Pyrolysis Chemistry of Poly(organosilazanes) to Silicon Ceramics

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The thermal evolution of a commercial and an in-house-prepared organosilazane polymer to silicon nitride and silicon carbide was examined systematically for temperatures up to 1400 °C. Characterization methods employed include thermal gravimetric analysis, X-ray powder diffraction, infrared spectroscopy, BET nitrogen surface area, solution ^1H and ^{29}Si NMR spectroscopy, cryoscopic and viscosimetric molecular weight determinations, and elemental analysis. In addition, the volatile gaseous pyrolysis byproducts were analyzed by gas-phase infrared spectroscopy and mass spectrometry. The commercial polymer, which shows enhanced solubility due to its lower fraction of higher molecular weight material and limited cross-linking, has a decreased pyrolytic ceramic yield due primarily to loss of volatile silazane species between 300 and 600 °C. This decreased yield can be offset by the addition of small quantities of a trichlorosilane prior to pyrolysis. The major gaseous byproduct from both polymers is methane which is evolved at temperatures greater than 450 °C. Under nitrogen and forming gas pyrolysis atmospheres there is evidence for some methylene bridge forming reactions. These phases are not found when an ammonia atmosphere is used in the pyrolyses.

Introduction

Silicon nitride and silicon carbide are important structural materials based on their resistance to corrosion under severe thermal and chemical environments, high hardness, low density, good thermal shock resistance, and retention of mechanical strength at elevated temperatures.[1,2] Some applications derived from these attributes include high-speed cutting tools, heat exchangers, abrasives, engine components, oxidation-resistant coatings, and furnace fixtures and heating elements.

The use of powders as precursors for either reaction-bonded or hot-pressed silicon ceramics limits the possible size and configuration of ceramic parts attainable. Preceramic polymers offer certain processing advantages over traditional powder metallurgy methods due to their rheology, solubility, low decomposition temperatures, and the ability to tailor the microstructure of the ceramic product. Polymers offer particular promise for specialty forms such as fibers and coatings which are essentially unattainable by conventional methods.

Until recently, preceramic polymer research has focused largely on polymer design and synthesis, in order to achieve high ceramic yields on pyrolysis as well as the desired ceramic material. Recent studies are beginning to probe the thermochemical evolution of preceramic polymers at intermediate temperatures during the polymer-to-ceramic conversion. Blum and co-workers followed the pyrolysis of polysilazanes using TGA and various mass spectral techniques.[3] The silazanes were synthesized by the reaction of organosilicon hydrides with ammonia under heat and pressure in the presence of a metal carbonyl catalyst. They noted the loss of a mixture of volatile silazane species up to 450 °C along with SiH_4 and methylamine. At higher temperatures, methane was evolved along with other hydrocarbons. The loss of silazanes was attributed to retroversion reactions in which additional cross-linking of the solid occurs during heating at the expense of volatile silazane compounds. The gaseous pyrolysis products of the silazanes formed by the reaction of hydrazine with diorganodichlorosilanes were investigated by Colombier using mass spectrometry.[4] In addition to hydrazine, the major species detected were CH_3SiH_3 (300 °C), NH_3 (250–500 °C), CH_4 (400–1000 °C), and H_2 (maximum at 800 °C).

Polysilazanes formed by the prolonged heating of hexamethyldisilazane and trichlorosilane mixtures were studied by Legrow et al.[5,6] A wide variety of ceramic characterization techniques was employed in the processing of these polysilazanes to ceramic fibers. During pyrolysis, volatiles including $(CH_3)_3SiCl$, NH_3, and silazane oligomers (300–500 °C); $(CH_3)_3SiH$, CH_4, and H_2 (500–700 °C); and CH_4 and H_2 (>700 °C) were evolved. Burns and co-workers[7] studied the pyrolysis of a number of silsesquiazanes, $(RSiNH_{1.5})_n$, formed by the reaction of ammonia with a variety of monosubstituted organosilanes. The organic pyrolysis volatiles were identified and quantified by GC/MS methods. Their results supported a thermal decomposition route involving Si–C bond cleavage. Ammonia and oligomeric species were not identified in the study. Peuckert and co-workers, using mass spectrometry, have analyzed the thermal decomposition volatiles evolved from a polysilazane similar in composition to the polymers investigated in this study.[8] The detected species were similar to our findings. The detected species were silazane compounds (200–500 °C), CH_4 and NH_3 (400–700 °C), and H_2 (300–800 °C). In addition to these systems, a number of other silazanes are receiving attention as ceramic precursors.[9-13] Detailed investigations of the pyrolysis

