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Synthesis and Polymerization of Cyclotetrasilazanes

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1,3,5,7-Tetrahydro-1,3,5,7-tetramethylcyclotetrasilazane and 1,3,5,7-tetrahydro-1,2,3,5,6,-7-hexamethylcyclotetrasilazane have been prepared by reaction of 1,3-dichloro-1,3-dihydro-1,3-dimethyldisilazane with ammonia and methylamine, respectively. The polymerization of these cyclotetrasilazanes by the action of catalytic quantities of potassium hydride and the pyrolysis of the resulting polymers in a stream of argon and in a stream of ammonia is reported. Comparisons are made with the polymers obtained by KH treatment of the ammonolysis product of CH_3SiHCl_2. © 1997 John Wiley & Sons, Ltd.

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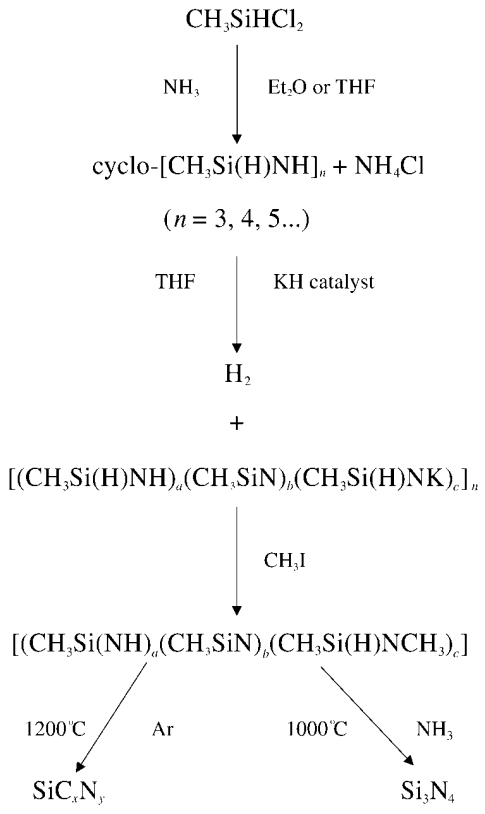
INTRODUCTION

The synthesis of polymeric silazanes the pyrolysis of which in an inert atmosphere gives silicon nitride/silicon carbide ('silicon carbonitride' when the pyrolysis residue is amorphous) has been of interest during the past 20 years, since the pioneering work of Verbeek.[1] A recent review gives excellent coverage of polysilazanes and their pyrolytic conversion to ceramic materials;[2] see also ref. 3. We became active in this area in the early 1980s.

In earlier reports we described the preparation of useful polymeric precursors for silicon carbonitride and silicon nitride by the procedure outlined in Scheme 1.[4–6] As shown, the ammonolysis of CH_3SiHCl_2 produces a mixture of cyclic oligomers of different ring sizes. While the composition of such mixtures may be studied by gas chromatography (GC), individual components, because of the lability of the system, cannot be isolated by GC or by distillation. The study of the subsequent polymerization of the CH_3SiHCl_2 ammonolysis product by the action of a catalytic quantity of potassium hydride (KH) is difficult because a mixture of cyclic oligomers is involved. A further complication is the formation of SiH_2CH_3 side groups, apparently by a ring-contraction process of the type reported by Klingebiel and his co-workers,[7,8] when the cyclo-$[CH_3Si(H)NH]_n$ product is left in contact with the NH_3- and NH_4Cl-containing reaction



Scheme 1

 CCC 0268–2605/97/100813–20 $17.50

mixture for some hours.[4–6]

In an attempt to gain a better understanding of the KH-catalyzed polymerization of the cyclo-$[CH_3Si(H)NH]_n$ mixture, we have prepared discrete cyclotetrasilazanes using known silazane chemistry and have studied their polymerization, as well as the pyrolytic conversion of the derived polysilazanes to ceramics.

RESULTS AND DISCUSSION

Preparation of the cyclotetrasilazanes

A known procedure for the preparation of cyclotetrasilazanes is the reaction of ammonia with 1,3-dihalodisilazanes.[9] A number of methods for the preparation of the latter have been reported.[10] The 1,3-dihalodisilazane required for our purposes was $[Cl(H)CH_3Si]_2NH$. A useful route to this disilazane had been reported by Pillot *et al*. In 1987,[11] with full details provided in 1994 (Eqn [1],[10] and this was used in the present study. 1,3-Dichloro-1,3-dihydro-1,3-dimethyldisilazane can be distilled (b.p. 39–41 °C/4 Torr), but it is thermally unstable, decomposing on standing at room temperature. It is extremely sensitive to atmospheric moisture and fumes on contact with air. Treatment of $[Cl(H)CH_3Si]_2NH$ with ammonia (NH_3) in diethyl ether at 0 °C gave the desired 1,3,5,7-tetrahydro - 1,3,5,7 - tetramethylcyclo - tetrasila - zane, **1** in 40–50% isolated yield (Eqn [2]) as a clear, mobile liquid. The average of three cryoscopic (benzene) molecular weight determinations (246 g mol^{-1}) agreed well with the value calculated for **1**, 236.6 g mol^{-1}. Once it has been isolated by distillation, this compound is stable, undergoing no alteration in composition on standing. A thermogravimetric analysis (TGA) experiment showed a rapid one-stage weight loss from 100 °C to 200 °C involving distillation of **1** with no residue.

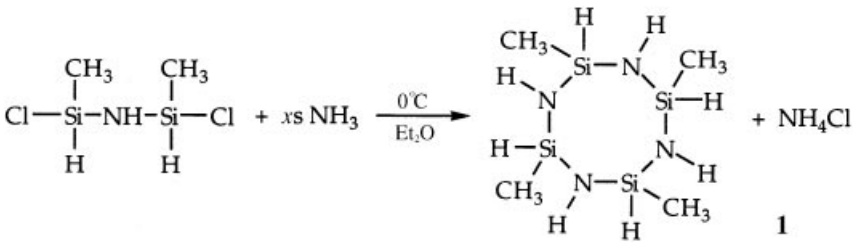
$$2\ CH_3\ Si\ HCl_2 + [(CH_3)_3Si]_2NH \xrightarrow{\Delta}$$

$$[Cl(H)CH_3Si]_2NH + 2(CH_3)_3SiCl \qquad [1]$$

The ^{1}H NMR spectrum of **1** (Fig. 1), like that of the cyclo-$[CH_3Si(H)NH]_n$ mixture obtained in the ammonolysis of CH_3SiHCl_2,[4–6] shows three major resonances: several CH_3Si peaks centered at δ 0.17, a broad NH peak centered at δ 0.9 and a somewhat broadened SiH peak at δ 4.64 ppm. There are some differences, however. The ^{1}H NMR spectrum of cyclo-$[CH_3Si(H)NH]_n$ shows three Si–H peaks in the δ 4.4–4.8 ppm region, while that of **1** shows only one which matches well with the center one of the three Si–H resonances of cyclo-$[CH_3Si(H)NH]_n$. Also, in the ^{1}H NMR spectrum of **1**, the CH_3Si resonance seems to be more distinct and less broad than that of cyclo-$[CH_3Si(H)NH]_n$. The CH_3Si resonance of **1** is composed of several closely spaced peaks, probably due to the presence of more than one geometric isomer. Figure 2 shows the four possible geometric isomers of **1**.

That the ammonolysis of $[Cl(H)CH_3Si]_2NH$ does not lead exclusively to **1** was shown by the ^{29}Si NMR spectrum of the crude reaction mixture before isolation of pure **1** (Fig. 3). In this spectrum a resonance at $\delta_{Si} -30$ to -32 ppm due to SiH_2[4–6] is apparent. The ^{29}Si NMR spectrum of **1** after its purification by distillation does not show this SiH_2 resonance. It is composed of at least five distinct peaks, indicative of the presence of geometric isomers.

Distilled **1** is stable on storage at room temperature in the absence of moisture for months as evidenced by its unchanged ^{29}Si NMR spectrum. Howver, contact of a 1 ml sample of distilled **1** with 0.5 g of NH_4Cl for 48 h at room temperature resulted in significant changes in the ^{29}Si NMR spectrum, including the appearance of a large SiH_2 resonance (Fig. 4), indicating the occurrence of the ring-contraction process noted earlier.



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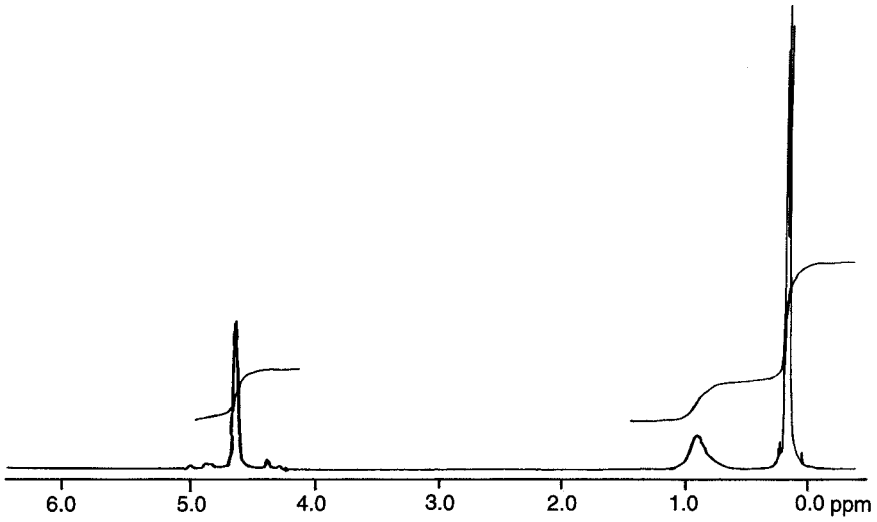


Figure 1 ^{1}H NMR spectrum of $(CH_3SiHNH)_4$.

The IR spectrum of **1** is unexceptional and essentially identical to that of cyclo-$[CH_3Si(H)NH]_n$, showing major absorptions at 3380 cm^{-1} (ν_{NH}), 3000–2800 cm^{-1} (ν_{CH}), 2120 cm^{-1} (ν_{SiH}), 1255 cm^{-1} (ν_{CH_3Si}), and broad, strong bands between 1200 and 1150 cm^{-1} (SiN framework vibrations).

Reaction of $[Cl(H)CH_3Si]_2NH$ with monomethylamine instead of ammonia gave a second cyclotetrasilazane, **2** (Eqn [3]) in 50–60% yield as a clear, mobile liquid, molecular weight 260 g mol^{-1} (cryoscopy in benzene) vs. a calculated value of 264.6 g mol^{-1}. Cyclosilazane **2** crystallized at temperatures below 0 °C, but

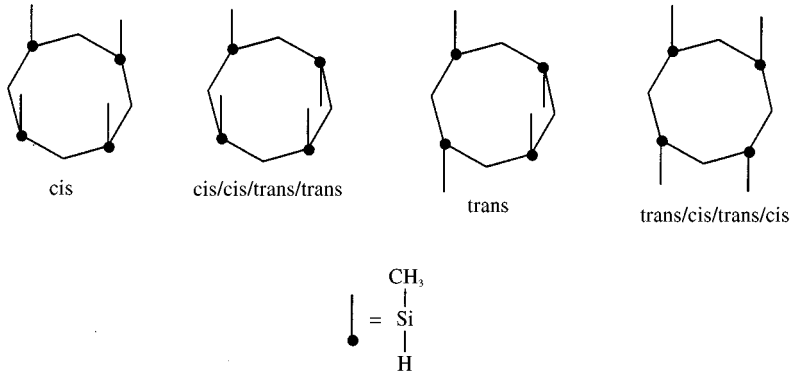
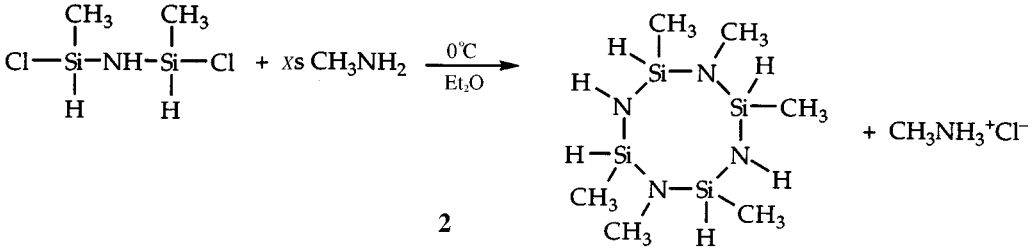


Figure 2 Geometric isomers of $(CH_3SiHNH)_4$.



