvent

Solvent	Yield (%)	Molecular Weight	Integration of ^1H NMR, SiH/NH
Ether	64	583	3.8 ^a
Methylene chloride	79	659	3.0
Benzene	23	637	4.6
Toluene	31	—	4.3
Hexane	~0	—	—

^a Average structure based on $\text{SiH}/\text{NH} = 3.8$: $(\text{H}_2\text{SiNH})_{0.63}[(\text{H}_2\text{Si})_{1.3}\text{N}]_{0.37}$.

~350 had formed, and chemical analysis suggested the approximate composition $(\text{H}_2\text{SiNH})_x$, $x \approx 7.8$.

We found that the reaction between H_2SiCl_2 and NH_3 proceeds much better in more polar solvents, such as diethyl ether or dichloromethane (Table 22.1). In our experiments, the polymer formed in benzene has a higher molecular weight than that reported by Stock and Somieski (637 vs. 350–400). Our analytical results (Table 22.2) also indicate that the polymer does not have the "ideal" structure, $(\text{H}_2\text{SiNH})_x$, suggested by Stock and Somieski. The IR spectrum of the polymer shows the expected N—H (3400 cm^{-1}), Si—H (2170 cm^{-1}), and Si—H ($1040\text{--}830\text{ cm}^{-1}$), frequencies. As seen in Table 22.1, the ^1H NMR spectrum of the polymer shows an integrated intensity ratio of SiH/NH always greater than the "ideal" value of 2 for H_2SiNH , indicating again that the structure of the polymer is more complicated than Stock's analysis would suggest. We feel that these data can best be accommodated by considering that the polymer contains at least two different structural units, depending on the degree to which the N—H bonds

Table 22.2 Elemental Analysis of a Dichlorosilane Ammonolysis Product (Reaction Solvent, Diethyl Ether)

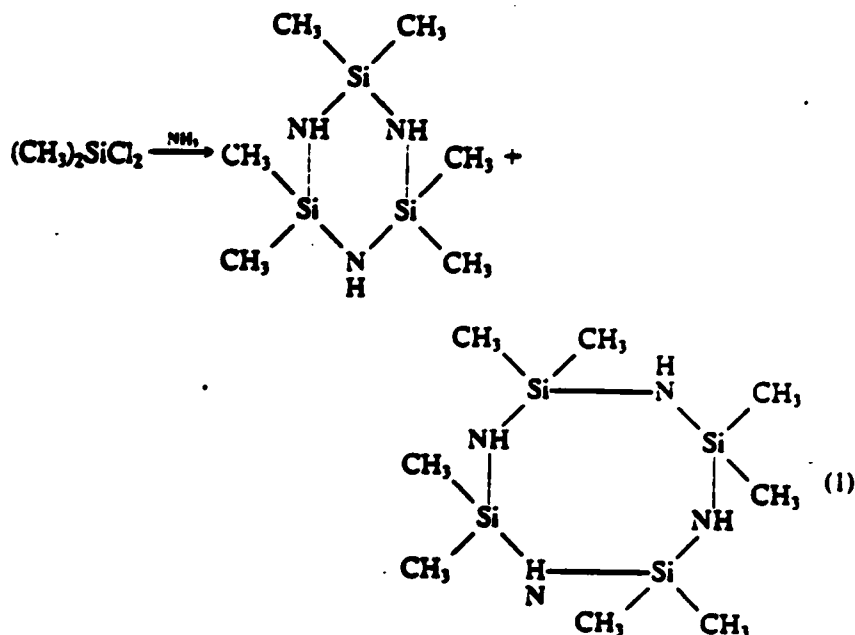
Product (%)	Calculated for H_2SiNH (%)	Found (%)	Calculated for $(\text{H}_2\text{Si})_{1.3}\text{N}$ (%)
Si	62.29	67.3 ^a	71.21
N	31.05	27.1 ^b	23.68
H	6.70	(5.6 ^c — by difference)	5.11

^a Average structure based on 67.3% Si = $(\text{H}_2\text{SiNH})_x[(\text{H}_2\text{Si})_{1.3}\text{N}]_y$; $x = 0.42$; $y = 0.58$.

