Poly(ureidosilazanes): Preceramic Polymeric Precursors for Silicon Carbonitride and Silicon Nitride. Synthesis, Characterization, and Pyrolytic Conversion to Si_3N_4/SiC Ceramics

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The mixture of cyclo-$[CH_3Si(H)NH]_n$ oligomers obtained in the ammonolysis of CH_3SiHCl_2 has been converted to material of higher molecular weight by the reaction with urea (between 4:1 and 12:1 $CH_3Si(H)NH$ unit/urea ratio) in pyridine at 85 °C. The resulting poly-(ureidosilazanes) (PUSZ) were obtained as white solids, gums or oils, depending on the CH_3-$Si(H)NH$/urea ratio used. Their pyrolysis in a flow of argon to 1000 °C gave black silicon carbonitride in high yield. In a flow of ammonia, their pyrolysis to 1000 °C resulted in grayish-white silicon nitride ceramics with a carbon content of less than 2%. DRIFTS, TGA-MS, TGA-FTIR, cross-polarization, and single-pulse magic angle spinning solid state NMR as well as solution-state NMR spectroscopy were employed in the characterization of the PUSZs and in the investigation of their pyrolytic conversion to ceramic materials. Selective isotopic labeling using ^{13}C- and ^{15}N-labeled urea was particularly useful in NMR studies aimed at determining the constitution of the poly(ureidosilanes).

Introduction

The application of preceramic polymers in the processing of advanced ceramics has become an established technology. Polymeric precursors for silicon-containing ceramics—silicon carbide, silicon oxycarbide, silicon nitride, silicon oxynitride, silicon carbonitride—have received the most attention during the development of this new area.[1] Among the organosilicon polymers that have been found to be useful precursors for silicon-based ceramics are the polysilazanes. They are prepared by ammonolysis of chlorosilanes, for the most part H_2SiCl_2, $RSiHCl_2$, R_2SiCl_2, $RR'SiCl_2$, and mixtures of these with each other and with trichlorosilanes, $HSiCl_3$ and $RSiCl_3$. In most cases such ammonolysis gives products of low molecular weight, usually mixtures of cyclic oligomers; e.g., $(RR'SiNH)_n$, where $n = 2, 3, 4, 5, ...$) in the case of $RR'SiCl_2$.[2] Such low molecular weight oligosilazanes are too volatile to serve as pyrolytic precursors for silicon carbonitride or silicon nitride.[3] For this purpose they must be converted by some means to materials of higher molecular weight that are branched and/or cross-linked to such an extent that their pyrolysis results, not in

conversion to volatile products, but rather in formation of a ceramic residue in high yield, with only minimal evolution of volatiles.

In earlier work we have described the conversion of a mixture of volatile, cyclic oligomeric methylhydridosilazanes obtained in the ammonolysis of methyldichlorosilane[2] to more complex polysilazanes of higher molecular weight by the action of a catalytic amount of a base strong enough to deprotonate the N–H functions of the cyclosilazane.[4] Such treatment, preferably with a catalytic amount of KH in THF, resulted in loss of H_2 and converted the liquid mixture of $[CH_3Si(H)NH]_n$ oligomers, after a quench with CH_3I, to a nonvolatile, but still soluble, white solid of composition (in terms of constituent groups) $[(CH_3Si(H)NH)_a(CH_3(SiN)_b(CH_3Si-(H)NCH_3)_c]_n$.[4] Pyrolysis of such a polysilazane in a stream of argon to 1000–1200 °C gave black, amorphous silicon carbonitride in 80–85% yield. On the other hand, pyrolysis in a stream of ammonia served to remove all CH_3 groups and left behind a white residue of essentially carbon-free silicon nitride.[1f] Such polysilazanes were found to be useful as binders in the processing of silicon-containing ceramic powders such as SiC and Si_3N_4[5] and in the preparation of ceramic-coating formulations for the protection of carbon/carbon composites against air oxidation at higher temperatures.[6]

[®] Abstract published in *Advance ACS Abstracts,* October 15, 1995.
(1) (a) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 250. (b) Peuckert, M.; Vaahs, T.; Brück, M. *Adv. Mater.* **1990**, *2*, 398. (c) Toreki, W. *Polym. News* **1991**, *16* (1), 6. (d) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297. (f) Seyferth, D. In *Silicon-Based Polymer Science—A Comprehensive Resource*; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; pp 565–591.
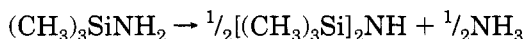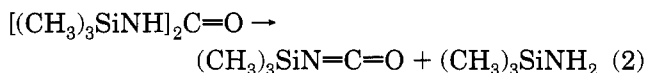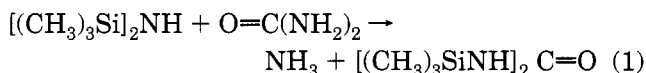(2) Brewer, S. D.; Haber, C. P. *J. Am. Chem. Soc.* **1948**, *70*, 3888.
(3) Except when the pyrolytic process involves gas-phase processes such as laser-induced vapor-phase pyrolysis; see, for instance: Du H.; Gallois B.; Gonsalves, K. E. *Chem. Mater.* **1989**, *1*, 569.

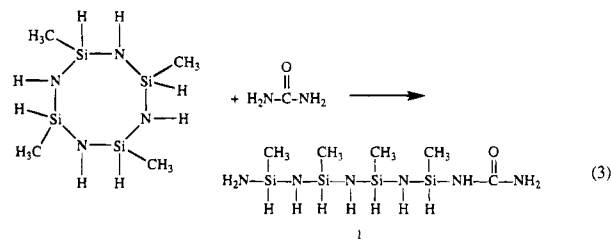(4) Seyferth, D.; Wiseman, G. H. *J. Am. Ceram. Soc.* **1984**, *67*, C-132; U.S. Patent 4,482,669, 1984.
(5) (a) Semen, J.; Loop, J. G. *Ceram. Eng. Sci. Proc.* **1991**, *12*, 1967. (b) Mohr, D.; Desai, P.; Starr, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 565.

Other procedures have been used to convert the $[CH_3\text{-}Si(H)NH]_n$ cyclic oligomers to less-volatile or nonvolatile preceramic materials. Thermal treatment,[7] especially in the presence of an acid catalyst,[1f,7b] a polymerization process that proceeds with elimination of ammonia, is one such procedure. Catalytic dehydrogenative NH/SiH condensation of the $[CH_3Si(H)NH]_n$ cyclic oligomers in the presence of a transition metal catalyst such as $Ru_3(CO)_{12}$[8] is another procedure that has been used.

During the course of our research on precursors for silicon-containing ceramics[1f] we were interested in developing other methods for the conversion of the volatile, cyclic $[CH_3Si(H)NH]_n$ oligomers to useful preceramic polymers. The high reactivity of the Si−N and N−H bonds in aminosilanes and silazanes has been demonstrated in many examples by previous workers,[9] and the older organosilicon literature provides many model reactions of simple organosilicon compounds that could be applicable to the synthesis of organosilicon polymers. In a search for known organosilicon chemistry that might be applied to the conversion of the cyclo-$[CH_3Si(H)NH]_n$ oligomers to useful materials of higher molecular weight, our attention was drawn to a report by Wannagat and co-workers[10] on the transamination reaction of hexamethyldisilazane with urea (eq 1), a reaction shown by use of ^{15}N-labeled hexamethyldisilazane to give $^{15}NH_3$ and unlabeled *N,N'*-bis(trimethylsilyl)urea.[10b] This product decomposed when heated to 222 °C (eq 2). Application of this reaction with urea

$$[(CH_3)_3Si]_2NH + O{=}C(NH_2)_2 \rightarrow$$
$$NH_3 + [(CH_3)_3SiNH]_2 C{=}O \quad (1)$$

$$[(CH_3)_3SiNH]_2C{=}O \rightarrow$$
$$(CH_3)_3SiN{=}C{=}O + (CH_3)_3SiNH_2 \quad (2)$$