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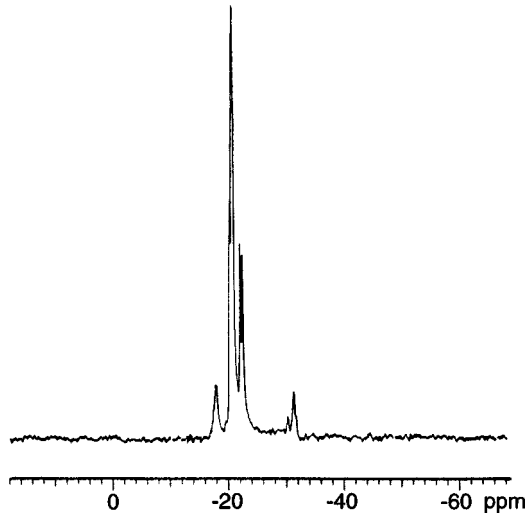


Figure 3 ^{29}Si NMR spectrum of the $(CH_3SiHNH)_4$ reaction mixture before distillation.

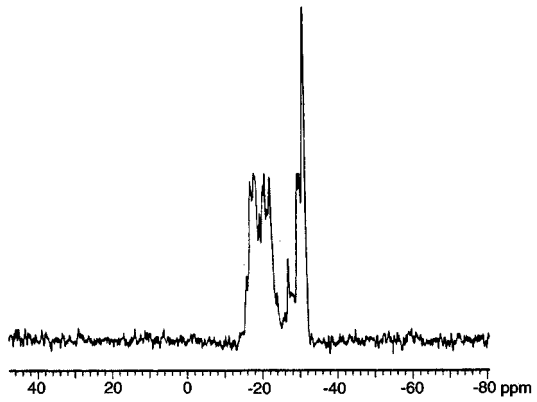


Figure 4 ^{29}Si NMR spectrum of the product of the reaction of $(CH_3SiHNH)_4$ and ammonium chloride.

attempts to obtain a crystal structure of this compound were unsuccessful. Arkles[12] had reported preparation of **2** in 1986 by a different but similar route, the ammonolysis of $[Cl(H)CH_3Si]_2NCH_3$.

There are 14 possible geometric isomers of **2** if there is no inversion at the NCH_3 sites, five if such inversion does occur. The NMR spectra of **2** indicate the presence of geometric isomers. The ^{1}H NMR spectrum of **2** shows four resonances: a broad multiplet at δ 0.1–0.4 ppm (CH_3Si), a broad, weak resonance at δ 2.4–2.6 ppm and a broad resonance at δ 4.5–4.7 ppm (SiH) (Fig. 5). Five resonances were observed in the ^{29}Si NMR spectrum of **2** at δ_{Si} −11, −14, −16, −18 and −20 ppm (Fig. 6).. The most intense of these, the one at −16 ppm, is split several times.

Preparation of polymers from the cyclotetrasilazanes

Most of the organosilicon preceramic polymers are of relatively low molecular weight (2000–10 000), so they are oligomers, not polymers. However, in the jargon of the field, which has become common usage, they are called polymers. The conversion of the CH_3SiHCl_2 ammonolysis product, cyclo-$[CH_3Si(H)NH]_n$, to material of higher molecular weight and greater molecular complexity as outlined in Scheme 1 is based on chemistry reported in a Monsanto patent (Eqn [4]).[13] Reaction of the potassium metal with the silylamine results in its conversion to KH, so the latter is the active catalyst. Therefore, in our work, we used KH rather than potassium metal.

$$2\,(CH_3)_2Si(H)NHR \xrightarrow{\text{catalytic K}} 2\,H_2 + \text{cyclo-}[(CH_3)_2Si(NR)]_2 \qquad [4]$$

Cyclotetrasilazane **1** has four sets of adjacent Si(H)–N(H) units. *If* all of these were to react in the sense of the reaction shown in Eqn [4], ring fusion via 1,3-cyclodisilazane rings would result in an array, as shown in Fig. 7, composed of linked cyclotetrasilazane rings. Such rings are not planar, so a flat sheet structure would not result. However, base-catalyzed dehydrogenative SiH/NH coupling to form Si–N single bonds is also a known process (Eqn [5]),[14–16] and both processes may be expected to take part in the polymerization of cyclo-$[CH_3Si(H)NH]_n$ and cyclotetrasilazanes **1** and **2**, giving a rather non-uniform structure.

$$\text{Si–H} + \text{N–H} \xrightarrow{\text{base}} H_2 + \text{Si–N} \qquad [5]$$

In the present investigation, the reaction solvent, THF, was loaded into a flask containing the KH catalyst. Subsequently, cyclotetrasilazane **1** was added dropwise by syringe and the reaction mixture was stirred under an inert atmosphere (argon or nitrogen) at room temperature or at reflux for varying lengths of time.

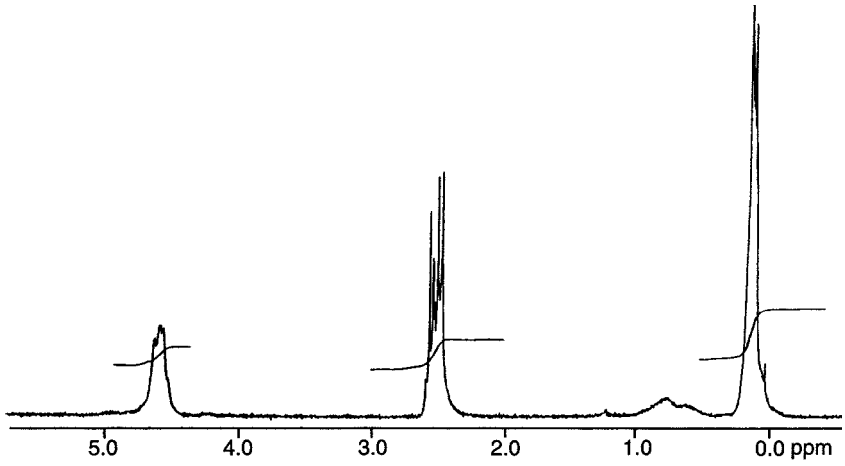


Figure 5 ^{1}H NMR spectrum of $[CH_3SiHN(CH_3)CH_3SiHN(H)]_2$.

Hydrogen was evolved during the reaction. Upon completion of the reaction, CH_3I was added to quench the residual reactive potassium silylamide sites in the polymer. After removal of the solvent, the residue was extracted with hexane, leaving behind KI. Evaporation of the hexane gave the polysilazane product in high yield as a white solid, which was soluble in all common non-protic organic solvents. These experiments are summarized in Table 1. The results of these experiments with cyclo-$[CH_3Si(H)NH]_4$ were very similar to the results obtained with the CH_3SiHCl_2 ammonolysis product, cyclo-$[CH_3Si(H)NH]_n$. The typical reaction (Expt. 1 in Table 1) was performed using 1 mol% KH catalyst in tetrahydrofuran (THF) at room temperature for 90 min. The white solid product had a cryoscopic molecular weight of 1090–1140 g mol^{-1} Cryoscopy in benzene was used in order to obtain some measure of comparison between the products of these experiments, although such measurements give no indication of components of higher molecular weight. Gel permeation chromatography has been used with only limited success in polysilazane molecular-weight determinations but did show that higher- molecular-weight components were present.[6] Its pyrolysis (TGA, to 950 °C at 10 °C min^{-1}) gave a ceramic residue uield of 79%, which showed that a more complex structure had been formed. Increasing the reaction time at room temperature (Expts 1 and 2) served to increase the molecular weight and the ceramic residue yield only slightly; the products were still soluble in common organic solvents. Increasing the concentration of the KH catalyst (Expts 5 and 6) increased molecular weight and ceramic residue yield in comparison with Expt 1. There was no benefit when the KH concentration was increased from 2 to 5%.

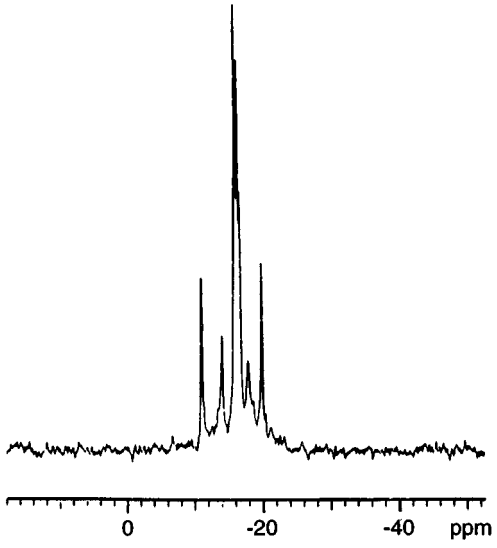


Figure 6 ^{29}Si NMR spectrum of $[CH_3SiHN(CH_3)CH_3SiHN(H)]_2$.

The use of solvents other than THF resulted in markedly different products (Expts 7–9). When diethyl ether, hexane and benzene were used, the product yields were lower and the products were sticky viscous liquids; their molecular weights were lower and their ceramic residue yields were markedly lower. The polysilazane obtained in the reaction carried out in diethyl ether could find application as a ceramic precursor when a liquid material is needed.

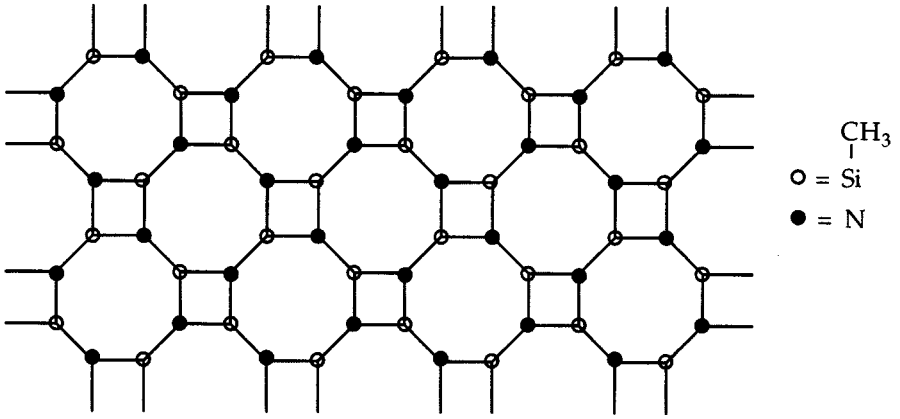


Figure 7 Proposed structure of polymer.