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chemistry of some other nonoxide preceramic polymer systems include, among others, polycarbosilanes (SiC),[14] polyborazenes (BN),[15-16] and aluminum–nitrogen polymers (AlN).[17,18]

The two polysilazanes investigated in the present work have been suggested to have a network structure formed by ring fusion of cyclic $[CH_3(H)SiNH]_n$ oligomers.[19] They are prepared by a three-step process involving ammonolysis of methyldichlorosilane to form a mixture of cyclic silazanes followed by a treatment of the latter with a catalytic amount of KH and, finally, quenching with an electrophile (CH_3I or a chlorosilane).[19-21] One of the two polysilazanes was obtained from the Ethyl Corp.,[22] and the second was prepared in-house as described in the Experimental Section.

The present study was undertaken to further clarify the details of the pyrolysis chemistry of the silazanes and the nature of the ceramic product formed under inert and reducing firing atmospheres. In addition, the subtle differences between the two preceramic polymers served to elucidate some of the factors affecting ceramic yield based on differences in pyrolysis chemistry.

Experimental Section

Polymers. The two polysilazanes used in this study are designated as A and B. Polymer A, prepared by a variation of our in-house procedure,[19-21] was donated by Ethyl Corp., Baton Rouge, LA.

Polymer B was prepared in-house by a similar process using a variant of a method described previously.[19-21] Freshly distilled methyldichlorosilane (CH_3SiHCl_2, 30 mL, 0.29 mol) was dissolved in 300 mL of dry THF (distilled from sodium benzophenone ketyl) in a three-necked flask equipped with a magnetic stirrer, dry ice reflux condenser, and a dry nitrogen bubbler purge. The flask was cooled in an ice bath and an excess of anhydrous gaseous ammonia was bubbled through the solution for 2 h. During this time, the flask was shaken periodically to break up the copious precipitate of NH_4Cl. Completion of the slightly exothermic reaction was indicated by a cooling of the flask from the condensing ammonia.

The supernatant solution was removed from the solid NH_4Cl using a Schlenk fritted glass filter. The salts were washed with a fresh portion of dry THF and filtered again to extract the remainder of the silazane. The silazane solution then was transferred slowly by cannula to a Schlenk flask equipped with a reflux condenser and containing the KH catalyst (0.064 g, 1.6 mmol). Evolution of hydrogen gas was immediate. After 15 min of stirring at room temperature, the clear solution was heated at reflux for 2 h. Longer reflux times result in increasingly less soluble cross-linked polymers. After this was cooled to room temperature, methyl iodide (0.16 mL, 1.6 mmol) was added to the solution to quench the "living" polymer which contained potassium amide functions. The solvent was removed under vacuum. The solid residue was redissolved in 100 mL of hexane, and the KI precipitate removed by centrifugation. Vacuum evaporation of the solvent yielded 13 g of polysilazane B (78% yield based on CH_3SiHCl_2), a white solid. The polymer formula was determined by ^1H NMR spectroscopy (see results section).

As a precaution, both polymers were stored in either a desiccator or a drybox when not in use. However, the prepared solid polymers are stable in air for a limited time[19] and were handled in air during transfers to furnaces, spectrometers, etc.