$$(CH_3)_3SiNH_2 \rightarrow {}^1/_2[(CH_3)_3Si]_2NH + {}^1/_2NH_3$$

would be expected to convert the cyclic $[CH_3Si(H)NH]_n$ oligomers to a complex mixture of products of higher molecular weight. The initial step would be ring opening as shown in eq 3, using the cyclic tetramer (i.e., n = 4) components of the mixture of cyclic oligomers as the example. Subsequent steps could involve ring closure of **1** with loss of NH_3 to give the 10-membered ureidosilazane **2** or attack of **1** at another cyclosilazane molecule to give a larger, linear molecule. Condensation of the Si−NH_2 terminus of **1** and other molecules containing such a function with the Si−NH_2 group of another molecule or with an SiNHSi unit with loss of NH_3 could establish new silazane links between mol-

ecules. Once linear ureidosilazanes have been formed, urea could react with SiNHSi functions of these species as well. Since the cyclosilazane oligomers in the contemplated experiments would be present in excess, a complex, nonuniform mixture of species of higher molecular weight composed of linear and cyclic components would be expected. The building blocks making up the components of these product mixtures would be **3**, **4**, and, possibly, some **5**. Terminal Si−NH_2 and NHC(O)-NH_2 groups should be negligible if present at all. Also
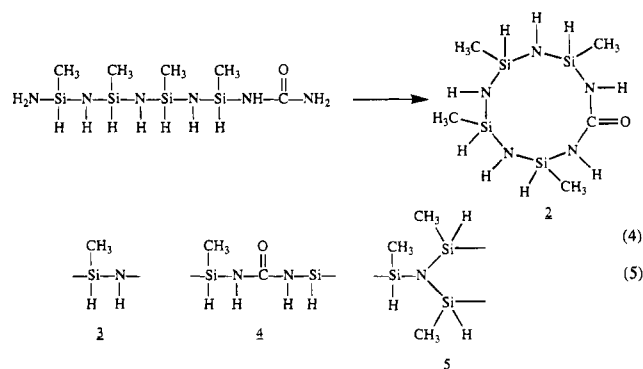
possibly contributing to some, probably lesser, extent to the formation of products of higher molecular weight might be the dehydrogenative condensation of cyclosilazanes induced by heating in the presence of pyridine, as has been substantiated by ^{29}Si solid state NMR.[11,13]

Given the simplicity of the reaction and the processing advantages that may be gained from the cyclo-$[CH_3Si(H)NH]_n$/urea reactions, we undertook an detailed investigation of this reaction. We report here the results of our studies including the synthesis and characterization of the products, the poly(ureidosilazanes).[11] Diffuse reflectance FTIR (DRIFTS), TGA-MS, TGA-FTIR, cross-polarization, and single-pulse magic angle spinning (MAS) solid-state NMR spectroscopy and powder X-ray diffraction were employed in our investigations of constituent components and bonding of these polymers and of their pyrolytic conversion to Si_3N_4/SiC ceramics. The use of these characterization techniques, in concert with ^{13}C and ^{15}N labeling, also allowed the unambiguous structural characterization of the urea incorporation, pyrolytic evolution and local order in these preceramic and ceramic materials.[12]

(6) Niebylski, L. M. U.S. Patents 4,921,925, 1990, and 5,009,961, 1991.

(7) (a) Yu, G.; Parrick, J.; Edirisinghe, M.; Finch, D.; Ralph, B. *J. Mater. Sci.* **1994**, *29*, 5569. (b) Porte, H.; Lebrun, J. J. Eur. Pat. Appl. EP 208,630, 1987; *Chem. Abstr.* **1987**, *106*, 13936y.

(8) (a) Blum, Y. D.; McDermott, G. A.; Hirschon, A. S. *Inorg. Organomet. Polym. Proc. IUPAC Symp. Macromol. 33rd, 1990*, **1991**, 161. (b) Blum, Y. D.; Schwartz, K. B.; Crawford, E. J.; Hamlin, R. D. *Mater. Res. Soc. Symp. Proc.* **1988**, 121 (*Better Ceram. Chem. 3*) 565. (c) Blum, Y. D.; Crawford, E. J. U.S. Patent 4,952,715, 1990.

(9) (a) Fessenden, R.; Fessenden, J. S. *Chem. Rev.* **1961**, *61*, 361. (b) Wannagat, U. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 225. (c) Fink, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 760. (d) Andrianov, K. A.; Khananashvili, *Organomet. Chem. Rev.* **1967**, *2*, 141. (e) Aylett, B. J. *Organomet. Chem. Rev.* **1968**, *3*, 151.

(10) (a) Wannagat, U.; Bürger, H.; Krüger, C.; Pump, J. *Z. Anorg. Allg. Chem.* **1963**, *321*, 208. (b) Wannagat, U.; Bürger, H.; Peach, M. E.; Hensen, K.; Lebert, K.-H. *Z. Anorg. Allg. Chem.* **1965**, *336*, 129.

(11) A preliminary report on this research has been published: Seyferth, D.; Strohmann, C.; Dando, N. R.; Perrotta, A. J.; Garnder, J. P. *Mater. Res. Soc. Symp. Proc.* **1994**, *327*, 191.

(12) While the present work was in progress, patents were issued which reported the reactions of coammonolysis products of CH_3SiHCl_2 and $CH_3(CH_2{=}CH)SiCl_2$ (Schwark, J. M. Ph.D. Thesis, Massachusetts Institute of Technology, **1987**) with organic isocyanates, isothiocyanates, amides, and N-substituted ureas and thioureas. The products were claimed to be polysilazane/N-substituted urea or thiourea hybrids: Schwark, J. M. U.S. patents 4,929,704, 1990, 5,001,090, 1991, 5,021,533, 1991, and 5,032,649, 1991, assigned to Hercules, Inc.

Results and Discussion

Synthesis and Preceramic Polymer Studies. The methylhydridosilazane which was the starting material used in this study was prepared by the ammonolysis of CH_3SiHCl_2. This reaction produced a mixture of mostly cyclic $[CH_3Si(H)NH]_n$ silazanes, where $n = 2, 3, 4, 5,$ .... If these cyclosilazanes are not separated immediately from the reaction mixture, rearrangements occur that result in formation of SiH_2CH_3 substituents.[13] Presumably, these arise *via* ring contraction processes of the type studied by Klingebiel and his co-workers.[14] For the most part, in the methylhydridosilazane preparations carried out in this study, the reaction products had been allowed to remain in contact with the reaction mixture overnight. As a result, the cyclosilazane contained some SiH_2CH_3 functionality.

The reaction of 4 mol equiv of $[CH_3Si(H)NH]_n$ cyclic oligomer mixture ($CH_3Si(H)NH$ taken as one molar unit) with one of urea in pyridine at 85 °C for 24 h resulted in the formation of a white soluble solid (pyridine was used because urea is soluble in this solvent, thus allowing a homogeneous reaction). This product was soluble in pyridine and THF but not in hydrocarbon solvents. (Reactions carried out in pyridine at reflux gave products that became insoluble on partial removal of the pyridine.) Spectroscopic studies (^{1}H NMR and IR) showed that N–H and Si–H bonds, Si-bonded CH_3 groups, and amide C=O functions were present in the product. Thermogravimetric analysis (TGA) at 10 °C/min to 950 °C in argon gave a black ceramic residue in 83% yield (a considerable increase over that obtained, 15–20%, in TGA experiments with the methylhydridosilazane oligomer mixture). This provided strong evidence that the 4 $CH_3Si(H)NH$/1 urea reaction product was a cross-linked polymer of higher molecular weight. Given the moisture sensitivity of the parent polysilazanes,[11,13] molecular weight determinations by VPO or GPC were not undertaken. A bulk pyrolysis (tube furnace to 1400 °C in a stream of argon) left a black residue in 73% yield whose elemental analysis gave C, 13.65%; N, 29.67%; Si, 49.19%. The difference from a 100% elemental accounting, 7.5%, may be due to the presence of oxygen, but, in view of the difficulty of obtaining accurate elemental analyses of ceramic materials, the amount of oxygen present may be less or even zero, given that solid state ^{29}Si NMR data did not indicate the presence of Si–O functionality in any of the ceramics presented here.