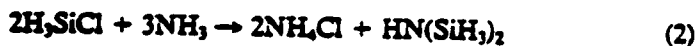
^b Average structure based on 27.1% N: $x = 0.46$; $y = 0.54$.

^c Average structure based on 5.6% H: $x = 0.31$; $y = 0.69$.

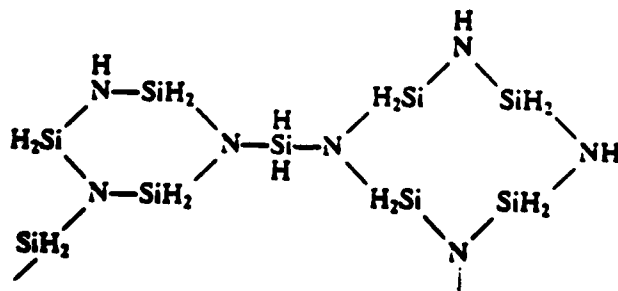
in NH_3 have been substituted. In most diorganodichlorosilanes [e.g., $(\text{CH}_3)_2\text{SiCl}_2$], the reaction with NH_3 produces stable cyclic silazanes (Eq. 1).⁽⁹⁾



However, in the case of the ammonolysis of H_3SiCl , the initially formed disilazane is unstable and disproportionates to give ammonia and a product with a trisubstituted nitrogen (Eqs. 2 and 3).⁽¹⁰⁾

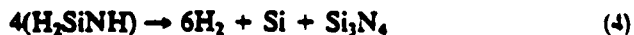


It is quite reasonable, then, that our initially formed polymer with the H_2SiNH structural unit may undergo similar disproportionation to give a more complicated structure with Si_3N as well as Si_2NH units. For example, such disproportionation of the linear polymer could result in a structure



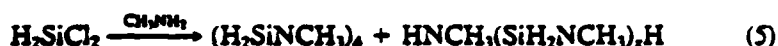
of type I, containing cyclic units with the gross composition $(\text{H}_2\text{SiNH})_3[(\text{H}_2\text{Si})_{1.3}\text{N}]_4$. At present, the exact constitution and structure of the oil obtained in the ammonolysis of H_2SiCl_2 is not known, and further studies aimed at its characterization are in progress.

We too have found that the H_2SiCl_2 ammonolysis product is not stable at room temperature or above. The oil produced initially increases in viscosity on standing at room temperature under nitrogen; after ~3 days, a hard glassy solid is formed. This process has a negligible rate at -30°C . As we reported,⁽¹⁾ thermogravimetric analysis (TGA) of the silazane oil (quartz sample boat, dry nitrogen or argon carrier gas) at a constant heating rate of $1^\circ\text{C}/\text{min}$ (room temperature to 1200°C) showed that the decomposition proceeded smoothly, beginning at about 50°C and ending at about 450°C , with a final polymer-to-ceramic yield of 69%. We followed this process by IR spectroscopy, stopping the heating at 100° intervals beginning at 200°C . When the initially liquid silazane oil was heated at 200°C for 1 hr, the IR spectrum of the resulting white brittle solid still contained a strong Si—H absorption, but had a significantly weaker N—H stretch. After 1 hr at 300°C , there was no change in the visual appearance of the sample or in the IR spectrum. After thermolysis at 400°C for 1 hr, the sample was a bright yellow solid whose IR spectrum showed an Si—H stretch of decreased intensity, as well as a further decreased N—H stretch. After 1 hr at 500°C , the sample was deep red in color and the IR spectrum showed no N—H and only a trace of Si—H absorption. In a separate pyrolysis experiment, the gases from the TGA unit were led into a mass spectrometer and their evolution was monitored as a function of temperature. We found that below $\sim 400^\circ\text{C}$, the major gaseous product was NH_3 , apparently formed by a disproportionation of silazane to produce ammonia and a more highly cross-linked polymer with more nitrogen atoms linked to three silicon atoms. This explains the reduction in the N—H stretch (IR) and correlates well with the known decomposition of other hydrosilazanes.⁽⁶⁾ At temperatures greater than 400°C , we found that the major gaseous product now was $\text{H}_2\text{SiNHSiH}_3$, which was identified by its parent ion at $m/z = 77$ and by comparison of the observed with the reported mass spectrum.⁽⁷⁾ Apparently, a second, more complex decomposition process occurs at higher temperatures and involves redistribution of the Si—H groups. Both of these reactions were previously observed in hydrosilazanes.⁽⁶⁾ In this experiment, we did not detect any small cyclic silazane oligomers, for example, $(\text{H}_2\text{SiNH})_3$ or $(\text{H}_2\text{SiNH})_4$, in the volatile pyrolysis products. The formation of low molecular weight rearrangement products ($\text{H}_2\text{SiNHSiH}_3$ and NH_3) accounts for our failure to achieve higher than 69% pyrolysis yields when, in theory, ~94% is possible if the pyrolysis had produced only H_2 , as in Eq. (4). With this information, further efforts