The ^{1}H NMR spectra of the polysilazanes obtained from **1** prepared in THF were used to obtain their composition in terms of component groups. There are three major resonances: a large, broad resonance between δ 0.1 and 0.4 ppm (CH_3–Si), a small, broad resonance at δ 0.8–1.0 ppm (N–H), another broad resonance at δ 4.6–4.9 ppm (Si–H) and a very weak signal at δ 2.5 ppm due to N–CH_3 groups introduced in the reaction of the living polymers with CH_3I (Fig. 8). This NMR spectrum is essentially identical to those of the polysilazanes produced by KH-catalyzed polymerization of the cyclic $[CH_3Si(H)NH]_n$ oligomer mixture. The inte-

Table 1. Results and conditions of the KH reactions of $(CH_3SiHNH)_4$

Expt no.	(%) KH	Solvent	Temp.	Time (h)	Yield (%)	Ceramic yield[a] (%)	MW (g/mol^{-1})[b]	Product
1	1	THF	RT	1.5	96	79	1090–1140	Solid
2	1	THF	RT	2.5	90	82	1580	Solid
3	1	THF	RT	3.0	95	84	1010–1175	Solid
4	1	THF	Reflux	0.5	90	82	940	Solid
5	2	THF	RT	1.5	90	86	1700	Solid
6	5	THF	RT	1.5	92	86	1590	Solid
7	1	Et_2O	RT	1.5	83	62	977	Thick oil
8	1	Hex	RT	1.5	89	34	430	Thick oil
9	1	Benzene	RT	1.5	71	51	720	Thick oil

[a] As determined by thermogravimetric analysis.
[b] Cryoscopy in benzene

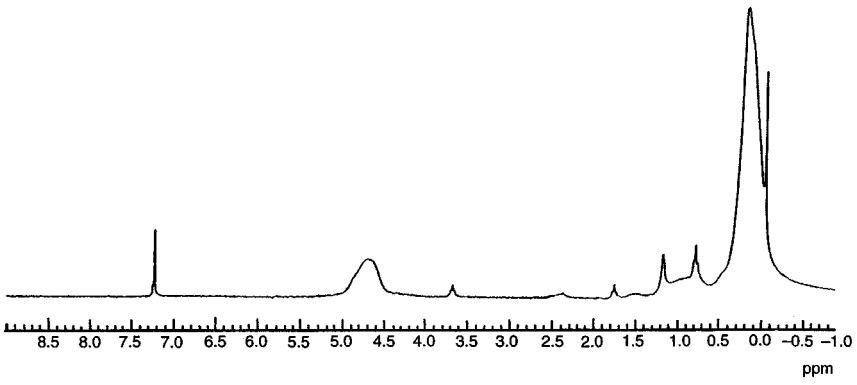


Figure 8 ^{1}H NMR spectrum of the $(CH_3SiHNH)_4$ derived polysilazane.

grated ^{1}H NMR spectrum allowed calculation of a composition $[(CH_3Si(H)NH)_a(CH_3SiN)_b]_n$ (neglecting the minor $CH_3Si(H)NCH_3$ units) with $a = 0.4$ and $b = 0.6$, which indicates that 60% of the silicon atoms are bonded to three nitrogen atoms, i.e. they are ring connection sites. The polysilazane obtained when the reaction was carried out in diethyl ether, a thick oil, was of the composition $[(CH_3Si(H)NH)_{0.53}(CH_3SiN)_{0.47}]_n$. In hexane the KH-catalyzed polymerization produced $[(CH_3Si(H)NH)_{0.59}(CH_3SiN)_{0.41}]_n$, also a thick oil. Thus, as expected, the non-solid polysilazanes have fewer ring connections.

The ^{29}Si NMR spectra of the polysilazanes obtained in the KH-catalyzed polymerization of **1** were not very informative. A typical ^{29}Si NMR spectrum is shown in Fig. 9. A broad, unresolved resonance between $\delta_{Si} -18$ and -26 ppm was observed. This is to be compared with the much sharper, more structured ^{29}Si NMR resonance group of **1** in the same range, -19 to -24 ppm. Unfortunately, these ^{29}Si NMR data give no evidence as to the 'structure' of the polysilazanes and leave the assumption of at least partial ring-fusion polymerization without support. The ^{29}Si NMR resonances of permethylated cyclosilazanes have been reported: δ_{Si} cyclo-$(Me_2SiNMe)_2$, 8.0; $(Me_2SiNMe)_3$, 0.62; $(Me_2SiNMe)_4$, 1.1 ppm.[17] In view of the relatively large difference between the ^{29}Si NMR resonances of the cyclodisilazane and those of the larger cyclosilazanes, we might have expected to see a downfield shift or a downfield resonance (vs. the ^{29}Si NMR resonance of **1**) representing the Si_2N_2 units in the polysilazane. Each silicon atom, however, would still be a member of an eight-membered ring. Each silicon atom of the CH_3SiN units would, as already noted, be bonded to three nitrogen atoms, which would result in an upfield shift of the ^{29}Si NMR resonances of **1** on going to the cross-linked polysilazane. Note in this connection the trend of δ_{Si} Me_3SiNMe_2, 6.52; $Me_2Si(NMe_2)_2$, -1.85; $MeSi(NMe_2)_3$, -16.80; $Si(NMe_2)_4$, -28.6 ppm.[18] Therefore the ^{29}Si NMR resonances of the polysilazane derived from **1** could well be in the same range as that of **1**, even if Si_2N_2 ring fusions were present. In view of these considerations, we are forced to the conclusion that the ^{1}H and ^{29}Si NMR spectra of the polysilazanes produced in the KH-catalyzed polymerization of cyclotetrasilazane **1** do not provide useful evidence concerning the exact nature of the dehydrogenative condensation processes taking place or of the connectivity between the cyclosilazane rings in the polysilazane.

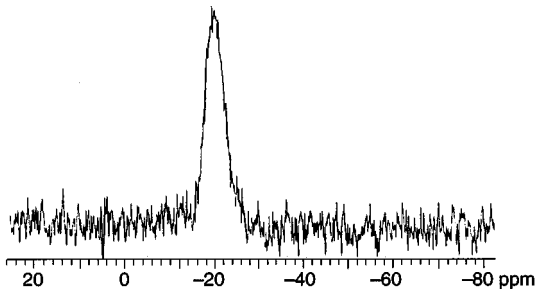


Figure 9 ^{29}Si NMR spectrum of the $(CH_3SiHNH)_4$-derived polyusilazane.

In whatever way the polymerization of **1** occurs, further experiments demonstrated that simple Si–H/N^-K^+ coupling can occur in reactions of **1**. Thus, treatment of a mixture of **1** and an excess of Et_3SiH with 2 mol% of KH in THF in the usual manner gave, after a CH_3I quench, a 69% recovery of Et_3SiH and a very viscous, cloudy oil as a residue. The ^{1}H NMR spectrum of the latter showed the presence of Et_3Si groups and integration of the ^{1}H NMR spectrum indicated a composition $(CH_3Si(H)NSiEt_3)_{0.42}$-$(CH_3SiN)_{0.58}$. In another experiment, a mixture of **1** and cyclo-$[(CH_3)_2SiNH]_3$(1:1 NH/NH ratio) was treated with 2 mol% KH in THF at room temperature. After the usual CH_3I quench, 55% of the originally charged cyclo-$[(CH_3)_2SiNH]_3$ was recovered by vacuum distillation. The white solid product that remained (ceramic residue yield only 57%) had a ^{1}H NMR spectrum whose CH_3–Si region showed the usual resonance at δ 0.4–1.0 ppm, but also a very sharp resonance at δ 1.0 ppm. The latter may be attributed to hexamethylcyclotrisilazane rings that had been incorporated into the polysilazane by N–H metallation followed by coupling with Si–H groups. The markedly decreased ceramic residue yield obtained on pyrolysis of this product is in agreement with this interpretation.

Cyclotetrasilazane **2** is not as highly functional in terms of adjacent Si(H)–N(H) units. As a consequence, rather harsh conditions, 19 h of heating with 5 mol% KH in refluxing THF, were required to obtain a material whose pyrolysis in argon to 950 °C (TGA) gave even a 64% ceramic residue yield. Table 2 summarizes the results of the experiments that were carried out with **2**. The products obtained ranged from viscous oils to sticky solids. All were soluble in organic solvents.

Table 2. Results and conditions of the KH reactions of $[CH_3SiHN(CH_3)CH_3$-$SiHN(H)]_2$

KH (%)	Solvent	Time (h)	Temp.	Yield (%)	Ceramic yield (%)[a]	Mol. wt. g/mol^{-1})[b]
1	THF	16	RT	69	14	300–400
2	THF	3	RT	80	17	470
1	THF	2.5	Reflux	80	21	400–450
1	THF	7.5	Reflux	68	47	610–655
2	THF	2.5	Reflux	93	24	500–600
5	THF	5	Reflux	90	49	600
		41	RT			
5	THF	19	Reflux	67	64	650–700

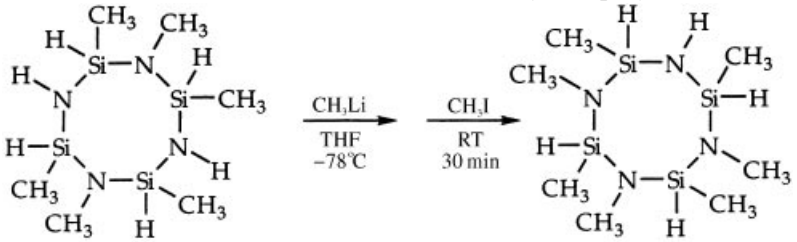
[a] As determined by thermogravimetric analysis.
[b] Cryoscopy in benzene.

In principle, if the KH-catalyzed process was that shown in Eqn [4], then the polymerization of **2** should give a ladder polymer in which the cyclotetrasilazane rings are linked via Si_2N_2 rings. However, as noted in that case of cyclotetrasilazane **1**, other condensation processes are possible, so such a unifom ladder polymer need not have been formed. NMR spectroscopy did not give useful information concerning these polymers, the ^{1}H NMR spectra showing broad resonances in the CH_3–Si region (δ 0.1–0.4 ppm), the CH_3–N region (δ 2.3–2.6 ppm), the Si–H region (δ 4.5–4.8 ppm), but not in the N–H region (in contrast to the polymers derived from **1**). The ^{29}Si NMR spectra showed a broad resonance at δ_{Si} -6 to -24 ppm.

Copolymerization of mixtures of cyclotetrasilazanes **1** and **2** was also investigated. Treatment of a mixture of one molar equivalent each of **1** and **2** with 1 mol% of KH in THF at reflux for 2 h, followed by a methyl iodide quench, gave a white solid in 84% yield. Pyrolysis of this product (TGA) left an 80% ceramic residue yield. It would appear that a reaction involving both cyclotetrasilazanes had occurred.

Since the experiments with cyclo-$[CH_3Si(H)NH]_4$ were inconclusive, leaving unresolved whether or not the polymerization of this cyclosilazane occurred via the process shown in Eqn [4] or that in Eqn [5] (or via both of these processes), we sought to answer this question by means of a model compound study. Conversion of **2** to the cyclotetrasilazane **3**, in which there is only one set of adjacent Si(H)–N(H) bonds, was effected as shown in Eqn [6]. A low reaction temperature was essential in order to avoid ring contraction processes of the intermediate silylamide anion.[7, 8]

Deprotonation of the N–H bond of **3** with one molar equivalent of KH in THF should give the respective cyclotetrasilazide anion. This species, if the process shown in Eqn [4] were operative, should give the coupled product **5**. On the other hand, if coupling via only a single Si–N bond had taken place, **6** would be the expected product if the reaction mixture had been quenched with CH_3I in order to methylate remaining amide anion sites. In view of the extensive methyl substitution of **3**, there should be considerable steric hindrance to the coupling of **3**-derived intermediates by either process. Also, since the KH-catalyzed polymerization is carried out at



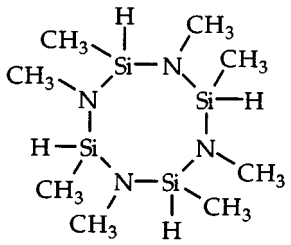
2 **3** [6]

room temperature or above, anionic rearrangements of the deprotonated **3** could occur. Nevertheless, a reaction of **3** with one molar equivalent of KH in THF at reflux for 75 min, followed by addition of CH_3I, was carried out. Two distillable, liquid products were obtained. One, not unexpectedly, was the permethylcyclotetrasilazane, **4**, in 25% yield. The second, higher-boiling product contained no N–H groups (by IR and ^1H NMR), but its ^1H and ^{29}Si NMR spectra and its elemental analyses did not allow us to distinguish between the presence of **5** or **6** or a mixture of the two.