Further experiments were undertaken to explore the effect of reactant stoichiometries. When greater $CH_3Si(H)NH$/urea ratios were used, products that were more soluble were obtained, most likely because a larger percentage of these products were linear and they were less cross-linked. For instance, the 6:1 $CH_3Si(H)NH$/urea product, also a white solid, was at least partially soluble in diethyl ether, benzene, and chloroform. The 10:1 product was a colorless gum that was completely soluble in diethyl ether and benzene but not in hexane. A liquid product was obtained in the reaction of 16 mol equiv of $CH_3Si(H)NH$ with 1 of urea, and the ceramic

(13) Dando, N. R.; Perrotta, A. J.; Strohmann, C.; Stewart, R. M.; Seyferth, D. *Chem. Mater.* **1993**, *5*, 1624.

(14) (a) Klingebiel, U. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *41*, 361. (b) Dippel, K.; Werner, E.; Klingebiel, U. *Ibid.* **1992**, *44*, 15.

Table 1. Elemental Analyses of the Ceramics Obtained by Pyrolysis of the Poly(ureidosilazanes)

PUSZ, $CH_3Si(H)NH$/ urea ratio	silicon, %	nitrogen, %	carbon, %
I. Two-Stage Pyrolysis to 1400 °C in Argon			
4:1	49.2	29.7	13.7
6:1	53.1	27.0	12.6
10:1	53.7	21.4	8.5
12:1	55.3	28.2	14.1
16:1	53.5	28.3	14.3
II. Two-Stage Pyrolysis to 1000 °C in NH_3 and Then to 1400 °C in Argon			
4:1	55.5	33.2	1.8
6:1	56.1	37.3	0.5
10:1	55.5	41.9	0.5
12:1	55.2	37.5	0.62
16:1	59.0	38.2	3.1

Table 2. Ceramic Residue Yields (%) Obtained in Furnace Pyrolysis Experiments with the Poly(ureidosilazanes)

PUSZ, $CH_3Si(H)NH$/ urea ratio	room temp to 1000 °C in NH_3	room temp to 1400 °C
I. In a Stream of Argon (Two-Stage Pyrolysis)		
4:1	73	73
6:1	76	76
10:1	76	75
12:1	73	72
16:1	62	61
II. In a Stream of Ammonia to 1000 °C and Then to 1400 °C in a Stream of Argon		
4:1	68	64
6:1	75	73
10:1	74	68
12:1	71	68
16:1	68	66

residue yield obtained from pyrolysis to 960 °C in argon in a TGA experiment was 62%. These experiments show that the physical nature of the product is changed as the $CH_3Si(H)NH$/urea ratio is increased: from solid to gum to liquid. Thus, the rheological behavior of these poly(ureidosilazanes) can be controlled with minimal sacrifice in ceramic residue yield. This is important in the context of potential applications of the poly(ureidosilazanes) (henceforth PUSZ) such as in the preparation of ceramic fibers, coatings, and in injection molding of ceramic or metal powder/PUSZ composites.

As was the case with the polysilazane obtained by KH-induced polymerization of the cyclo-$[CH_3Si(H)NH]_n$ oligomers, pyrolysis to 1000 °C of the PUSZ products in a stream of ammonia (rather than argon) gave a grayish-white residue in high yield that contained less than 2% carbon. In the best experiment, such a pyrolysis of the 12:1 PUSZ left a whitish solid whose elemental analysis was 55.20% Si, 41.87% N, and less than 0.5% C. When larger quantities of urea were used, the carbon contents of the resulting ceramics were a bit higher (see Table 1). In all cases the silicon and nitrogen contents (plus the C content) did not add up to 100%. The difference could, but need not, be due to a small oxygen content. As discussed above, no Si–O species were observed in any of the systems discussed here. (In our experience, commercial analyses of silicon nitride materials are not very reliable.) Further heating (to 1400 °C under argon) of the ceramic obtained from the pyrolysis of the PUSZs under ammonia to 1000 °C, in a different tube furnace, gave a small weight loss (1–6%; see Table 2) and left a gray-black residue. It is probable that some of the silicon nitride had decomposed

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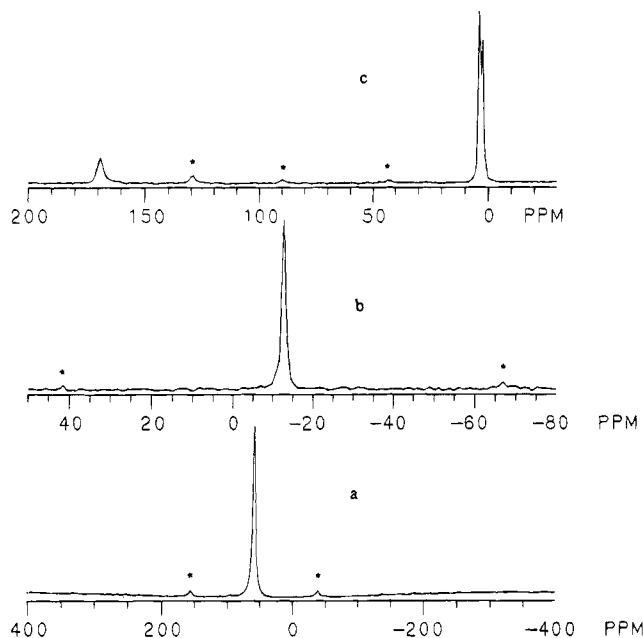
Figure 1. (a) ^{15}N, (b) ^{29}Si, and (c) ^{13}C CPMAS NMR spectra of N,N'-bis(dimethylsilyl) urea. Spinning sidebands are marked with an asterisk.
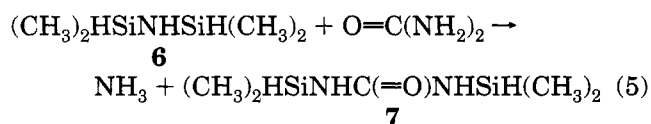

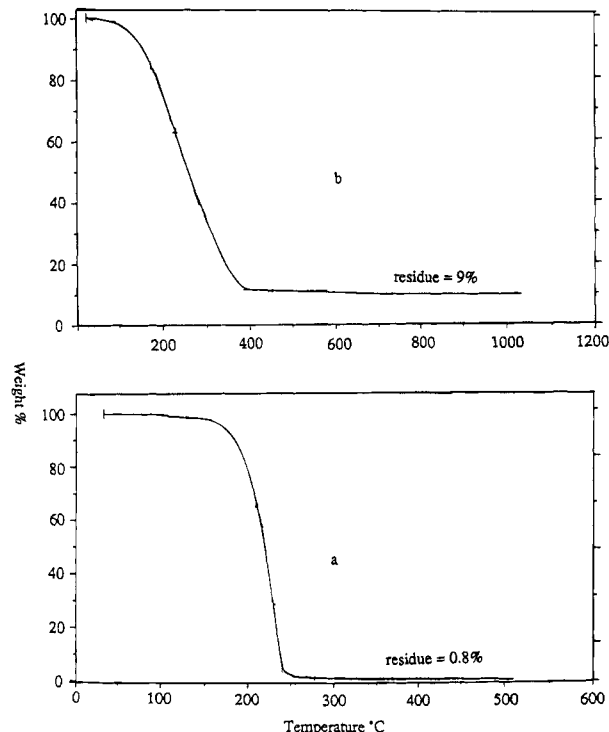**Figure 2.** TGA data (10 °C/min, N_2) for (a) bis(dimethylsilyl) urea and (b) the $[CH_3Si(H)NH]_n$ oligomer mixture.

on heating to 1400 °C, giving N_2 and elemental silicon.

The PUSZ prepared by the 6 $CH_3Si(H)NH/1$ urea reaction melted when heated, and fibers several meters in length could be drawn by hand in air from a melt of the polymer. After a 1-h air cure, pyrolysis of the green fibers in a furnace in a stream of argon gave black ceramic fibers.

Characterization of the Poly(ureidosilazanes). As noted above, the IR spectrum of PUSZ indicated retention of the urea reactant in the product polymer (as had been expected from the model reaction[10]). This suggested several opportunities for direct insertion into, and monitoring of, the reaction products by using ^{15}N- and ^{13}C-labeled urea.