can now be focused on optimizing the pyrolysis yield.

We have also studied the reaction of H_2SiCl_2 with monomethylamine (CH_3NH_2) in the hope of producing a non-cross-linked polymer (the CH_3N group will not be reactive toward $\text{Si}-\text{Cl}$ groups). When a diethyl ether solution of H_2SiCl_2 (at 0°C) was treated with an excess of CH_3NH_2 ,⁽⁹⁾ filtration and vacuum distillation of the solvent left an oil in 90% yield. Gas chromatographic analysis of this oil showed that only one volatile product was present, which was identified as $(\text{H}_2\text{SiNCH}_3)_4$ by its elemental analysis, mass spectrum, ^1H and ^{29}Si NMR spectra, and IR spectrum. The molecular weight of the crude oil, however, was 323 [the molecular weight of $(\text{H}_2\text{SiNCH}_3)_4$ is 236], indicating that a nonvolatile component of higher molecular weight was present in addition to the volatile tetrasilazane. The volatile tetrasilazane was removed from the reaction product by vacuum distillation and the residual oil was identified as $(\text{H}_2\text{SiNCH}_3)_x$ (MW = 566 by cryoscopy in benzene, $x \approx 10$) by its ^1H and ^{29}Si NMR spectra, elemental analysis, and IR spectrum. The IR spectrum showed the presence of $\text{N}-\text{H}$ in trace concentration, suggesting that the polymer is probably a linear silazane, capped by $-\text{N}(\text{H})\text{CH}_3$ groups (Eq. 5).



where $x \approx 10$.

We found that this polymer could also be converted to a black ceramic product by heating it in the TGA apparatus at $5^\circ\text{C}/\text{min}$. The ceramic yield was 38%. The IR spectrum of this product showed only the broad absorption for Si_3N_4 ($1130-700\text{ cm}^{-1}$) and no absorptions for elemental carbon ($\sim 1600\text{ cm}^{-1}$). Further characterization is in progress.

Thus far, we have described products produced from the ammonolysis of H_2SiCl_2 . Since these oils have an approximately 1:1 ratio of $\text{Si}:\text{N}$, pyrolysis leads to a mixture of Si_3N_4 and elemental Si , despite the complicated rearrangements that occur. Unfortunately, the crystallization temperature of Si_3N_4 is lowered by the presence of free Si ,⁽¹⁰⁾ and this effect is clearly seen in our ceramic products. After pyrolysis at 1200°C for 12 hr under nitrogen, the grains have grown sufficiently to produce sharp X-ray diffraction peaks for Si_3N_4 . In practice, this grain growth probably would lead to a decrease in the mechanical strength of any body made by the pyrolysis of these polymers. For such high temperature applications, the presence of a second refractory phase might not only be acceptable, but also highly desirable to prevent this grain growth problem. In experiments directed toward this end, we began an investigation of the synthesis of alkyl(hydrido)silazanes, $(\text{RSiH}_2\text{NH})_2$, which presumably would produce a mixture of Si_3N_4 and SiC on pyrolysis.