Pyrolysis Studies. The pyrolyses were conducted in one or more of the following instruments: (1) a CM Furnaces rapid temperature, horizontal tube furnace Model 1625, (2) a Netzsch TGA/DTA Model STA-429, and (3) a Perkin-Elmer TGA Model TGS-2. All pyrolyses were performed under precisely controlled Matheson Gas Products atmospheres, whether inert (ultrahigh purity, UHP, N_2) or reactive (95%/5% N_2/H_2 (forming gas) or 99.999% NH_3). The gas flow rate was maintained at approximately 60 cm^3/min except for the gas-phase IR experiments, which were measured at a gas flow rate of 10 cm^3/min. All of the polymer samples were pyrolyzed as loose powders.

Gas-phase IR and mass spectra of thermolysis volatiles were obtained using an Ametek Model M200 mass spectrometer (ionization voltage 30 eV) coupled with a Model IR-85 IBM FTIR spectrometer, with a liquid N_2 cooled mercury cadmium telluride detector. Powder samples (50 mg) were heated to 1000 °C at a rate of 10 °C/min inside a short section of 1-cm-diameter fused silica tube in a small tube furnace under a 10 cm^3/min flow of dry nitrogen atmosphere. The silica tube outlet was connected to a 1-mm-diameter by 12-cm-long gas cell in the IR beam path. The mass spectrometer capillary probe was inserted at the outlet of the beam path in order to obtain IR spectra and mass spectra simultaneously.

General Characterization Procedures. Powder X-ray diffraction measurements were made using a Model RU-300 Rigaku diffractometer (Cu Kα radiation). Samples were finely ground in an alumina mortar and pestle, slurried in acetone, and spread on glass slides. Diffraction was performed in step scan mode at 55 kV and 250 mA power settings. The starting angle was 10° and the stopping angle was 90°, with a 0.02° step and a 1-s counting time.

The possible presence of potassium which might remain in the polymers after workup was checked by atomic emission spectroscopy on an Ebert 3.4 Meter spectrometer. (None was present.)

Solids IR spectra were obtained on a Model IR-44 IBM Fourier transform infrared (FTIR) spectrometer. The samples were prepared by finely grinding the pyrolytic residue with potassium bromide (KBr) in an alumina mortar and pestle and then pressing into pellets.

Cryoscopic molecular weight determinations were made using 17 wt % polymer solutions in rigorously dried benzene. Viscosity measurements were taken at four polymer concentrations in THF using an Ostwald viscometer in a 25 °C constant-temperature bath.

Surface areas of solids were determined on an Quantasorb Instrument (Quantachrome Corp.) by single-point BET at N_2 P/P_0 = 0.30 after outgassing at 250 °C for 3 h.

Proton NMR spectra were measured in $CDCl_3$ solutions using a Bruker Instruments AC 250-MHz spectrometer. Silicon NMR for polymer A was measured in C_6D_6 solution with a TMS standard on a Varian 300-XL spectrometer.

Elemental analyses of the unpyrolyzed polysilazanes were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. Elemental analyses of the pyrolyzed solids were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

The approximate formula for polymer B as determined by ^1H NMR spectroscopy is $(CH_3SiHNH)_{0.32}(CH_3SiNHCH_3)_{0.02}(CH_3SiN)_{0.66}$.[23] The approximate formula for A as determined by a combination of ^1H and ^{29}Si NMR spectroscopy is $(CH_3SiHNSi(CH_3)_3)_{0.14}(CH_3SiHNH)_{0.58}(CH_3SiN)_{0.28}$.[23] The (CH_3SiN) functionality represents cross-linking sites, i.e., silicon atoms that are linked to three

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[23] Polymer A: ^1H NMR (250 MHz, $CDCl_3$) δ 0–0.7 (br, 0.772 H, $SiCH_3$), 0.7–1.4 (br, 0.12 H, NH), 4.4–5.1 (br, 0.104 H, SiH). ^{29}Si NMR (300MHz C_6D_6) δ −11 to −14 (br, 0.073 Si, $Si(CH_3)_3$), −16 to −26 (br, 0.927 Si, $SiCH_3$, SiH). Polymer B: ^1H NMR (250 MHz, $CDCl_3$) δ 0–0.6 (br, 0.78 H, $SiCH_3$), 0.6–1.4 (br, 0.12 H, NH), 2.3–2.6 (br, 0.018 H, NCH_3), 4.5–5 (br, 0.084 H, SiH).