To gain a better understanding of the structural effects of urea incorporation into the polysilazane $[CH_3Si(H)NH]_n$ framework, the model reaction of urea with 1,1,3,3,-tetramethyldisilazane, **6**, was examined (eq 3). ^{15}N, ^{29}Si, and ^{13}C solid-state cross-polarization magic angle spinning NMR (CPMAS NMR) spectra of the reaction product, bis(dimethylsilyl) urea, **7**, are shown in Figure 1. Solid-state, rather than solution, data were acquired because of the moisture sensitivity of **7**. A single sharp resonance was observed for both the ^{15}N and ^{29}Si NMR spectra, indicating the presence of a single species, consistent with eq 5. The ^{13}C CPMAS NMR spectrum (Figure 1c) exhibited line broadening and peak splitting at the carbonyl and methyl carbon signals at 158 and 3 ppm, respectively, owing to local unaveraged packing effects in the solid powder. The single pulse (i.e., not cross-polarized) ^{15}N, ^{13}C, and ^{29}Si MAS NMR spectra of **7** (not shown) were observed to be identical with the cross-polarized spectra.

$$(CH_3)_2HSiNHSiH(CH_3)_2 + O=C(NH_2)_2 \rightarrow$$
$$\mathbf{6}$$
$$NH_3 + (CH_3)_2HSiNHC(=O)NHSiH(CH_3)_2 \quad (5)$$
$$\mathbf{7}$$

When it was heated to 210 °C, **7** decomposed to give a range of products, including NH_3, CH_4, $(CH_3)_2Si(H)$-

NCO, $(H_2N)_2CO$, HNCO, $(CH_3)_2SiH_2$, and the cyclic dimer $(HNCO)_2$, as determined by comparative analyses using TGA-MS and TGA-FTIR. The complexity of the mass spectra suggests that a number of linear and cyclic recombination products, such as the cyclodisilazane $[CH_3Si(H)NH]_2$, m/z 118, were formed, either during the thermal decomposition or following electron impact in the ionization source. By 440 °C **7** is lost completely due to what appears to be a single-stage, monotonic thermal decomposition as indicated by the TGA profile shown in Figure 2a. In a similar manner, the starting $[CH_3Si(H)NH]_n$ oligomer mixture decomposes to a 9% residue by 400 °C, as shown in Figure 2b.

The PUSZ obtained in the 6 $CH_3Si(H)NH/1(H_2N)_2C=O$ reaction was chosen for more detailed study. The ^{1}H NMR spectrum of 6:1 PUSZ, shown in Figure 3b, is quite similar to that of the $[CH_3Si(H)NH]_n$ cyclic oligomer mixture (Figure 3a) showing, in addition to the CH_3-Si signal (at 0.2 ppm) several peaks in the $Si-H$ region, but with slight peak broadening owing to the increased molecular weight and greater diversity of local structure in the polymer. The resonance in the ^{1}H NMR spectrum of the methylhydridocyclosilazane oligomers (Figure 3a) due to the SiH_2CH_3 group (at 4.45 ppm) was retained in the ^{1}H NMR spectrum of the 6:1 PUSZ (Figure 3b), which is in agreement with the process shown in eq 2 (i.e., reaction with urea involves the Si–N, not the Si–H bonds). Confirmation of this observation also provided by the ^{29}Si MAS-NMR spectrum of the 6:1 PUSZ (Figure 4) which clearly shows a signal due to SiH_2 functionality at -30 ppm, in addition to the $Si-H$ signal at -20 ppm.

The integration of urea into the methylcyclosilazane may be investigated directly by ^{13}C NMR spectroscopy or by the use of labeled ureas such as $(H_2 {}^{15}N)_2CO$ or $(H_2N)_2{}^{13}CO$. Figure 5a shows the ^{13}C MAS NMR spectrum of unlabeled 6:1 PUSZ. The signals observed
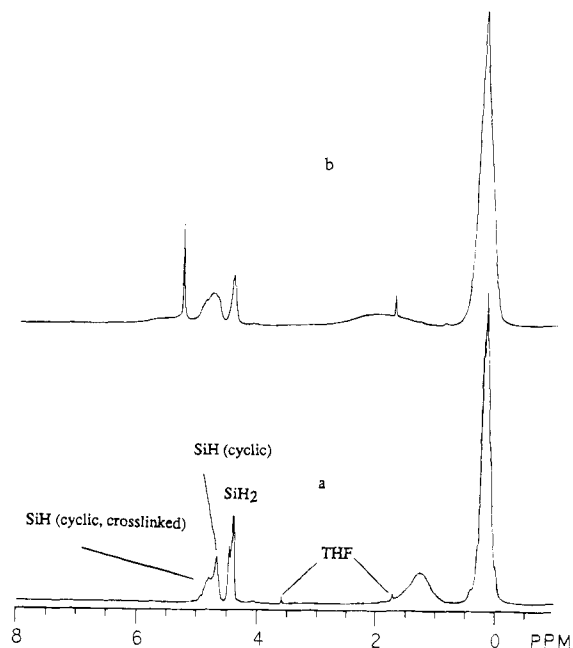
Figure 3. ¹H NMR spectra of (a) [CH₃Si(H)NH]ₙ oligomer mixture and PUSZ (6:1 CH₃Si(H)NH/urea).
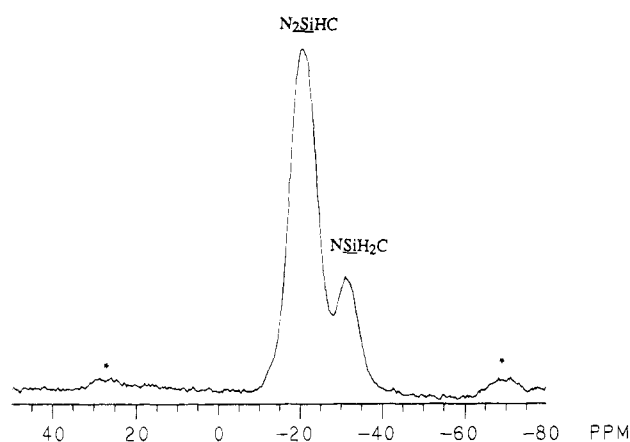
Figure 4. ²⁹Si MAS NMR spectrum of 6:1 CH₃Si(H)NH/urea PUSZ. Spinning sidebands are marked with an asterisk.

Figure 5. ¹³C MAS NMR spectra of (a) 6:1 CH₃Si(H)NH/urea PUSZ and (b) same polymer prepared using (H₂N)₂ ¹³CO; (c) ¹³C CPMAS NMR spectrum and (d) liquid-state ¹³C NMR spectrum of the same PUSZ (¹³C-labeled urea). Spinning side bands are marked with an asterisk.

Figure 6. DRIFT spectrum of 6:1 CH₃Si(H)NH/urea PUSZ.