As expected, the reaction of $\text{CH}_3\text{SiHCl}_2$ with anhydrous ammonia in diethyl ether produced a mobile oil in high yield (70–85%).⁽¹¹⁾ Elemental analysis and spectroscopic investigation of this oil suggested that it possessed a

cyclic structure, with no cross-linking through tertiary nitrogens. The molecular weight of the crude oil was 290 (Eq. 6).



where $x = 4.9$. Thermogravimetric analysis of the oil ($2^\circ\text{C}/\text{min}$, room temperature to 1000°C) produced a 20% yield of a black solid. This ceramic product was heated at 1200°C for 6 hr, but after this treatment it showed no X-ray diffraction peaks for Si_3N_4 or SiC . The IR spectrum of the product showed only a broad absorption from $1190\text{--}680\text{ cm}^{-1}$ (no band at 1600 cm^{-1}), indicating that again no free carbon seems to be present. Further microstructural characterization of this product is in progress.

Our characterization of the oil, $(\text{CH}_3\text{SiH}_2\text{NH})_x$, has been hampered by its thermal instability. Gas chromatography using low (150°C) injection port and detector temperatures indicated the presence of at least three compounds tentatively identified as $(\text{CH}_3\text{SiH}_2\text{NH})_3$, $(\text{CH}_3\text{SiH}_2\text{NH})_4$, and $(\text{CH}_3\text{SiH}_2\text{NH})_5$. We also studied the reactions of $(\text{CH}_3)_2\text{CHSiHCl}_2$, $(\text{CH}_3)_3\text{CSiHCl}_2$, and $\text{C}_6\text{H}_5\text{CH}_2\text{SiHCl}_2$ with NH_3 in diethyl ether. These reactions produced thermally stable cyclic silazanes, $(\text{RSiH}_2\text{NH})_x$, where $x = 3$ and 4. The results are summarized in Table 22.3.

We have also investigated the use of catalysts to effect the ring-opening polymerization of these cyclic silazanes before pyrolysis. The desired consequence of this polymerization was to prevent the distillation of the volatile oligomers [e.g., $(\text{CH}_3\text{SiH}_2\text{NH})_3$] that apparently caused the low pyrolysis yield. Krüger and Rochow showed that catalytic amounts of ammonium halides (e.g., NH_4Cl) cause the polymerization of hexamethylcyclotrisilazane, $((\text{CH}_3)_2\text{SiNH})_3$, to give nonvolatile oils or waxy, rubbery solids.⁽¹²⁾ In the TGA unit, we heated the crude $(\text{CH}_3\text{SiH}_2\text{NH})_x$ with 2.7% by weight NH_4Cl as a catalyst at 120°C for 14 hr (under nitrogen). The temperature then was increased at $2^\circ\text{C}/\text{min}$ to 1000°C . This increased the ceramic yield to 39%. This method of polymerization produces intractable (i.e., insoluble, very hard) solids that are unsuitable for our purposes. We are actively investigat-

Table 22.3 Alkyl(hydro)silazanes, $(\text{RSiH}_2\text{NH})_x$, Obtained by Ammonolysis of RSiHCl_2

R	$x = 3$ (%)	$x = 4$ (%)	$x = 5$ (%)
CH_3	28	54	17 (by NMR)
$(\text{CH}_3)_2\text{CH}$	64	36	—
$(\text{CH}_3)_3\text{C}^a$	100	—	—
$\text{C}_6\text{H}_5\text{CH}_2$	52	48	—

^a An unidentified, nonvolatile oil was also present in this reaction mixture, but no higher cyclic species were observed.

ing other methods for the polymerization of these low molecular weight cyclic silazanes, which will hopefully produce high-yield polymer precursors to $\text{Si}_3\text{N}_4/\text{SiC}$ mixtures.

ACKNOWLEDGMENT

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