Pyrolysis of the cyclotetrasilazane-derived polymers

The TGA (10 °C min^{-1} under argon) trace of the polysilazane prepared from cyclotetrasilazane **1** in Expt 3 (Table 1) is shown in Fig. 10. A slow 4–5 % weight loss during heating from 50 °C to around 500 °C was followed by a greater rate of weight loss between 550 °C and 650 °C, with no further weight loss to 960 °C. This behavior is very similar to that observed in TGA experiments with the polysilazane prepared in a similar manner from the ammonolysis product of CH_3SiHCl_2.

Bulk pyrolysis of the polysilazanes was effected in a stream of either argon or ammonia to 1000 °C in a tube furnace. They were further pyrolyzed in a stream of argon to 1500 °C until they were crystalline (Scheme 2). Typically, the ceramics produced in the pyrolysis of the polysilazane derived from **1** to 1500 °C in a stream of argon had an oveall composition (by wt) of 70–74% Si_3N_4 + 15–23% SiC + 5–11% C. As the ceramics formed at 1000 °C are amor-



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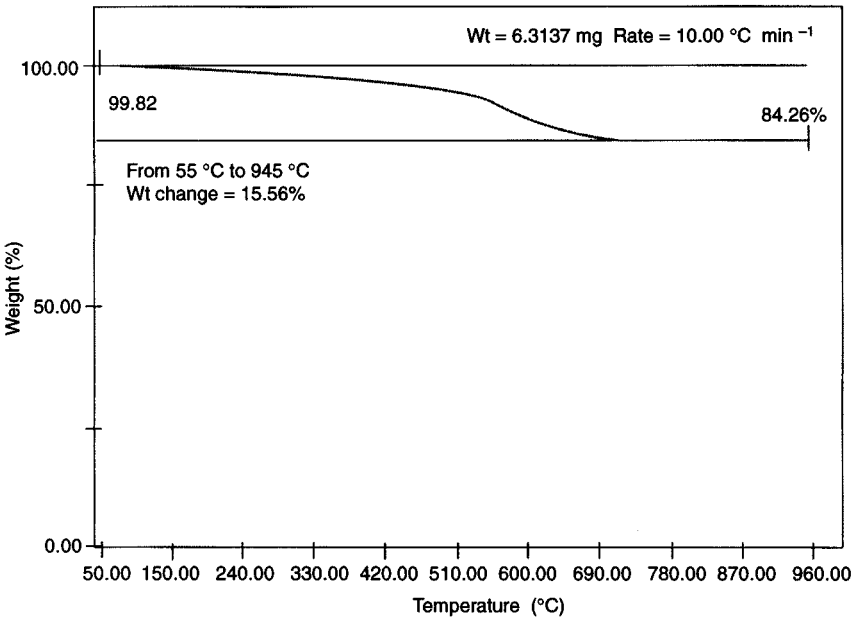
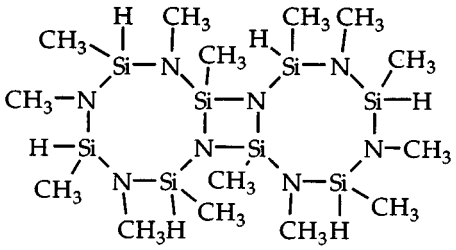


Figure 10 Thermogravimetric analysis of the $(CH_3SiHNH)_4$-derived polysilazane.



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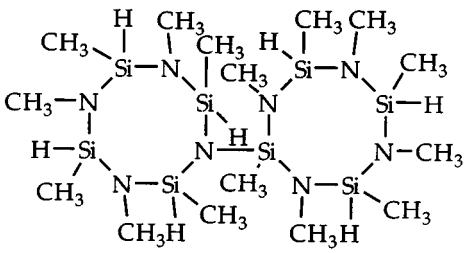

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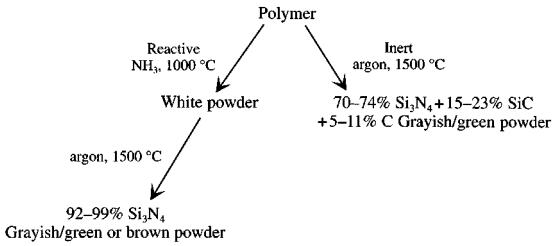
phous, no segregation into crystalline Si_3N_4 and SiC has occurred, so such compositions have no physical meaning. However, *if* Si_3N_4, SiC and free carbon were present, this is the composition that one would calculate from the elemental analysis, assuming that all N is combined with Si to Si_3N_4, any Si left over is combined with C to SiC. That generally leaves some residual carbon. The analysis of such a sample after it has been heated to 1500 °C to induce crystallization of Si_3N_4 and SiC generally is not greatly different from that calculated for the 1000 °C sample. The ceramics produced in the pyrolysis of polysilazane **1** to 1000 °C in a stream of ammonia and then to 1500 °C in a stream of argon had an overall composition (by wt) of 92–99% Si_3N_4. The remainder of the samples was usually composed of excess silicon or carbon.



Scheme 2 Pyrolysis of polysilazanes.

Several of the ceramics were examined by X-ray powder diffraction (XRD), diffuse reflectane FTIR (DRIFT) and solid-state ^{29}Si NMR spectroscopy.[6] The XRD pattern of a ceramic sample that had been pyrolyzed in a stream of ammonia to 1000 °C, and then in a stream of argon to 1500 °C, is shown in Fig. 11. This ceramic had a

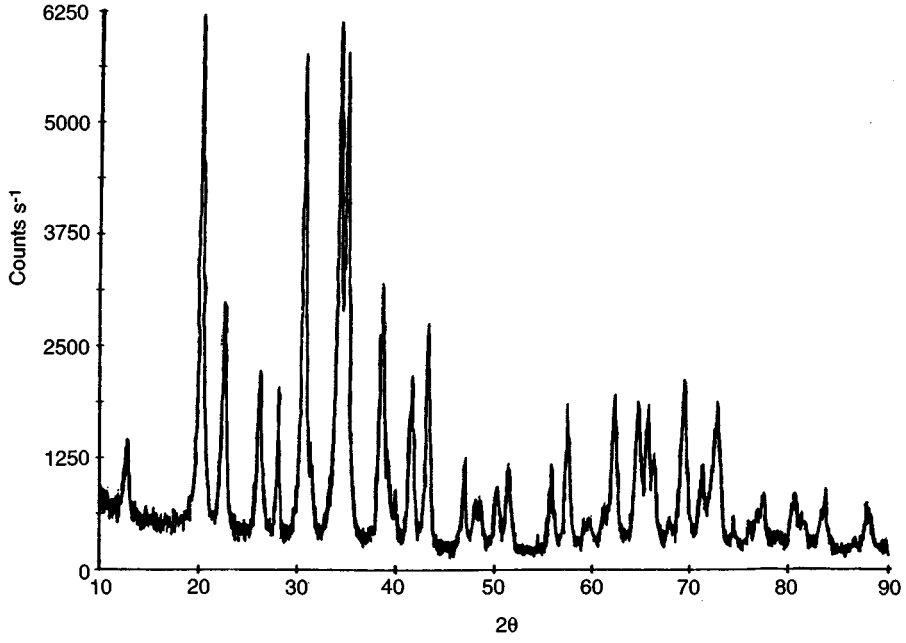


Figure 11 X-ray powder diffraction pattern of the ceramic (formed by pyrolysis in NH_3) from the $(CH_3SiHNH)_4$-system polysilazane.

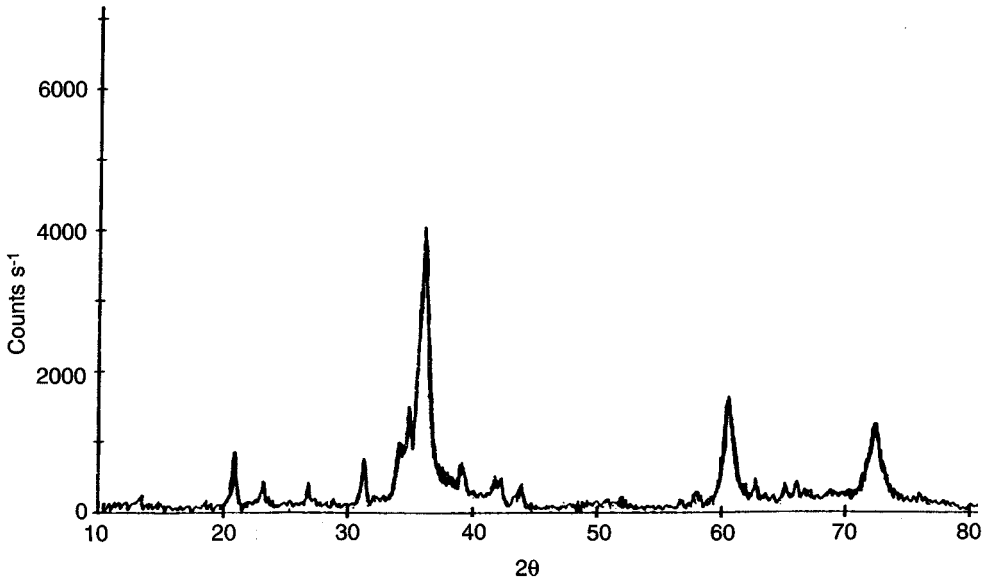


Figure 12 X-ray powder diffraction pattern of the ceramic (formed by pyrolysis in argon) from the $(CH_3SiHNH)_4$[system polysilazane.

composition (elemental analysis, by wt) of 93% Si_3N_4 + 2% SiC + 5% Si. The XRD pattern shows that the only major crystalline phase present is α-Si_3N_4. Pyrolysis of the same polysilazane sample to 1500 °C in a stream of argon gave a ceramic with a composition (elemental analysis, by wt) of 71% Si_3N_4 + 20% SiC + 9% C. Figure 12 shows the XRD pattern of this ceramic. The major peaks are due to β-SiC, although it is only a minor component of the ceramic, while the small peaks represent α-Si_3N_4.