at 5 and 165 ppm indicate the presence of CH₃–Si and ureido C=O carbon atoms, respectively. On the basis of natural abundance ¹³C NMR data alone, the urea incorporation appears to be straightforward, without side reactions. However, on investigating the ¹³C(urea)-labeled 6:1 PUSZ (Figure 5b), a third carbon peak was observed near 125 ppm. This peak indicates that some side reaction did occur and suggests the presence of isocyanate or, less likely, some other double-bonded carbon atom in the polymer. The ¹³C CPMAS NMR spectrum of the ¹³C(urea)-labeled PUSZ (Figure 5c) clearly exhibits significant signal enhancement for the 165 ppm peak but not for the 125 ppm peak. This observation also suggests that the latter peak is due to a carbon atom that is not directly protonated, which is in line with the NCO assignment. The local structural diversity at the site of urea incorporation in the 6:1 PUSZ is further evident in the liquid state ¹³C NMR spectrum (Figure 5d). The apparent, slight shift of the peak between the solid- and liquid-state spectra is due to solution effects, as well as the external referencing of the solid state data (vs internal referencing for the liquid-state data). This spectrum also suggests the
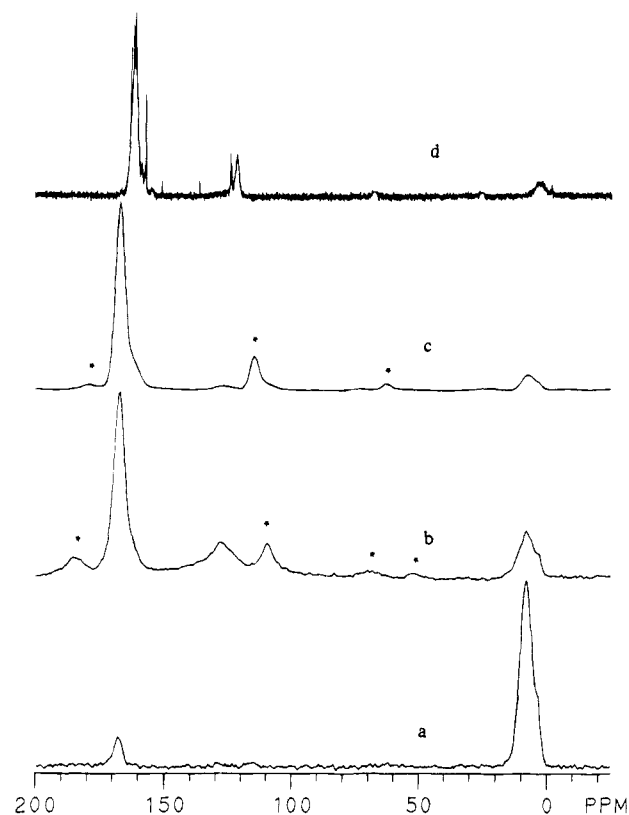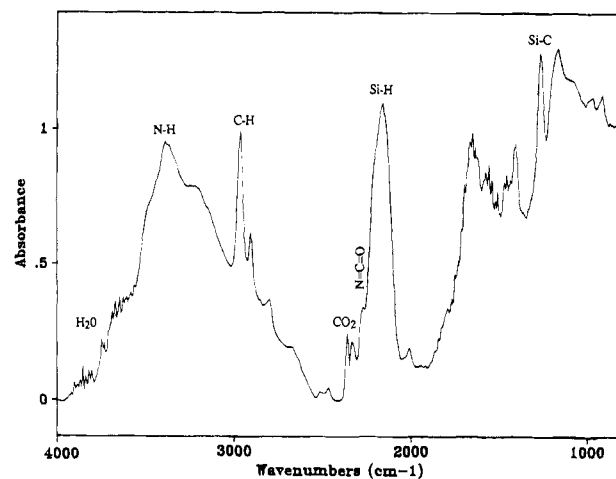
presence of a small amount of unreacted urea, as indicated by the very sharp peak at 161 ppm. These observations, it should be noted, would not have been possible from natural-abundance ¹³C NMR studies alone.

Further support for the presence of NCO functionality in 6:1 PUSZ (most likely formed from minor thermal decomposition of the PUSZ during the preparative reaction in refluxing pyridine for 24 h) is evident from the DRIFT spectrum of the polymer (Figure 6). The NCO band is observed at 2270 cm⁻¹ as a shoulder on the large Si–H adsorption at 2160 cm⁻¹. (The NCO band of silyl isocyanates is in the region 2275–2297 cm⁻¹.[10a] The low NCO concentration in the polymer
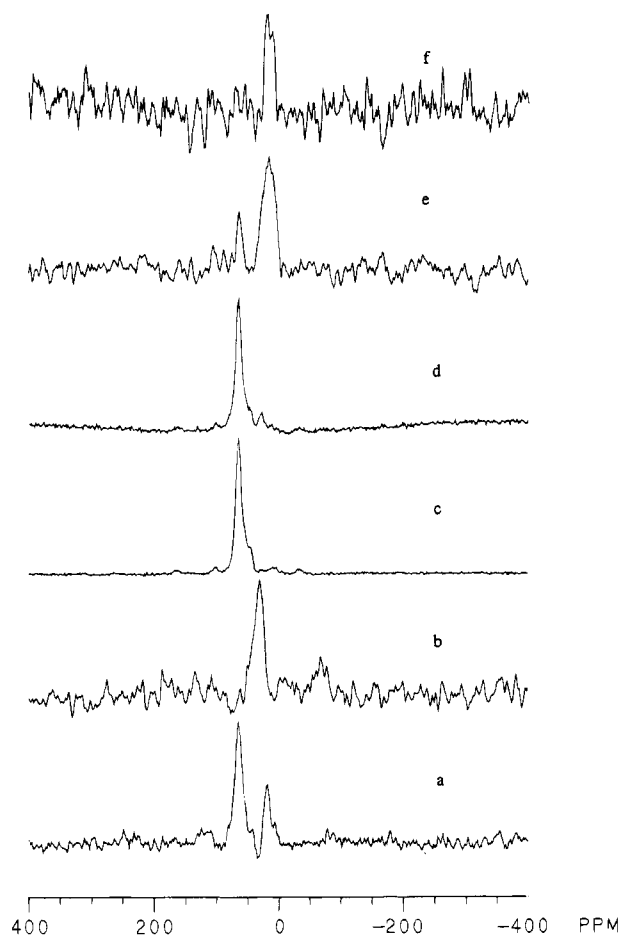
Figure 7. (a) Proton-decoupled and (b) proton-coupled ^{15}N MAS NMR spectra of ^{15}N-labeled (urea) 6:1 CH$_3$Si(H)NH/urea PUSZ; (c) 1 ms and (d) 5 ms contact time ^{15}N CPMAS NMR spectra of ^{15}N-labeled (urea) 6:1 CH$_3$Si(H)NH/urea PUSZ; (e) ^{15}N CPMAS NMR spectrum of unlabeled 6:1 CH$_3$Si(H)NH/urea PUSZ; (f) of KH cross-linked methylhydridopolysilazane.

Figure 8. TGA weight loss trace (10 °C/min) for 6:1 CH$_3$Si-(H)NH/urea PUSZ in a flow of nitrogen.

along with the large overlapping Si–H absorption could preclude unambiguous assignment of the NCO band on the basis of the DRIFT data alone.

The structural characterization of the ureido nitrogen in the 6:1 PUSZ was investigated directly using a PUSZ sample prepared using (H$_2$^{15}N)$_2$CO, as indicated by the proton-decoupled ^{15}N MAS NMR spectrum of the ^{15}N-labeled polymer (Figure 7a). This spectrum indicates the presence of at least two species as evidenced by peaks at 65 and 18 ppm. When the ^{15}N MAS NMR spectrum of this polymer was acquired without proton decoupling (Figure 7b), only a single, new peak was observed at 40 ppm. This suggests that the nitrogen atom in the species responsible for this signal is not directly protonated, and it may, in fact, be separated by several bonds from a proton-bearing atom, as opposed to the species giving rise to the peaks at 65 and 18 ppm. These have been broadened into the baseline in Figure 7b owing to dipolar coupling to directly bound protons or protons on adjacent (SiH$_x$) groups in the polymer. Such a nitrogen atom is that in an NCO group, so this observation provides further, although indirect, evidence for the presence of NCO functions in the 6:1 PUSZ. This rationale is further supported by the ^{15}N CPMAS NMR spectra of the 6:1 PUSZ shown in Figure 7c,d. Upon comparing the spectra acquired using short and long CP contact times (1 and 5 ms, respectively), the 65 ppm
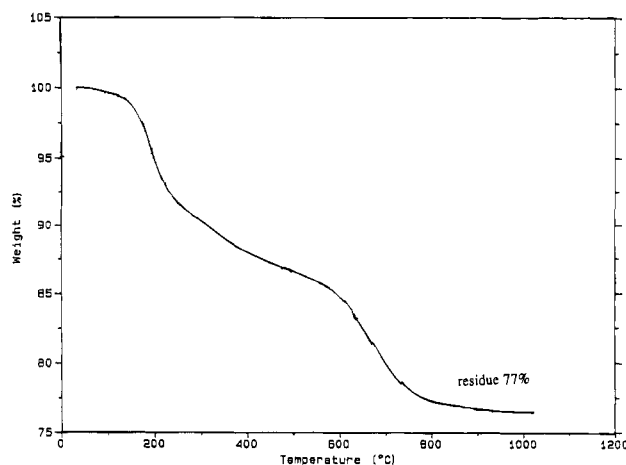
peak is enhanced under both conditions, whereas the 40 ppm peak is only significantly enhanced at long contact times, suggesting that this latter species either is more mobile (if directly protonated) or, more likely, is enhanced by protons on adjacent nuclei, as opposed to directly bonded protons. The formation of Si–NCO linkages must occur by thermal chain cleavage as shown in eq 2. However, the H$_2$NSi(H)(CH$_3$)-terminated fragment also formed surely would condense with SiNH$_2$ or SiNHSi groups in other polymer molecules, increasing the molecular weight.