Table I. Characteristic IR Absorption Bands for Unpyrolyzed A and B

wavenumber, cm^{-1}	assignment
3400	N-H str
3000-2800	C-H str
2140	Si-H str
1550	$SiNH_2$ bend
1420	CH_3 asym str
1270	CH_3 sym str
1180-1140	N-H bend
1000-800	Si-N-Si and Si-C str

nitrogen atoms. Since B contains a greater percentage of this moiety per polymer unit, the relative degree of cross-linking in B is greater than in A. A contains $Si(CH_3)_3$ groups in lieu of NCH_3 functions because the quenching of the potassium amide containing "living" polymer was effected with trimethylchlorosilane rather than methyl iodide. In the case of the A polymer, it was not possible to assign a quantity to the contribution of trimethylsilyl groups from the quenching agent to the molecular formula by ^1H NMR as these resonances overlap with those of the other methylsilyl groups. However, using ^{29}Si NMR, it was possible to distinguish the contribution of $Si(CH_3)_3$ functions in A from the broad resonance due to the other silicon environments. The difference in the properties of polymers A and B might be partly attributed to the different quenching agents used. However, other factors such as reflux time in the presence of potassium hydride prior to quenching and choice of polymerization solvent (both of which were not known for polymer A) have a marked effect on the polymer properties.[19-21]

The greater cross-linked fraction in B is manifest as an increase in the solution viscosity and a decrease in solubility, but does not contribute to the freezing point depression. The intrinsic viscosity in THF was determined for A to be 10.8 mL/g and for B to be 28.1 mL/g. This result indicates that the weight average molecular formula for B should be, at minimum, greater than 2 times that of A. However, the number averaged molecular weights of the polymers were similar at approximately 1200 amu, as determined by cryoscopy in benzene. The solubility of the A polymer in THF or toluene is approximately 0.5 g/mL of solvent while that of B is about half of this value.

Elemental percent compositions for each of the polymers differ by less than 1% for Si, C, H, and N as determined by elemental analysis.[24] The discrepancy between the elemental composition calculated from the integrated ^1H NMR spectrum and elemental analysis data for polymer B is less than 1%. The discrepancy for polymer A based on its ^1H and ^{29}Si NMR derived formula and elemental analysis data is slightly greater. The polymers are essentially free of KH, KI, or KCl since atomic emission spectroscopy showed no evidence for the presence of potassium.

Although differences between the polymers can be detected by NMR and viscometry, little difference can be seen by elemental analysis, cryoscopy in benzene, or FTIR. Figure 4 (top spectrum) shows the IR spectrum of unpyrolyzed A. This spectrum is identical to that of polymer B. The assigned major absorptions[25] in the complex spectra are compiled in Table I. The weak NH_2 band at 1550 cm^{-1} is not seen in the IR spectra of the cyclic silazanes prepared by ammonolysis of CH_3HSiCl_2 prior to polymerization by KH catalysis. Other workers have noted this band in the IR spectra of silazanes prepared by an alternative method.[26] The persistence of this band in the solids IR spectra of the polymers fired under ammonia as opposed to a nitrogen atmosphere supports the assignment (vide infra).

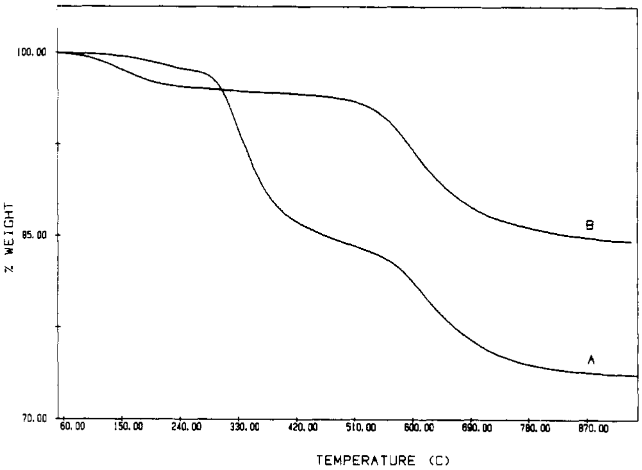

Figure 1. Weight retention TGA traces of A and B pyrolyzed to 950 °C at 10 °C/min under UHP N_2.