Figure 13 shows the DRIFT spectra of a polysilazane sample which had been pyrolyzed in a stream of ammonia to 1000 °C (Fig. 13a) and then in a stream of argon to 1500 °C (Fig. 13b). After pyrolysis to 1000 °C, possibly due to residual N–H, C–H and Si–H bonds, small bands above 1000 cm^{-1} are observed, and a broad band is centered at 1000–800 cm^{-1}. After further pyrolysis to 1500 °C in a stream of argon (Fig. 13b) these bands are no longer observed, and there are now strong, distinct bands at 1050, 950 and 850 cm^{-1}. Figure 14 shows the DRIFT spectra of the same polysilazane sample pyrolyzed to 1000 °C in a stream of argon (Fig. 14a) and then to 1500 °C (Fig. 14b) also in argon. As with the previous sample, there are still bands present in Fig. 14(a). After further pyrolysis to 1500 °C, these bands are no longer apparent and there is one distinct band centered at 960 cm^{-1}

One of the polysilazanes (that derived from **1**) was used to produce two ceramic bars, as described in the Experimental section. They were

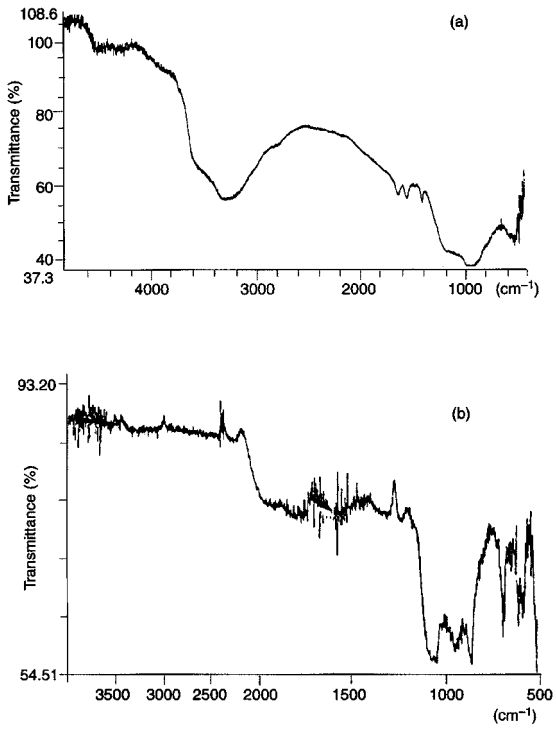


Figure 13 DRIFT spectra of the ceramic from the $(CH_3SIHNH)_4$-system polysilazane: (a) formed by pyrolysis in NH_3 to 1000 °C; (b) as in (a), then pyrolyzed in argon to 1500 °C.

each pyrolyzed to 1000 °C, one in a stream of argon and the other in a stream of ammonia. Both bars retained their shape, did not bloat or crack, and could not be broken by hand. The bar which had been pyrolyzed in a stream of argon was black, while the bar which had been pyrolyzed in a stream of ammonia was white. Table 3 gives the dimensions and densities of the bars before and after the pyrolyses. Both bars showed about a 20% reduction in weight, length, width and height; this is comparable to the loss upon pyrolysis of a bulk powdered sample of the polysilazane. The density of each bar had increased from 1.07 to 1.76 cm^{-3} (NH_3 pyrolysis) and from 1.06 to 1.94 $g\,cm^{-3}$ (argon pyrolysis).

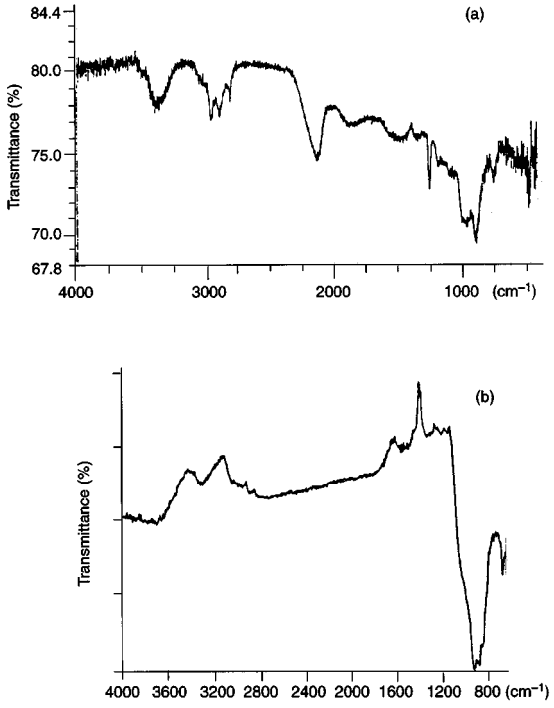


Figure 14 DRIFT spectra of the ceramic from the $(CH_3SiHNH)_4$-system polysilazane: (a) formed by pyrolysis in argon to 1000 °C; (b) as in (a), then pyrolyzed in argon to 1500 °C.

CONCLUSION

We have shown that a discrete monomeric compound, $[CH_3SiHNH]_4$, can be prepared which produces polysilazanes via KH-catalyzed reactions; these monomers are similar to those produced from the mixture of cyclic $(CH_3SiHNH)_n$ oligomers. Pyrolysis of the polysilazanes produced high yields of mixed Si_3N_4/SiC/C ceramic materials as well as ceramic materials which consist of almost pure Si_3N_4. Monolithic ceramic bodies have also been prepared.

EXPERIMENTAL

General comments

All reactions and manipulations were performed under a prepurified nitrogen or argon atmosphere using standard Schlenk techniques, or a nitrogen-filled Vacuum Atmospheres drybox. Tetrahydrofuran (THF), diethyl ether, toluene and benzene were distilled under nitrogen from sodium benzophenone ketyl. Hexane was distilled under nitrogen from $LiAlH_4$. All chlorosilanes were purchased from Petrarch Systems, Inc., or Silar, Inc., and distilled from magnesium chips before use. Methylamine was purchased from Matheson, Inc., and used as received. Anhydrous ammonia was purchased from Matheson, Inc., and dried by passing through a 3-ft (91.4-cm) KOH tower. Potassium hydride (KH) was purchased from Alfa as a

Table 3. Dimensional analysis of the ceramic bars

	NH_3			Argon		
	Before pyrolysis	After pyrolysis	Retention (%)	Before pyrolysis	After pyrolysis	Retention (%)
Weight (g)	3.0371	2.4765	82	3.0190	2.4194	80
Length (mm)	37.5	29.8	80	38.0	27.5	72
Width (mm)	5.90	4.72	80	5.84	4.56	78
Height (mm)	12.87	10.1	78	12.88	9.96	77
Density ($g/cm^{\times 2}$)	1.07	1.76	—	1.06	1.94	—

20–25 wt% slurry in mineral oil. This was filtered in the drybox and the KH was washed with hexane until the oil was completely removed. The KH was dried on a fritted funnel and then stored in the drybox without further purification. Methyl iodide (CH_3I) was distilled under nitrogen from P_2O_5.

Proton NMR spectra were obtained using either a Bruker WM-250 or a Varian XL-300 spectrometer operating at 250 or 300 MHz, respectively, using CDCl(3/$CHCl_3$ as the reference at 7.24 ppm downfield from tetramethylsilane. ^{29}Si NMR spectra were obtained using a Varian XL-300 spectrometer operating at 59.59 MHz in $CDCl_3$ with 0.05 M $Cr(acac)_3$ (acac = acetylacetonate) as a relaxation reagent. Tetramethylsilane (at 0.00 ppm) was used as an external standard. As indicated in the experiments below, some ^{29}Si NMR spectra were obtained using a DEPT[19, 20] pulse sequence. Infrared spectra were obtained using either a Perkin–Elmer Model 1430 ratio recording infrared spectrophotometer or a Perkin–Elmer model 1600 FTIR spectrophotometer, and are referenced to polystyrene film.

Thermogravimetric analysis (TGA) of samples was performed using a Perkin–Elmer TGS-2 system under a 40 $cm^3\,min^{-1}$argon flow. All samples were heated from 50 to 950 °C at 10 °C min^{-1}. TGA yields are then reported as the percentage weight that the sample retained after the heating cycle was complete.

Pyrolyses to 1000 °C (under Ar or NH_3) were performed using a Lindberg model 59344 tube furnace equipped with a Eurotherm model E5 controller and a quartz tube. Fused silica boats were used to contain the polymer in the quartz tube. For pyrolyses conducted under Ar, the following temperature program was used: 25 to 550 °C at 10 °C min^{-1}, hold at 550 °C for 0.5 h, 550 to 1000 °C at 10 °C min^{-1}, hold at 1000 °C for 1 h. For pyrolyses conducted under NH_3, the following temperature program was used: 25 to 550 °C at 6 °C min^{-1}, hold at 550 °C for 0.5 h, 550 to 1000 °C at 6 °C min^{-1}, hold at 1000 °C min^{-1} for 1 h. In both the pyrolyses under NH_3 and under Ar, an initial furnace purge of at least 300 $cm^3\,min^{-1}$ was run for 15 to 30 min after the samples were introduced into the furnace, to ensure removal of oxygen before heating. The gas flow was then decreased and a flow of 100 $cm^{-3}\,min^{-1}$ was used during the pyrolysis and subsequent cooling of the sample. Following pyrolysis, all bulk samples were placed in vials and immediately purged with argon.

Pyrolyses to 1500 °C under argon were performed using a Lindberg model 59545 tube furnace equipped with a Eurotherm model E5 controller and a mullite tube. Samples were placed in a graphite boat on a six-inch (5.2-cm) Al_2O_3 D-tube inside the mullite tube. The following temperature program was used for all samples pyrolyzed to 1500 °C: 25 to 1000 °C at 10 °C min^{-1}, hold at 1000 °C for 1 h, 1000 to 1500 °C at 10 °C min^{-1}, hold at 1500 °C for 5 h. The furnace was initially purged with Ar for at least 0.5 h before the sample was introduced, then purged for an additional 0.5 h before pyrolysis was begun. Following pyrolysis, all ceramic samples were placed in vials and immediately purged with argon.

Diffuse reflectance FTIR spectra (referred to as 'DRIFT' in the following experiments) were obtained on a Perkin–Elmer model 1600 FTIR spectrophotometer. Samples were prepared by physically grinding (in an agate mortar and pestle) KBr powder together with a few milligrams of ceramic powder which had been first ground with an agate mortar and pestle.

X-ray powder diffraction data were obtained on ceramic samples (pyrolyzed to 1500 °C for 5 h) using a Diano generator with Cu Kα (λ = 1.5418 Å) radiation and a nickel filter. A 2θ range of 20–80° was scanned for each sample.

Ceramic analyses were performed by Galbraith Laboratories, Knoxville, TN, USA. The calculated ceramic compositions were made with the assumption that all of the nitrogen, silicon, and carbon present in the ceramic were accurately accounted for in the elemental analyses. This was not necessarily the case, as often the analyses added up to less than 99%. SiC and Si_3N_4 ceramics are quite difficult to analyze for silicon and we have not been able to obtain totally reliable analyses on such materials. Silicon analyses of polymer samples also appeared to be of doubtful reliability.

In the following experimental discussion, 'trap-to-trap' distillation at 25 °C and 0.01–0.03 mmHg was used to distill solvents from the reaction mixtures into a trap cooled by liquid nitrogen.

Reaction of methyldichlorosilane with hexamethyldisilazane[10, 11]

A 1 L, three-necked, round-bottomed flask equipped with a stir-bar, a reflux condenser, a gas

inlet tube, a glass stopper and a septum was flame-dried under argon. The apparatus was charged with 126 mL (1.21 mol) of CH_3SiHCl_2 and 64 mL (49.53 g, 0.307 mol) of $[(CH_3)_3Si]_2NH$. The reaction mixture was heated at a mild reflux for 6 h. (After several minutes of reflux, the solution became cloudy.) The solution was cooled to room temperature overnight and filtered through a Schlenk frit to give a slightly cloudy solution. The excess chlorosilanes were removed from the solution by trap-to-trap distillation to leave a cloudy liquid. The product, $[CH_3Si(H)Cl]_2NH$, was distilled at 4 mmHg/39–41 °C (36.31 g, 0.2085 mol, 68% yield). The product was not sufficiently stable for prolonged periods at room temperature to permit elemental analysis.