The information gained from the ^{15}N-labeling experiment discussed above facilitates the interpretation of the natural abundance ^{15}N CPMAS NMR spectrum of unlabeled 6:1 PUSZ, shown in Figure 7e. Nitrogen atoms associated with the ureido carbonyl group give rise to the peak at 65 ppm, while the backbone silazane nitrogen atoms give rise to the peak envelope centered around 20 ppm. It is interesting to note that these latter peaks were barely evident in the data acquired on labeled PUSZ, showing how isotope labeling studies can be employed to focus on the local structure about the urea insertion sites. Further support for the above assignments is shown in Figure 7f, the natural abundance ^{15}N MAS NMR spectrum of the unlabeled polysilazane prepared by KH-catalyzed dehydrogenative condensation of the cyclic [CH$_3$Si(H)NH]$_n$ oligomers. This polymer does not contain ureido linkages and exhibits only an envelope at 20 ppm due to the nitrogen atoms in the polysilazane units.

Pyrolysis of the Poly(ureidosilazanes). As noted in the section on synthesis and preceramic polymer studies, pyrolysis of the PUSZ results in formation of silicon-containing ceramics in high yield. Figure 8 shows the thermogravimetric analysis trace of the 6:1 PUSZ (heated in nitrogen to 1000 °C). The two-step thermal decomposition profile is similar in shape to that of the polysilazane obtained in the KH-catalyzed polymerization of cyclic [CH$_3$Si(H)NH]$_n$ oligomer mixture.[4,15] The lower degree of cross-linking of the PUSZ is evidenced in the higher weight loss (15%) to 500 °C relative to that of the KH-derived polysilazane (3%), owing to the high amount of linear content of the PUSZ. Stacked FTIR plots (Figure 9) and mass spectra of the
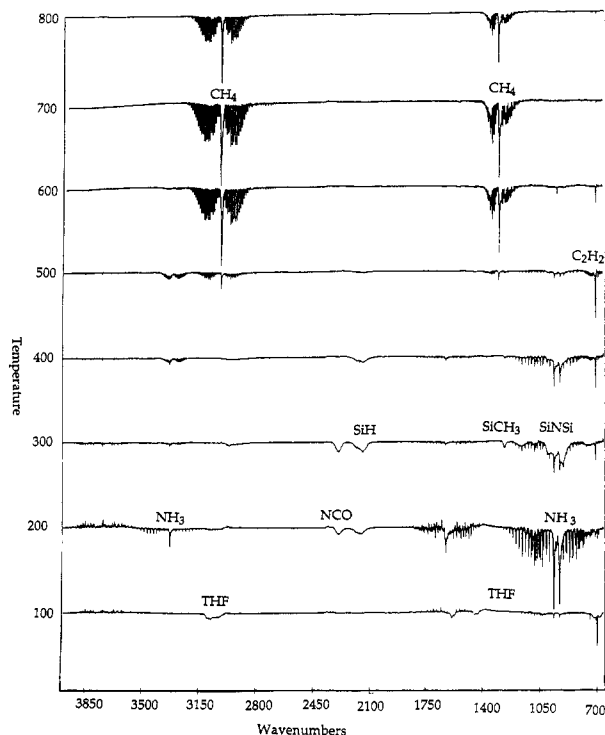
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(15) Han, H.; Lindquist, D. A.; Haggerty, J. S.; Seyferth, D. *Chem. Mater.* **1992,** *4,* 705.

Figure 9. TGA-FTIR spectra of volatiles evolved from the 6:1 CH₃Si(H)NH/urea PUSZ at temperatures ranging from 100 to 800°C.

gaseous products evolved during pyrolysis under nitrogen serve to clarify the TGA findings. Between 100 and 500 °C, the spectra in Figure 9 show significant losses of silicon-containing species (with multiple Si—H bands centered around 2140 cm⁻¹, Si—CH₃ absorption at 1263 cm⁻¹, and a broad SiNSi absorption centered at 900 cm⁻¹), as well as absorptions due to NH₃, NCO, C₂H₂, and residual solvent (THF). The above assignments were all corroborated by TGA-MS data, which also suggested evolution of minor amounts of (CH₃)₂Si(H)-NCO and CH₃SiH₂NCO.

The second step of the weight loss profile (∼500 °C), involving primarily methane evolution due to methyl group cleavage, is virtually identical to that of the KH-derived polysilazane. Both TGA/FTIR (Figure 9) and TGA/MS data confirm that only CH₄ and trace amounts of acetylene are evolved at temperatures exceeding 500 °C. The evolution of H₂, which must have been a major gaseous product, was not monitored.

The ceramic product obtained in PUSZ pyrolysis under nitrogen or argon is amorphous to 1400 °C. In fact, heating at 1500 °C for 8 h failed to induce crystallization of Si₃N₄ or SiC. As shown previously,[13] the pyrolytic phase evolution in these systems can be informatively interrogated using single-pulse and CP-MAS NMR spectroscopy. Figure 10 shows the ¹³C CPMAS NMR spectra of the solids obtained when ¹³C-(urea)-labeled, 6:1 PUSZ was heated for 1 h at 200, 500, and 800 °C. Single-pulse ¹³C MAS NMR data (not shown) show a large probe background signal and provide little additional information. The isotropic chemical shift peaks in Figure 10a are at 165, 125, and 5 ppm, as deduced from variable spinning speed data (not shown). These peaks correspond to urea C=O, —C=C—, or — C=N— and Si—CH₃ moieties, respectively. After the sample had been heated to 500 °C
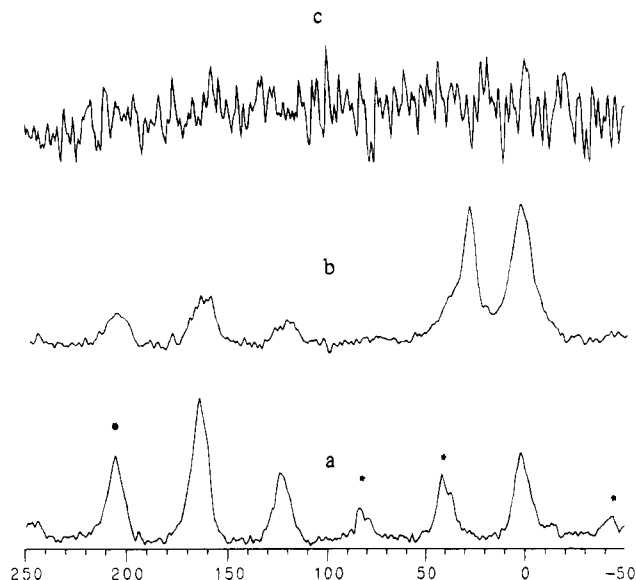

Figure 10. ¹³C CPMAS NMR spectra of ¹³C-labeled (urea) 6:1 CH₃Si(H)NH/urea PUSZ after 1 h pyrolysis at (a) 200, (b) 500, and (c) 800 °C. Spinning sidebands are marked with an asterisk.

there was loss of urea C=O functionality and new peaks appeared at 28 and 38 ppm. These correspond to amorphous SiC and preceramic SiCH$_n$/Si₃N₄, where n = 0, 1, or 2. These latter assignments are supported by variable cross-polarization contact time (2−19 ms) experiments, consistent with previous ¹³C NMR studies of SiC ceramics.[13,16] It is important to note that the loss of C=O functionality occurs primarily via volatilization as HNCO or RNCO species, as indicated by the TGA-FTIR and TGA-MS data. The urea C=O carbon is not involvled in SiCH$_n$/Si₃N₄ phase development, which occurs in a manner identical to that observed in the neat polysilazanes.[13] All methyl groups are lost upon pyrolysis to 800 °C as evidenced by the absence of any cross-polarizable carbon species as shown in Figure 10c. Single-pulse ¹³C MAS NMR data of the 800 °C pyrolysate simply show a broad peak at 25 ppm, due to amorphous SiC. From the ¹³C NMR data presented above, the complete loss of C=O functionality, coupled with hydrogen disproportionation and conversion to amorphous SiC can readily be observed as a function of pyrolysis temperature.