Table II. Total Weight Loss in A from TGA and Horizontal Tube Furnace Pyrolyses Based upon Original Polysilazane Sample Weight[a]

	weight loss, %		
temp, °C	under UHP N_2 (TGA/furnace)	under 95%/5% N_2/H_2 (TGA furnace)	under 99.999% NH_3 (furnace)
200	0.69/1.55	0.69/2.84	2.87
350	9.25/11.02	5.38/5.48	13.09
550	15.75/18.25	6.90/6.21	15.28
800	25.34/24.71	24.08/24.87	15.91
900	26.44/27.09	24.56/27.66	20.90
1000	NA/27.10	NA/27.69	22.36
1100	NA/27.15	NA/27.72	25.69
1200	NA/27.11	NA/27.78	27.39
1300	NA/27.46	NA/27.64	32.53
1400	NA/27.27	NA/27.84	33.19

[a] NA = not available.

Differences between the polymers arise in their thermal decomposition behavior. Figure 1 shows TGA traces for both polysilazanes heated from room temperature to 950 °C at 10 °C/min under UHP N_2. The primary difference is that B consistently yields approximately 10 wt % more ceramic residue. B exhibits only very gradual weight losses to 550 °C. A shows significant loss around 350 °C. These results are consistent with B having a higher degree of cross-linking. The weight losses between 550 and 900 °C for both polymers are quite close, ranging from approximately 11 to 13 wt %. Additional TGA traces, not illustrated here, obtained using a forming gas atmosphere, show similar ceramic yields for A and B as those measured under nitrogen.

More solids characterization data were obtained for polymer A than for B. It is believed that since both polymers behaved similarly during pyrolysis at the higher temperatures, the conclusions drawn from the A results can be applied to B.

Table II summarizes the weight loss results obtained for polymer A by TGA and in the tube furnace. As we have

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[24] Elemental analysis: polymer A 22.11% C (calcd for ^1H and ^{29}Si NMR derived formula 24.8%), 7.28% H (calcd 8.16%), 22.42% N (calcd 20.40%), 47.75% Si (calcd 46.6%). Polymer B 21.49% C (calcd for ^1H NMR derived formula 21%), 7.00% H (calcd 6.5%), 23.22% N (calcd 24%), 48.3% Si (calcd 48%).

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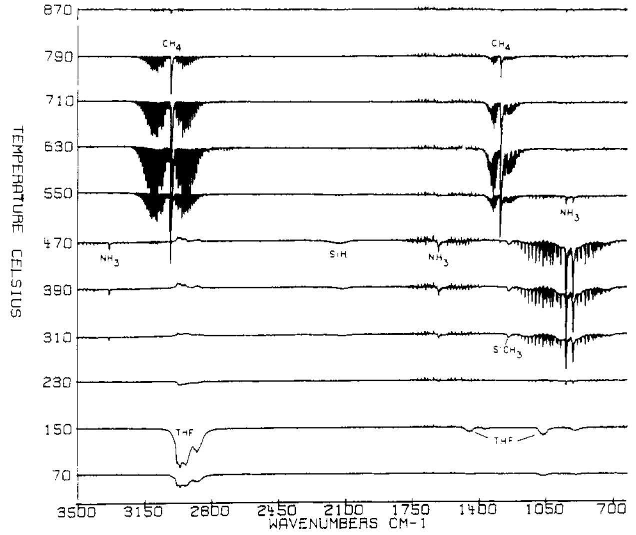

Figure 2. Stacked IR absorbance spectra of the gaseous products evolved during pyrolysis of B to 870 °C at 10 °C/min under N_2.