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.59 (d, J=2 Hz, 6H, $SiCH_3$), 1.86 (broad, 1H, NH), 5.13 ppm (q, J=2 Hz ^{2}H, SiH). ^{29}Si NMR (59 59 MHz, $CDCl_3$/$(CH_3)_4Si$): δ_{Si} −4.62 ppm (s). IR (thin film, cm^{-1}): 3360 (vs), 3125 (s), 3050 (s), 2970 (s), 2905 (sh), 2200 (vs), 1640 (w), 1585 (w), 1410 (s), 1260 (vs), 1205–1160 (broad, vs), 1100 (m), 1050 (sh), 975–940 (broad, vs), 910–830 (broad, vs), 810 (s), 760–750 (broad, vs), 700 (w), 680 (w), 635 (w). Molecular weight (cryoscopy in C_6H_6): 170–180 g mol^{-1}. Calcd: 174 g mol^{-1}.

Reaction of $[CH_3Si(H)Cl]_2NH$ with ammonia

A 1 L, three necked, round-bottomed flask equipped with a dry ice/acetone condenser, a septum and an overhead mechanical stirrer was flame-dried and purged with argon. The apparatus was charged with 500 mL of diethyl ether and 10 mL (10.75 g, 62.86 mmol) of $[CH_3Si(H)Cl]_2NH$ and cooled to 0 °C in an ice bath. Anhydrous ammonia was bubbled through an 8-inch (~20-cm) stainless-steel needle into the solution until an excess was observed on the −78 °C condenser. Immediately upon addition of the ammonia, a salt precipitated. The reaction mixture was warmed to room temperature overnight and then filtered in the drybox. The ammonium chloride precipitate was washed with two 50-mL portions of diethyl ether. The ether was removed by trap-to-trap distillation and the product $[CH_3Si(H)NH]_4$, **1**, was distilled at 1.1 mmHg/57–59 °C (6.491 g, 27.43 mmol, 40%).

Analysis: Calcd for $C_4H_{20}N_4Si_4$: C, 20.31; H, 8.52; N, 23.68%. Found: C, 20.12; H, 8.46; N, 23.29%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.17 (m, 12H, $SiCH_3$), 0.90 (broad, 4H, NH), 4.64 (m, 4 H, SiH ppm). ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4Si$): δ_{Si} −22.8, −22.3, −21.2, −21.0, −20.6 ppm (all s). IR (thin film, cm^{-1}): 3380 (s), 2960 (s), 2900 (m), 2800 (vw), 2120 (vs), 1530 (w), 1410 (m), 1255 (vs), 1200–1150 (broad, vs), 1050 (w), 960–860 (broad, vs), 800 (s), 770 (sh), 730 (s), 610 (w). Molecular weight (cyroscopy in benzene): 230–265 g mol^{-1} Calcd. 236.6 g $mol.^{-1}$.

Reaction of $[CH_3Si(H)Cl]_2NH$ with monomethylamine

The apparatus described in the previous experiment was charged with 650 mL of diethyl ether and 24.83 g (142.5 mmol) of $[CH_3Si(H)Cl]_2NH$ and cooled to 0 °C in an ice bath. Monomethylamine was bubbled through an 8-inch (~20 cm) stainless-steel needle into the solution until an excess was observed on the −78 °C condenser. Immediately upon addition of the monomethylamine, a salt precipitated. The reaction mixture was washed with two 50-mL portions of diethyl ether. The ether was removed by trap-to-trap distillation and the product $[CH_3Si(H)N(CH_3)CH_3SiHNH]_2$, **2**, was distilled at 0.03 mm Hg/44–46 °C (9.84 g, 37.19 mmol, 52%).

Analysis: Calc'd for $C_6H_{24}N_4Si_4$: C, 27.73; H, 9.14; N, 21.17%. Found: C, 27.72; H, 9.14; N, 21.10% H NMR (250 MHz, $CDCl_3$; δ 0.15 (d, J=3.6 Hz, 12H, $SiCH_3$), 0.86 (broad, 2H, NH), 2.46–2.56 (m, 6H, NCH_3), 4.56 ppm. (q, J=3.6 Hz, SiH). ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4Si$/DEPT): δ_{Si} −11 to −21 ppm (complex m). IR (thin film): 3390 (s), 2960 (vs), 2930 (sh), 2890 (vs), 2810 (s), 2125 (vs), 1465 (m), 1430 (sh), 1260 (s), 1410 (m), 1255 (vs), 1200–1150 (broad, vs), 1100–1050 (broad, vs), 1020 (sh), 970–850 (broad, vs), 800 (s), 760 (s), 735 (s), 620 (w). Molecular weight (cryoscopy in benzene): 240–275 g mol^{-1}. Calcd: 264.6 g mol^{-1}.

Reaction of $[CH_3Si(H)NH]_4$, 1, with 1 mol% KH in THF at room temperature

A 50-mL, three-necked, round-bottomed flask equipped with a gas inlet tube, a reflux con-

denser, a glass stopper, a stir-bar, and a septum was flame-dried under argon. (This will hereafter be termed the 'standard polymerization apparatus'). This set-up was charged with 0.02 g (0.499 mmol) of KH in the drybox. The apparatus was connected to a Schlenk line (under argon) equipped with an oil bubbler and then charged with 20 mL of THF. The mixture was stirred for 10 min. By syringe, 1.978 g (8.36 mmol) of $[CH_3Si(H)NH]_4$ was added to the catalyst over 30 min. Gas evolution was observed. The reaction mixture was stirred for an additional 90 min and then CH_3I (0.20 mL, 3.23 mmol) was added. An immediate white precipitate formed. The reaction mixture was stirred for an additional 30 min at room temperature and then the solvent was removed by trap-to-trap distillation. The residue was extracted with 15 mL of hexane and the resulting mixture was centrifuged to precipitate the KI. The supernatant solution was cannulated into a 100-mL one-necked flask which had been flame-dried under argon. The hexane was removed by trap-to-trap distillation (this will hereafter be termed the 'standard polymer work-up') to leave a white solid weighing 1.899 g (96% yield based on the weight of the cyclotetrasilazane used). The product was soluble in THF, hexane, $CHCl_3$, CCl_4 and benzene (henceforth, a solid that is soluble in these solvents is termed 'soluble').

Analysis: C, 19.17; H, 6.96; N, 23.95; Si, 44.29% ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 7.0H, $SiCH_3$, 0.80–0.95 (broad, 1.0H, NH), 4.6–4.9 ppm (broad, 1.0H, SiH). Integration established the composition $(CH_3SiHNH)_{0.43}(CH_3SiN)_{0.57}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/DEPT): δ_{Si} -18 to -24 ppm (broad).

IR (CCl_4, cm^{-1}): 3400 (w), 2960 (m), 2890 (vw), 2125 (m), 1580 (sh), 1565 (s), 1555 (m), 1405 (vw), 1260 (s), 1190–1140 (broad, m), 1020–970 (broad, s), 910 (vs), 810 (vs), 800–750 (broad, vs), 610 (vw).

Molecular weight (cryoscopy in benzene): 1090–1140 g mol^{-1}. Ceramic residue yield (by TGA): 79%.

Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.788 g of the white solid produced 0.620 g (78%) of a black ceramic foam. Black ceramic analysis: C, 14.95; H, 0.66; N, 28.66; Si 54.69% (Σ 98.96%). A 0.438 g sample of the above ceramic was pyrolyzed in a stream of argon to 1500 °C and 0.394 g (90%) of a greenish ceramic was obtained. Greenish ceramic analysis: C, 15.42; H, <0.10; N, 28.29; Si, 56.02%. The calculated composition, $Si_3N_4+0.9$ SiC + 1.6 C., is equivalent to 72% Si_3N_4 + 17% SiC + 11% C, by weight.

Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 0.285 g of the white solid produced 0.489 g (79%) of a white ceramic foam. White ceramic analysis: C, 0.38; H, 0.87; N, 36.70; Si, 51.61%. A 0.285 g sample of this ceramic was pyrolyzed in a stream of argon to 1500 °C and 0.1982 g (70%) of a grayish-white ceramic was obtained. Grayish-white ceramic analysis: C, 0.62; H, <0.10; N, 34.28; Si, 59.06%. The calculated composition, $Si_3N_4+0.08$ SiC + 0.34 Si, is equivalent to 92% Si_3N_4 + 2% SiC + 6% Si, by weight.

In another experiment, the standard polymerization apparatus was charged with 0.07 g (1.746 mmol) of KH and 60 mL of THF was added to the flask. The mixture was stirred for 10 min. By syringe, 10.501 g (44.38 mmol) of $[CH_3Si(H)NH]_4$ was added over 30 min. Gas evolution was observed. The reaction mixture was stirred for 2.5 h at room temperature. CH_3I (0.30 mL, 0.684 g, 4.851 mmol) was added and an immediate white precipitate formed. The reaction mixture was stirred for an additional 30 min and then the standard polymer work-up was done. The product was a soluble, white solid (89% yield). Analysis: C, 21.30; H, 7.54; N, 23.58; Si, 46.91%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 8.8H, $SiCH_3$), 0.8–1.0 (broad, 1.0H, NH), 4.6–4.9 ppm (broad, 1.0H, SiH). Integration enabled calculation of the composition $(CH_3SiHNH)_{0.34}(CH_3SiN)_{0.66}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/DEPT): δ_{Si} -16 to -25 ppm (broad). Molecular weight (cryoscopy in C_6H_6): 1580 g mol^{-1}. Ceramic residue yield (TGA): 82% (black ceramic).

Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 1.0855 g of the white solid produced 0.8413 g (78%) of a black ceramic. A 0.8393 g sample of the latter was pyrolyzed in a stream of argon to 1500°C and 0.6412 g (76%) of a greenish-gray ceramic was obtained.

Ceramic analysis: C, 15.01; H, <0.10; N, 27.94; Si, 55.91%. A composition of Si_3N_4 + SiC + 1.5 C. Or 71% Si_3N_4 + 20% SiC + 9% C. (by weight) was calculated.

X-ray powder diffraction (d, Å): 3.14 (α-Si_3N_4), 2.51 (β-SiC), 1.93, 1.64 (α-Si_3N_4), 1.54, 1.31 (β-SiC).

Large-scale tube furnace pyrolysis in a stream of ammonia to 1000 °C of 1.1020 g of the white solid produced 0.8953 g (79%) of a white ceramic powder. A 0.8827 g sample of the latter was pyrolyzed in a stream of argon to 1500 °C and 0.6637 g (75%) of a grayish ceramic was obtained. Ceramic analysis: C, 0.71; H, <0.10; N, 35.61; Si, 60.11% A composition of 93% Si_3N_4+2% SiC+5% Si. (by weight) was calculated. DRIFT (cm^{-1}): 1050, 950, 850. X-ray powder diffraction (*d*, Å): 4.31, 3.92, 3.38, 3.14, 2.88, 2.59, 2.54, 2.31, 2.16, 2.08, 1.91, 1.64, 1.60, 1.48, 1.43, 1.35, 1.30, 1.25, 1.23, 1.11 (α-Si_3N_4).

In the drybox, approximately 3.0 g of this polysilazane was ground in a mortar and pestle. The ground polysilazane was placed in a 1.5 in × 0.5 in (3.8 cm × 3.8 cm) rectangular stainless-steel die and uniaxially pressed to 5000 psi (34×10^3 kPa) for 15 min. The resulting bar was loaded into a rubber bag and isostatically pressed at 40 000 psi (276×10^3 kPa) for 2 min. This bar was removed from the die and placed in a fused-silica boat and pyrolyzed to 1000 °C in a stream of argon. A second bar was prepared and pyrolyzed to 1000 °C in a stream of ammonia.

Further experiments on the polymerization of $[CH_3Si(H)NH]_4$, 1

Essentially the same procedure as that described above was used in these experiments. Only the results are given.