The ¹⁵N CPMAS NMR data obtained on pyrolysates of 6:1 PUSZ synthesized from (H₂¹⁵N)₂CO are shown in Figure 11. The 200 °C pyrolysate (Figure 11b) evidences a spectrum virtually identical to that shown in Figure 7c, with the main peak due to the ureido nitrogen atoms at 65 ppm. Upon heating to 500 °C, the main peak is replaced by one at 40 ppm, coincident with Figure 7b, lending further support to the previously discussed assignment of this peak to nondirectly protonated ureido nitrogen functionality. This transition probably results from both loss of methyl groups and reaction (cross-linking) of any remaining (cyclic or terminal) NH functionality. As with the ¹³C NMR data above, the 800 °C pyrolysate does not contain any appreciable NH as evidenced by a lack of observable ¹⁵N CPMAS NMR signal (Figure 11c). Single-pulse ¹⁵N NMR data for this

(16) Dando, N. R.; Tadayyoni, M. A. *J. Am. Ceram. Soc.* **1990**, *73*, 2242.
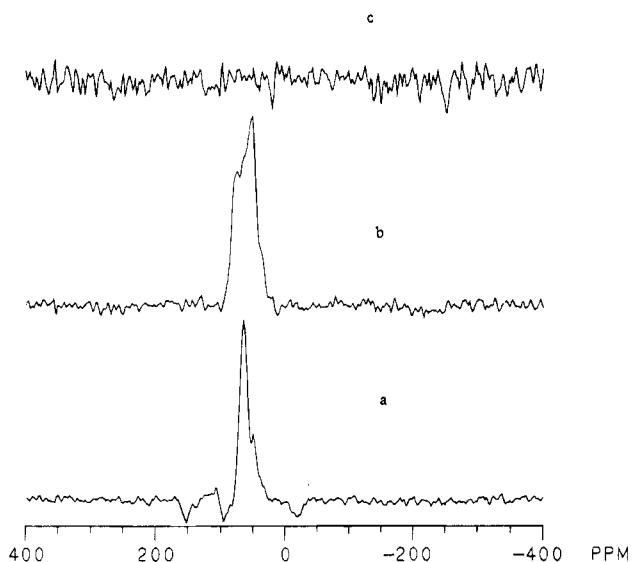
Poly(ureidosilazanes): Preceramic Polymeric Precursors

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Figure 11. ^{15}N CPMAS NMR spectra of ^{15}N-labeled (urea) CH$_3$Si(H)NH/urea PUSZ after 1 h pyrolysis at (a) 200, (b) 500, and (c) 800 °C.

pyrolysate showed a single broad peak, consistent with that expected for amorphous Si$_3$N$_4$. This observation indicates that the loss of NH functionality is due to volatilization (most likely as H$_2$, since no NH$_3$ was observed above 500 °C in the TGA-FTIR data) and conversion to Si$_3$N$_4$. After pyrolysis to 800 °C or higher, the MAS-NMR spectra of this system (^{15}N, ^{13}C, and ^{29}S) are virtually identical to those observed in neat polysilazanes (i.e., mixtures of amorphous SiC and Si$_3$N$_4$), as have been reported previously.[11,13]

Conclusions

This study has developed a simple procedure for converting the mixture of methylhydridocyclosilazane oligomers obtained in the ammonolysis of CH$_3$SiHCl$_2$ to material of higher molecular weight whose pyrolysis in a flow of argon, nitrogen, or ammonia gives silicon-containing ceramics in high yield. These products, shown by spectroscopic techniques to be poly(ureidosilazanes), are isolated as oils, gums, or white solids, depending on the CH$_3$Si(H)NH/urea ratio used in their synthesis. This brings useful flexibility in their applications in ceramics processing. Another potential advantage is that the poly(ureidosilazanes) do not contain alkali-metal or transition-metal ions. These polymers should find useful application in ceramics fabrication.

Experimental Section

Synthesis. *Synthesis of the Cyclo-[CH$_3$Si(H)NH]$_n$ Oligomer Mixture.* A 3 L, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dry Ice condenser, and a rubber septum was charged with 2 L of diethyl ether (distilled from sodium benzophenone ketyl) and 200 mL of CH$_3$SiHCl$_2$ (distilled from Mg chips) (d_4^{20}) = 1.195 g/cm^3, 1.92 mol). The solution was cooled in an ice bath. Ammonia (dried by passing it through a tower filled with anhydrous KOH) was bubbled into the cold, stirred solution at such a rate that a gentle reflux of ammonia was maintained. Ammonium chloride precipitated during the course of the addition. Completion of the reaction was evidenced by an increase in the ammonia reflux rate and at that point the addition of ammonia was stopped. The reaction mixture (maintained under dry nitrogen) was allowed

to warm to room temperature overnight. The reaction mixture then was filtered under nitrogen through a Schlenk (fritted) filter. The separated NH$_4$Cl was washed with several portions of ether (1 L total). The combined ether solutions were distilled (trap-to-trap) at reduced pressure to remove solvent. The residue was maintained in high vacuum at room temperature for 3 h to remove residual volatiles. The yield of liquid residue, the methylhydridocyclosilazane oligomers, was in the range 80−85%. For product characterization, see refs 4 and 13. Note that this product contains some SiH$_2$CH$_3$ functionality.

Reaction of 1,1,3,3-Tetramethyldisilazane with Urea. A 100 mL, three-necked flask equipped with a reflux condenser topped with a gas inlet/outlet tube connected to the Schlenk line, a stir-bar, and two septa was charged with 1.2 g (20.0 mmol) of urea and 11.0 g (82.6 mmol) of the disilazane. The mixture was stirred and heated at reflux for 5 h. Subsequently, all volatiles were removed in vacuo, leaving 2.6 g of a white solid, *N,N'*-bis(dimethylsilyl)urea. The product was purified by sublimation at 100 °C at 0.1 Torr. NMR data are shown in the Results and Discussion sections. IR (principal bands, cm^{-1}) 3432, 3320 (NH), 2964, 2908 (CH), 2148 (SiH), 1654, 1607 (C=O), 1496, 1248 (SiCH$_3$). EI/MS (*m/z*, rel intensity): 175 (100, [M − H]$^+$), 173 (10, [M − 3H]$^+$), 161 ([M − CH$_3$]$^+$, 159 ([M − CH$_3$ − 2H]$^+$), 132 ([M − SiHCH$_3$]$^+$.

Reactions of the Methylhydridocyclosilazane Oligomer Mixture with Urea. 1. CH$_3$Si(H)NH/Urea Ratio = 4:1. The reaction apparatus described in the experiment above was charged with 1.2 g (20.0 mmol) of urea, 4.73 g (80.0 mmol of CH$_3$Si(H)NH units) of [CH$_3$Si(H)NH]$_n$ cyclic oligomer mixture and 40 mL of dry pyridine (distilled from calcium hydride). The mixture was stirred and heated at 85 °C under nitrogen for 24 h. Subsequently, the pyridine was removed in vacuo, and the residue was dissolved in 40 mL of dry diethyl ether. Removal of volatiles at reduced pressure left a white solid (4.9 g) which was soluble in pyridine and THF, less soluble in CHCl$_3$. Anal. Found: C, 22.29; H, 6.34; N, 20.81. Calcd assuming all of the urea reacted: C, 21.48; H, 7.57; N, 25.03. IR (principal bands, cm^{-1}) 3386 (NH), 2960, 2902 (CH), 2199 (SiH), 1664 (C=O, 1440, 1258 (SiCH$_3$)). Ceramic residue yield (TGA) 83%.