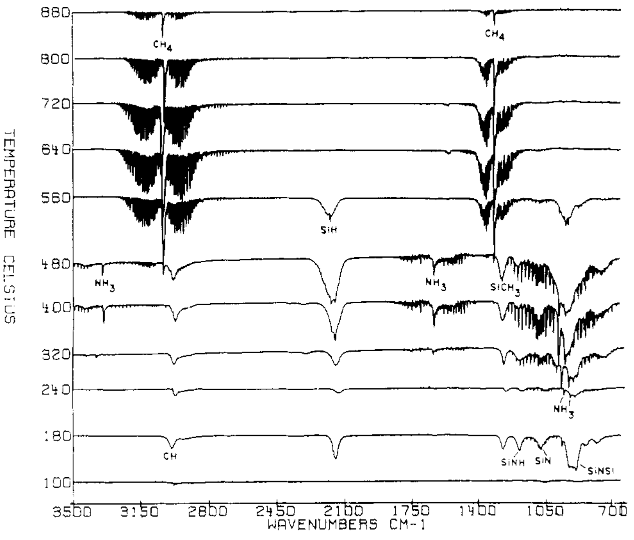

Figure 3. Stacked IR absorbance spectra of the gaseous products evolved during pyrolysis of A to 880 °C at 10 °C/min under N_2.

generally found, the ceramic yields in multigram tube furnace samples are slightly lower than in the TGA experiment. The pyrolyses performed in the tube furnace at 10 °C/min to 1400 °C show that most (99%) of A's weight loss is concluded after heating to 900 °C under UHP N_2 as well as under forming gas. However, pyrolyses performed in a stream of NH_3 in the tube furnace under the same conditions, indicate that only 64% of A's total weight loss is completed after heating to 900 °C. At 900 °C the ceramic yield of A under ammonia is 79% as compared to 73% under N_2. At 1400 °C the yield is reduced to 67% in ammonia and 72% under N_2 or forming gas. This delay in weight loss in an ammonia atmosphere may be the result of the formation of amino functions in the solid which are progressively lost at temperatures greater than 900 °C. The ceramic residues obtained under ammonia were shiny, translucent, glassy solids. Those obtained under N_2 or forming gas were shiny black solids.

Elemental analyses of polymer A samples pyrolyzed to 1400 °C under N_2 and under forming gas found carbon contents of 14.67 and 14.17 wt %, respectively.[27] However, in A pyrolyzed to 1400 °C under ammonia, elemental analysis found the carbon content to be <0.5 wt %. In all three residues, the hydrogen content was <0.5 wt %. These results indicate that the forming gas was an unexpectedly ineffective reducing agent for removing the carbon functionalities from the polysilazane during pyrolysis. Alternatively, as expected, the ammonia was a highly effective reducing agent.

All of the ceramic residues fired above 800 °C for both polymers under the three pyrolysis atmospheres were examined for crystalline phases by powder X-ray diffraction. No crystalline material was detected in the samples pyrolyzed up to 1400 °C except for the polymer B sample heated to 1400 °C under 95%/5% N_2/H_2. The diffraction pattern of this sample exhibited small crystalline peaks at 2θ = 35°, 31°, and 34.5°, with the corresponding intensities of I = 100, 85, and 75. These peaks and their intensities match those of α-Si_3N_4. Further high-temperature studies are in progress to determine the temperatures and conditions under which the solids crystallize and the nature of the phases formed.