Reaction of $[CH_3Si(H)NH]_4$ with 1 mol% KH in THF for 3 h at room temperature

The product, obtained in 95% yield, was a soluble, white solid Analysis: C, 20.31; H, 6.02; N, 21.42; Si, 47.50%. ^{1}H NMR (250 MHz, $CDCl_3$): δ0.1–0.4 (broad, 120H, $SiCH_3$), 0.87–1.0 (broad, 13H, NH), 2.5 (broad, 1.0H, NCH_3), 4.6–4.9 ppm (broad, 13H, SiH). Calcd composition: $(CH_3SiHNH)_{0.32}$ $(CH_3SiN)_{0.67}$ $(CH_3SiHNCH_3)_{0.01}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4Si$/DEPT): δ_{Si} –17 to –24 ppm (broad). Molecular weight (cryoscopy in C_6H_6): 1010–1175 g mol^{-1}. Ceramic residue yield (TGA): 84%.

Large-scale tube furnace pyrolysis in a stream of argon to 1000 °C of 1.2309 g of the white solid produced 0.9394 g (76%) of a black ceramic. A 0.9361 g sample of this material was pyrolyzed in a stream of argon to 1500 °C and 0.6981 g (76%) of a greenish-gray ceramic was obtained. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 1.1414 g of the white solid produced 0.8951 g (78%) of a white ceramic powder. A 0.8933 g sample of this ceramic was pyrolysed in a stream of argon to 1500 °C and 0.6253 g (70%) of a grayish ceramic was obtained.

Reaction of $[CH_3Si(H)NH]_4$ with 2 mol% KH in THF for 90 min at room temperature

The product, a soluble, white solid, was isolated in 90% yield. Analysis: C, 21.03; H, 6.96; N, 20.46; Si, 42.98%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 13.0H, $SiCH_3$), 0.8–0.9 (broad, 1.0H, NH), 4.55–4.9 ppm (broad, 2.0H, SiH). Calcd composition: $(CH_3SiHNH)_{0.23}(CH_3SiN)_{0.77}$. Molecular weight (cryoscopy in C_6H_6): 1700 g mol^{-1}. Ceramic residue yield (TGA): 86%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.4052 g of the white solid produced 0.3139 g (78%) of a black ceramic.

Reaction of $[CH_3Si(H)NH]_4$ with 5 mol% KH in THF for 90 min at room temperature

A soluble white solid was obtained in 92% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.5 (broad, 7.3H, $SiCH_3$), 0.8–1.0 (broad, 1.0H, NH), 4.55–4.9 ppm (broad, 1.0H, SiH). Calculated composition: $(CH_3SiHNH)_{0.27}(CH_3SiN)_{0.73}$ IR (CCl_4, cm^{-1}): 3400 (m), 2960 (m), 2920 (m), 2860 (m), 2120 (vs), 1260 (vs), 1140 (m), 1000 (vs), 900 (vs), 800–750 (broad, vs). Molecular weight (cryoscopy in C_6H_6): 1590 g mol^{-1}. Ceramic residue yield (TGA): 86%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.2696 g of the white solid produced 0.2145 g (80%) of a black ceramic.

Reaction of $[CH_3Si(H)NH]_4$ with 1 mol% KH in diethyl ether for 90 min at room temperature

The product was a soluble, very viscous oil weighing 1.35 g (83% yield). Analysis: C, 20.31; H, 7.40; N, 22.88; Si, 50.90%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 5.6H, $SiCH_3$), 0.75–1.0 (broad, 1.2H, NH)), 4.4 (broad s, 0.1H, SiH), 4.6–5.0 ppm (broad, 0.9H, SiH). Calcd composition: $(CH_3SiHNH)_{0.54}(CH_3SiN)_{0.46}$. Molecular weight (cryoscopy in C_6H_6): 977 g mol^{-1}. Ceramic residue yield (TGA): 62%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.2136 g of the

white solid produced 0.0813 g (38%) of a black ceramic.

Reaction of $[CH_3Si(H)NH]_4$ with 1 mol% KH in hexane for 90 min at room temperature

The product was a soluble, very viscous oil (89% yield). Analysis: C, 20.27; H, 7.68; N, 22.43; Si, 47.91%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 5.0H, $SiCH_3$), 0.8–1.0 (broad, 1.3H, NH), 4.4 (broad, 0.1H, SiH), 4.6–4.9 ppm (broad, 0.9 H, SiH). Calcd composition: $(CH_3SiHNH)_{0.59}(CH_3SiN)_{0.41}$. Molecular weight (cryoscopy in C_6H_6): 430 g mol^{-1}. Ceramic residue yield (TGAS): 34%.

Reaction of $[CH_3Si(H)NH]_4$ with 1 mol% KH in benzene for 90 min at room temperature

The product, obtained in 71% yield, was a soluble, very viscous oil. Analysis: C, 20.56; H, 7.40; N, 23.06; Si, 47.12%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 8.7H, $SiCH_3$), 0.8–1.0 (broad, 1.5H, NH), 4.5–4.9 ppm (broad, 1.5H, SiH). Calcd composition: $(CH_3SiHNH)_{0.52}(CH_3SiN)_{0.48}$. ^{29}Si NMR (59.59 MHz, $CDCl_3/(CH_3)_4Si$/DEPT): δ_{Si} −16 to −24 ppm (broad). Molecular weight (cryoscopy in C_6H_6): 720 g mol^{-1}. Ceramic residue yield: 51% (TGA). Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.1792 g of the white solid produced 0.0597 g (32%) of a black powder.

Reaction of $[CH_3Si(H)NH]_4$ with 1 mol% KH in THF for 30 min at reflux

The product was a soluble white solid (90% yield). Analysis: C, 21.34; H, 6.93; N, 22.07; Si, 45.18%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.5 (broad, 7.0H, $SiCH_3$), 0.8–1.0 (broad, 1.0H, NH), 4.6–5.0 ppm (broad, 1.0H, SiH). Calcd composition: $(CH_3SiHNH)_{0.43}(CH_3SiN)_{0.57}$. Molecular weight (cryoscopy in C_6H_6): 940 g mol^{-1}. The ceramic residue yield (TGA): was 82%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.8057 g of the white solid produced 0.6056 g (81%) of a black ceramic foam. A 0.6526 g sample of the above ceramic was pyrolyzed in a stream of argon to 1500 °C and 0.4924 g (75%) of a greenish-gray ceramic was obtained. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 0.3834 g of the white solid produced 0.3187 g (83%) of a white powder.

Reaction of $[CH_3Si(H)NH]_4$ and 12 molar equivalents of Et_3SiH with 2 mol% KH

The standard apparatus was charged with 0.036 g (0.898 mmol) of KH. By syringe, 40 mL of THF was added and the mixture was stirred for 10 min. By syringe, 2.485 g (10.5 mmol) of $[CH_3SiHNH]_4$ and 10.124 g (87.05 mmol) of Et_3SiH were added to the flask over 10 min. Gas evolution was observed. The reaction mixture was heated at reflux for 30 min and then cooled to room temperature. CH_3I (0.20 mL, 3.23 mmol) was added and an immediate white precipitate formed. The reaction mixture was stirred for an additional 30 min and then the standard polymer work-up was performed. The product was a soluble, very viscous, cloudy oil weighing 2.287 g. A GC analysis (internal standard, C_8) of the volatiles showed that 6.9 g (60 mmol, 69%) of unreacted Et_3SiH was recovered in the trap. ^{1}H NMR (250 MHz, $CDCl_3$: δ 0.0–0.4 (broad, 9.3H, $SiCH_3$), 0.4–0.6 (broad, 2.9H, Si–$\underline{CH_2}$–CH_3), 0.8–1.2 (broad, 3.8H, $SiCH_2\underline{CH_3}$ and possibly N–H), 4.6–5.0 ppm (broad, 1.0H, SiH). The calculated composition was $(CH_3SiHNSiEt_3)_{0.42}$ $(CH_3SiN)_{0.58}$. ^{29}Si NMR (59.59 MHz, $CDCl_3/(CH_3)_4Si$/ DEPT): δ_{Si} 0.1, −0.2 (both very small), −17 to −26 ppm (broad). IR (CCl_4, cm^{-1}): 3400 (m), 2960 (s), 2900 (m), 2130 (vs), 1550 (w), 1255 (vs), 1000–950 (broad, vs), 900 (vs), 800–740 (broad, vs). Molecular weight (cryoscopy in C_6H_6): 400 g mol^{-1}. Ceramic residue yield (TGA): 56%.

Reaction of $[CH_3Si(H)NH]_4$ and $[(CH_3)_2SiNH]_3$ with 2 mol% KH

The standard apparatus was charged with 0.025 g (0.623 mmol) of KH. By syringe, 40 mL of THF was added and the mixture was stirred for 10 min. By syringe, 1.021 g (4.32 mmol) of $[CH_3Si(H)NH]_4$ and 1.076 g (4.96 mmol) of $[(CH_3)_2SiNH]_3$ were added to the flask over 10 min. Gas evolution was observed. The reaction mixture was stirred at room temperature for 2 h. CH_3I (0.30 cm^3, 0.68 g, 4.85 mmol) was added and an immediate white precipitate formed. The reaction mixture was stirred for an additional 30 min and then most of the solvent was removed by trap-to-trap distillation. Unreacted $[(CH_3)_2SiNH]_3$ (0.59 g, 55%) was distilled from the residue at 16 mmHg/77–79 °C. The product was a soluble, white solid weighing

0.901 g. ^{1}H NMR (250 MHz, $CDCl_3$: δ 0.1–0.4 (broad, 55H, $SiCH_3$), 0.8–1.0 (broad, 7.0H, NH), 2.4–2.6 (broad, 1.0H, NCH3), 4.6–5.0 ppm (broad, 5.0H, SiH). Calcd composition: $(CH_3SiHN)_{0.37}(CH_3SiN)_{0.42}$ $(CH_3Si(NSi(CH_3)_2NH)_{0.18}(CH_3SiHNCH_3)_{0.03}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/ DEPT): δ_{Si} −17 to −27 ppm (broad). Molecular weight (cryoscopy in C_6H_6): 400 g mol^{-1}. Ceramic residue yield (TGA): 57%.

The product of this reaction was dissolved in 15 mL of THF. By syringe, 3.609 g (16.48 mmol) of $[(CH_3)_2SiNH]_3$ was added to the clear solution. This solution was stirred for two days at room temperature. After the THF had been removed by trap-to-trap distillation, 3.5 g (97% recovery) of $[(CH_3)_2SiNH]_3$ was distilled out of the reaction mixture. The residue was a white solid whose characterization matched that of the original product, and it was collected in 95% yield (based on the weight of the polysilazane used).

Reaction of $[CH_3Si(H)NCH_3–CH_3Si(H)NH]_2$, 2, with 1 mol% KH at room temperature

The standard polymerization apparatus was charged with 0.01 g (0.249 mmol) of KH in the drybox. By syringe, 25 mL of THF was added and the mixture was stirred for 10 min. By syringe, 5.249 g (19.84 mmol) of the cyclotetrasilazane **2** was added over 30 min. Gas evolution was observed. The reaction mixture was stirred at room temperature for 16 h. CH_3I (0.20 cm^3, 0.456 g, 3.23 mmol) was added and an immediate white precipitate formed. The reaction mixture was stirred for an additional 30 min and then the standard polymer work-up was done. The product was a soluble, very viscous oil weighing 3.625 g (69% yield). Analysis: C, 27.14; H 8.07; N, 21.01; Si, 36.84%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 4.5H, $SiCH_3$), 2.4–2.6 (broad, 2.1H, NCH_3), 4.5–4.9 ppm (broad, 1.0H, SiH). Calcd composition: $(CH_3SiHNH)_{0.20}(CH_3SiN)_{0.33}(CH_3SiHNCH_3)_{0.47}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/DEPT): δ_{Si} −7 to −22 ppm (broad). IR (Ccl_4, cm^{-1}): 3400 (m), 2960 (s), 2940 (sh), 2890 (s), 2815 (s), 2125 (vs), 1470 (m), 1435 (sh), 1415 (m), 1375 (m), 1260 (vs), 1195 (s), 1100 (vs), 1060 (sh), 1020–880 (broad, vs), 800(vs), 760 (vs). Molecular weight (cryoscopy in C_6H_6): 300–400 g mol^{-1}. Ceramic residue yield (TGA): 14% (black foam). Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.6255 g of the white solid produced 0.1006 g (16%) of a black solid. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 0.3792 g of the white solid produced 0.0766 g (20%) of a flaky white, solid.