2. CH$_3$Si(H)NH/Urea Ratio = 6:1. The same procedure was used in the reaction of 0.8 g (13.3 mmol) of urea with 4.73 g (80.0 mmol of CH$_3$Si)H)NH units) of [CH$_3$Si)H)NH]$_n$ cyclic oligomer mixture in 40 mL of pyridine. A white solid (4.9 g) was isolated. This product was soluble in pyridine and THF, partially soluble in benzene, diethyl ether, and chloroform. Anal. Found: C, 22.75; H, 6.70; N, 24.09. IR (principal bands, cm^{-1}) 3394, 2958, 2898, 2276, 2194, 2142, 1654. Ceramic residue yield (TGA) 83%.

The same procedure was used in reactions of 6 mol equiv of CH$_3$Si(H)NH cyclic oligomer mixture with one of (H$_2$^{15}N)$_2$CO and (H$_2$N)$_2$^{13}CO.

3. CH$_3$Si(H)NH/Urea Ratio = 10:1. The same procedure was used in the reaction of 0.48 g (8.0 mmol) of urea with 4.73 g (80.0 mmol of CH$_3$Si(H)NH units) of the methylhydridocyclosilazane oligomer mixture in 40 mL of pyridine. A colorless gum (4.8 g) remained after removal of volatiles in vacuo. Anal. Found: C, 21.24; H, 6.85; N, 21.21. IR (principal bands, cm^{-1}) 3395, 2961, 2898, 2284, 2134, 1653. Ceramic residue yield (TGA) 82%.

4. CH$_3$Si(H)NH/Urea Ratio = 12:1. The same procedure was used in the reaction of 0.40 g (6.7 mmol) of urea with 4.73 g (80.0 mmol of CH$_3$Si(H)NH units) of methylhydridocyclosilazane oligomer mixture in 40 mL of pyridine. Removal of volatiles left 4.9 g of a colorless gum. Anal. Found: C, 24.14; H, 7.09; N, 22.21. IR (principal bands, cm^{-1}) 3395, 2958, 2898, 2278, 2136, 1653. Ceramic residue yield (TGA) 78%.

5. CH$_3$Si(H)NH/Urea Ratio = 16:1. The same procedure was used in the reaction of 0.3 g (5.0 mmol) of urea with 4.73 g (80.0 mmol of CH$_3$Si(H)NH units) of methylhydridocyclosilazane oligomer mixture of 40 mL of pyridine. Removal of volatiles left 4.8 g of a colorless oil. Anal. Found: C, 21.35; H, 7.51; N, 22.76. IR (principal bands, cm^{-1}) 3392, 2959, 2903, 2136, 1654. Ceramic residue yield (TGA) 62%.

Reaction of [(CH₃)(CH₂=CH)₀.₂Si(H)₀.₈NH]ₙ Cyclic Oligomers with Urea. A solution of 1.2 g (20.0 mmol) of urea and 5.15 g (80.0 mmol of "monomer" units) of the title cyclosilazane mixture (prepared by coammonolysis of CH₃SiHCl₂ and CH₃-(CH₂=CH)SiCl₂) in 40 mL of pyridine was stirred under nitrogen at 85 °C for 24 h. After removal of the pyridine at reduced pressure, 40 mL of ether was added to the residue. Subsequent removal of volatiles left 5.0 g of a white solid. It was soluble in most organic solvents and melted on being heated. Anal. Found: C, 26.44; H, 6.42; N, 22.67. IR (principal band, cm⁻¹) 3386, 3050, 2958, 2902, 2212, 1661. Ceramic residue yield (TGA) 79%.

Pyrolysis of the Poly(ureidosilazanes). Bulk pyrolyses to 1000 °C were carried out using a Lindberg Model 59344 tube furnace equipped with a Eurotherm Model E5 controller and a quartz tube. Pyrolyses to 1400 and 1500 °C were performed using a Lindberg Model 59545 tube furnace equipped with a Eurotherm E5 controller and a mullite tube. Samples were placed in a graphite boat on a 6-in. aluminum tube inside the mullite tube. The furnace initially was purged with argon for 30 min before the sample was introduced and then purged for an additional 30 min before pyrolysis was begun.

1. Pyrolysis under Argon. A 1.0 g sample of the PUSZ was charged into an alumina boat and placed in the argon-flushed tube furnace. Argon was passed through the furnace at a rate of about 100 mL/min while the sample was heated from room temperature to 250 °C at a rate of 5 °C/min. After a hold at 250 °C for 1 h, further heating to 1000 °C (under argon) at 5 °C/min followed. The sample then was kept at 1000 °C for 2 h. Subsequently, the sample was allowed to cool to room temperature (under argon) and transferred to a boron nitride boat which was placed in the 1500 °C furnace in a mullite tube. Further heating at 10°C/min under argon to 1400 °C followed, with a terminal 4 h hold at that temperature. The final ceramic product was a black solid which XRD showed to be amorphous. For experimental details (ceramic residue yields, analyses), see Tables 1 and 2.

2. Pyrolysis under Ammonia. A 1.0 g sample of the PUSZ (6:1) was charged into an alumina boat and placed into an argon-flushed tube furnace. Gaseous ammonia (dried by passing it through a tower of anhydrous KOH) was passed through the tube at a rate of 50 mL/min while the sample was heated to 250 °C at a rate of 5 °C/min. After a 1 h hold at 250 °C, the sample was heated under a flow of ammonia to 1000 °C at 5 °C/min and was kept at 1000 °C for 2 h. The sample was allowed to cool to room temperature in a stream of argon; at this point it was grayish-white in color. This material then was transferred into a BN boat which was placed in a mullite tube in a tube furnace and heated under a stream of argon to 1400 °C at 10 °C/min. It was heated at 1400 °C for 4 h. The residue generally was gray-black in color. XRD showed it to be amorphous. Experimental details (ceramic residue yields and ceramic element analyses) are given in Tables 1 and 2.

In later experiments, 20.0 g samples of PUSZ were heated at 7.5 °C/min from room temperature to 200, 500, and 800 °C under argon or ammonia and held at the respective temperature for 1 h or more before ramping the oven back to room temperature.

Characterization. Thermal analyses (TGA) were performed under flowing argon or nitrogen using a Perkin Elmer

TGS-2 or a duPont Model 9900 system at a heating rate of 10 °C/min to 950 °C. Ceramic residue yield (%) = weight of residue/weight of sample × 100. TGA-MS analyses were performed on a TA Instrument 951 interfaced with a VG quadrupole mass spectrometer. Samples were heated at a rate of 20 °C/min. Diffuse reflectance FT infrared (DRIFT) spectra were acquired using samples that had been ground in an agate mortar and pestle on a Digilab FTS-60 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector and Harrick DRA Praying Mantis accessory. All DRIFT spectra were acquired at 4 cm⁻¹ resolution.

NMR analyses were performed using a GE GN-300 wide bore instrument with a 7.05 T cryomagnet and Chemagnetics solids accessories. ²⁹Si, ¹³C, and ¹⁵N spectra were acquired at 58.6, 75, and 30.4 MHz, respectively. Liquid-state NMR spectra were acquired of sample solutions in THF-d₈. Quantitative data were ensured by first measuring spin–lattice relaxation times and employing relaxation delays ≥5 T_1. All solid-state magic angle spinning (MAS) NMR data were acquired under conditions of gated high-power decoupling at sample spinning rates of 4 kHz. The magic angle was adjusted using the ⁷⁹Br resonance of KBr.[17] ¹H, ¹³C, and ²⁹Si chemical shift values are referenced to external tetramethylsilane. ¹⁵N chemical shift values are referenced externally to glycine.

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku RU 300 (Cu Kα radiation) instrument. Samples were finely ground in an alumina mortar and pestle, slurried in acetone, and spread on glass slides. Diffraction analyses were performed in step-scan mode at 55 kV and 250 mA power settings. The starting angle was 10° and the stopping angle 90°, with a 0.02° step and 1-s counting time. Elemental analyses of the polymers were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark; elemental analyses of ceramic samples by Galbraith Laboratories, Knoxville, TN. Gas-phase IR spectra of the thermolysis volatiles were obtained using an IBM Model IR-85 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. Powder samples were heated at a rate of 10 °C/min inside a short section of silica tube inside a small tube furnace under 10 cm³/min flow of dry nitrogen. The silica tube was connected to a 12 cm long gas cell in the FTIR beam path.

(17) Frye, J.; Maciel, G. *J. Magn. Reson.* **1982**, *48*, 125.