Reaction of $[CH_3Si(H)NCH_3–CH_3Si(H)NH]_2$ with 1 mol% KH in THF for 7.5 h at reflux

The product was a soluble, sticky solid (68%). $_1$H NMR (250 MHz, $CDCl_3$) δ 0.1–0.4 (broad, 11.0H, $SiCH_3$), 0.8–0.9 (broad, 1.0H, NH), 2.4–2.6 (broad, 3.8H, NCH_3), 4.6–4.9 ppm (broad, 1.8H, SiH). Calcd composition: $(CH_3SiHNH)_{0.27}(CH_3SiN)_{0.38}(CH_3SiHNCH_3)_{0.35}$. Molecular weight (cryoscopy in C_6H_6): 610–655 g mol^{-1}. Ceramic residue yield: 47%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.6057 g of the white solid produced 0.3695 g (61%) of a black chunky solid. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of the white solid produced 0.4732 g (72%) of a flaky, white solid.

Reaction of $[CH_3Si(H)NCH_3–CH_3Si(H)NH]_2$ with 5 mol% KH in THF for 19 h at reflux

The product was a soluble, very sticky solid, 3.544 g (67% yield). Analysis: C, 27.75; H, 7.62; N, 21.18; Si, 36.97%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 6.8H, $SiCH_3$), 2.3–2.6 (broad, 3.5H, NCH_3), 4.5–4.8 ppm (broad, 1.0H, SiH). Calcd composition: $(CH_3SiN)_{0.46}(CH_3SiHNCH_3)_{0.54}$. ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/DEPT): δ_{Si} −6 to −24 (broad). Molecular weight (cryoscopy in C_6H_6): 650–700 g mol^{-1}. Ceramic residue yield (TGA): 64%. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 0.5310 g of the white solid produced 0.2205 g (42%) of a flaky, white solid. Ceramic analysis: C, 0.59; H, 0.96; N, 40.98; Si, 54.92%.

Reaction of $[CH_3Si(H)NH]_4$ and $[CH_3Si(H)NCH_3–CH_3Si(H)NH]_2$, 2, with 1 mol% KH in THF for 2 h at reflux

The standard polymerization apparatus was charged with 0.02 g (0.499 mmol) of KH. By syringe, 30 mL of THF was added and the reaction mixture was stirred for 10 min. Then 1.741 g (7.36 mmol) of $[CH_3Si(H)NH]_4$ and 1.95 g (7.37 mmol) of **2** were added over 30 min. Gas evolution was observed. The reaction mixture was heated at reflux for 2 h and then cooled

to room temperature. CH_3I (0.30 cm^3, 0.68 g, 4.85 mmol) was added. An immediate white precipitate formed. The reaction mixture was stirred for 30 min and then the standard work-up was done. The product was a soluble, white solid weighing 3.111 g (84% yield based on the weight of the cyclotetrasilazanes used). Analysis C, 21.67; H, 6.88; N, 19.45; Si, 45.58%. ^{1}H NMR (250 MHz, $CDCl^3$): δ 0.1–0.4 (broad, 13.4H, $SiCH_3$), 0.9–1.0 (broad, 1.0H, NH), 2.4–2.6 (broad, 2.4H, NCH_3), 4.6–4.9 ppm (broad, 1.8H, SiH). Calcd composition: $(CH_3SiHNH)_{0.22}(CH_3SiN)_{0.60}(CH_3SiHNCH_3)_{0.18}$. Molecular weight (cryoscopy in C_6H_6): 740–780 g mol^{-1}. Ceramic residue yield (TGA): 80% (black ceramic). Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 1.011 g of the white solid produced 0.738 g (73%) of a foamy, black solid. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 1.201 g of the white solid gave 0.889 g (74%) of a foamy white, solid.

Reaction of $[CH_3Si(H)NH]_4$ and $2[CH_3Si(H)NCH_3–CH_3Si(H)NH]_2$, 2, with 1 mol% KH in THF for 30 min at reflux

The same procedure was used in the reaction of 0.914 g (3.86 mmol) of $[CH_3Si(H)NH]_4$ and 1.75 g (6.61 mmol) of **2** with 0.012 g (0.299 mmol) of KH in 25 mL of THF at reflux for 30 min. The product was a soluble, white solid weighing 2.213 g (83% yield based on the weight of the cyclotetrasilazanes used). Analysis: C, 24.11; H, 7.32; N, 19.27; Si, 42.49%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.4 (broad, 10H, $SiCH_3$), 0.8–0.9 (broad, 1.0H, NH), 2.4–2.6 (broad, 2.2H, NCH_3), 4.5–4.9 ppm (broad, 1.6H, SiH). Calcd composition: $(CH_3SiHNH)_{0.30}(CH_3SiN)_{0.48}(CH_3SiHNCH_3)_{0.22}$. Molecular weight (cryoscopy in C_6H_6): 630 g mol^{-1}. Ceramic residue yield (TGA): 60%. Large-scale tube-furnace pyrolysis in a stream of argon to 1000 °C of 0.749 g of the white solid produced 0.419 g (56%) of a foamy, black solid. Large-scale tube-furnace pyrolysis in a stream of ammonia to 1000 °C of 0.873 g of the white solid produced 0.786 g (90%) of a white solid.

Reaction of $[CH_3Si(H)NCH_3–CH_3Si(H)N(H)]_2$, 2, with methyl-lithium in THF with CH_3I quench

A 200-mL three-necked, round-bottomed flask equipped with a gas inlet tube, a stir-bar, and two septa was flame-dried under argon. By syringe, 100 mL of THF and 10.819 g (40.89 mmol) of **2** were added to the flask, which was cooled to − 78 °C in a dry ice/acetone bath. Then 34 mL of a 1.2 M solution of CH_3Li (40.80 mmol) was added dropwise over 15 min. The solution was stirred at − 78 °C for an additional 15 min. CH_3I (3.0 mL, 6.84 g, 48.51 mmol) was added by syringe; a white precipitate formed. The reaction mixture was stirred for an additional 30 min at room temperature and then the solvent was removed by trap-to-trap distillation. The residue was extracted with 30 mL of hexane and the resulting mixture was centrifuged to precipitate lithium iodide which had been carried along. The supernatant liquid was cannulated into a 100-mL one-necked flask which had been flame-dried under argon. The hexane was removed from the supernatant layer by trap-to-trap distillation to leave a clear liquid. The latter, cyclo{$[CH_3$-Si(H)N(CH_3)CH_3-Si(H)N(CH_3)CH_3Si(H)N(CH_3), CH_3Si(H)N(CH_3)CH_3Si(H)NH} **3**, was distilled at 0.15 mmHg/58–60 °C (5.69 g, 20.42 mmol, 50%). Analysis: Calcd for $C_7H_{26}N_4Si_4$: C, 30.17; H, 9.40; N, 20.10%. Found: C, 30.09; H, 9.32; N, 20.08%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.25 (complex m, 12H, $SiCH_3$), 0.6 (broad, 1H, NH), 2.45–2.55 (complex m, 9H, NCH_3), 4.5–4.7 ppm (complex m, 4H, SiH). ^{29}Si NMR (59.59 MHz, $CDCl_3$/$(CH_3)_4$Si/DEPT): δ_{Si} − 6 to − 20 ppm (complex m). There was no signal in the SiH_2 region. IR (thin film, cm^{-1}): 3420 (m), 3400 (sh), 2960 (s), 2940 (SH), 2890 (s), 2810 (s), 2140–2100 (broad, vs), 1470 (m), 1400 (m), 1370 (m), 1255 (vs), 1200 (vs), 1110–1060 (broad, vs), 1000–850 (broad, vs), 750 (vs). Molecular weight (cryoscopy in C_6H_6): 250–300 g mol^{-1}. Calcd: 278.6 g mol^{-1} TGA yield: 0%.

Reaction of cyclotetrasilazane 3 with KH in THF

The standard polymerization apparatus was charged with 2.35 g (58.6 mmol) of KH in the drybox. By syringe, 100 mL of THF was added to the flask and the mixture was stirred for 10 min. Then 16.4 g (58.86 mmol) of silazane **3** was added over 10 min. Gas evolution was observed. The reaction mixture was stirred at room temperature for 75 min. CH_3I (11.40 g, 80.85 mmol) was added by syringe and an immediate white precipitate formed. The reac-

tion mixture was stirred for an additional 30 min and then the standard work-up was done. The products were distilled from the resulting solution: $[CH_3SiHNCH_3]_4$ (**A**) was distilled at 0.01 mmHg/38–40 °C (4.257 g, 14.54 mmol, 25%), and a second fraction (**B**) distilled at 0.01 mmHg/67–78 °C (4.3857 g).

(**A**) Analysis: Calcd for $C_8H_{28}N_4Si_4$: C, 32.83; H, 9.64; N, 19.14%. Found: C, 32.99; H, 9.56; N, 19.13%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.25 (broad m, 12H, $SiCH_3$), 2.4–2.6 (broad m, 12.0, NCH_3), 4.4–4.7 ppm (broad m, 4H, SiH). ^{29}Si NMR (59.59 MHz, $CDCl_3/(CH_3)_4Si$/DEPT): δ_{Si} -2 to -15 (broad), six major peaks between -8 and -15 ppm. IR (CCl_4, cm^{-1}): 2960 (vs), 2940 (sh), 2900 (vs), 2820 (vs), 2120 (vs), 1470 (w), 1410 (w), 1255 (vs), 1190 (s), 110–1050 (broad, vs), 1000–850 (broad, vs), 760 (m). Molecular weight (cryoscopy in C_6H_6): 260–300 g mol^{-1}. Calc.: 288.6 g mol^{-1}.
(**B**) Analysis: Calcd for **5**, $C_{14}N_{48}N_8Si_8$: C, 30.39; H, 8.74; N, 20.25%. Calcd for **6**, $C_{15}H_{42}N_8Si_8$: C, 31.64; H, 9.21; N, 19.68%. Found: C, 31.43; H, 8.62; N, 18.49%. Found: C, 32.20; H, 9.34; N, 19.59%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.1–0.2 (broad, 4.1H, $SiCH_3$), 2.5 (broad m, 3.4H, NCH_3), 4.4–4.6 ppm (broad m, 1.0H, SiH). ($SiCH_3/NCH_3 = 1.21$; this ratio for **5** is 1.3, for **6** 1.14). ^{29}Si NMR (59.59 MHz, $CDCl_3/(CH_3)_4Si$/DEPT): δ_{Si} -4 to -14 ppm (broad). IR (CCl_4, cm^{-1}): 2960 (vs), 2900 (vs), 2820 (vs), 2120 (vs), 1470 (w), 1410 (w), 1255 (vs), 1190 (s), 1100–1050 (broad, vs), 1000–850 (broad, vs), 760 (m). Molecular weight (cryoscopy in C_6H_6): 500–600 g mol^{-1}. Calcd molecular weight: 553.3 g mol^{-1} for **5**, 569.3 g mol^{-1} for **6**.

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