Stacked IR plots (Figures 2 and 3) and mass spectra of the gaseous products evolved during pyrolyses under N_2 clarify some of the TGA findings. The absorbance axes of the IR spectra are compressed to allow display of several spectra simultaneously. Between 120 and 600 °C, the spectra in the case of A show large losses of silicon-containing species (with multiple SiH bands centered around 2140 cm^{-1}, $SiCH_3$ 1263 cm^{-1}, and a broad SiNSi absorption at 900 cm^{-1}). Mass ions for the silicon compounds suggest the formation of the silazane dimer $[CH_3SiHNH]_2$ (*m/e* 119, 118, 59, 58, 57) and the disilazane compounds $[CH_3SiH_2]_2NH$ (*m/e* 105, 104) and $(CH_3)_3SiNHSiH_2CH_3$ (*m/e* 133, 73, 72). No higher molecular weight compounds (up to 200 amu) were detected. In the case of B only very small losses of such compounds (SiH 2140 cm^{-1}, $SiCH_3$ 1270 cm^{-1}) were detected. Mass spectra data confirmed the silicon compounds from B to be silane, SiH_4, and methylsilane, CH_3SiH_3 (*m/e* 32, 31, 30, 45, 44, 43). No higher molecular weight silicon species were detected from B. Concomitant with the evolution of volatile silicon species is the loss of NH_3 from both polymers (3333, 1626, 966, and 933 cm^{-1}; *m/e* 17, 16, 15, 14). Polymer B also shows the loss of THF up to approximately 225 °C. After B has been isolated, some THF still remains in the solid. This can be removed prior to pyrolysis through prolonged drying in vacuum. Methane loss begins at 400 °C for A and 450 °C for B; this is the only volatile product detected above 600 °C by IR (3019 cm^{-1}, 1302 cm^{-1}; *m/e* 16, 15, 14, 13, 12). Methane continues to be evolved at the temperature limits of the experiment (1000 °C). Additionally, hydrogen gas is found in the mass spectra throughout the temperature range in which methane evolution occurs with maximum loss at about 850 °C for both polymers. Only about 2% of the weight loss in B is due to volatiles other than methane and residual THF. Both polymers lose about 12% of their weight under nitrogen or forming gas in the same temperature range (500–950 °C) as methane and hydrogen are evolved. Since the unpyrolyzed polymers contain approximately 21% carbon by weight, about half of the total carbon content is lost as methane gas under these two atmospheres.

The difference in ceramic yield for the two polymers then stems primarily from the greater loss of silicon compounds from A below 600 °C. The amounts of methane and hydrogen evolved above 600 °C are quantitatively similar for both polymers. The addition of small quantities

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[27] Elemental analysis: polymer A pyrolyzed to 1400 °C under UHP N_2 14.67% C, <0.5% H, 26.92% N, 54.90% Si. Polymer A pyrolyzed to 1400 °C under 95%/5% N_2/H_2 14.17% C, <0.5% H, 27.23% N, 58.08% Si. Polymer A pyrolyzed to 1400 °C under NH_3 <0.5% C, <0.5% H, 38.42% N, 55.28% Si. Polymer B pyrolyzed to 1400 °C under 95%/5% N_2/H_2 14.53% C, <0.5% H, 28.18% N, 55.84% Si.

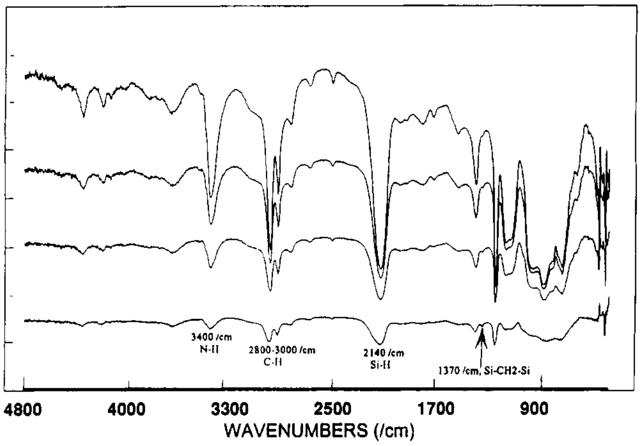

Figure 4. Stacked IR transmission spectra of unpyrolyzed A (top) and A residues at 200, 350, and 550 °C (bottom) pyrolyzed under UHP N_2.

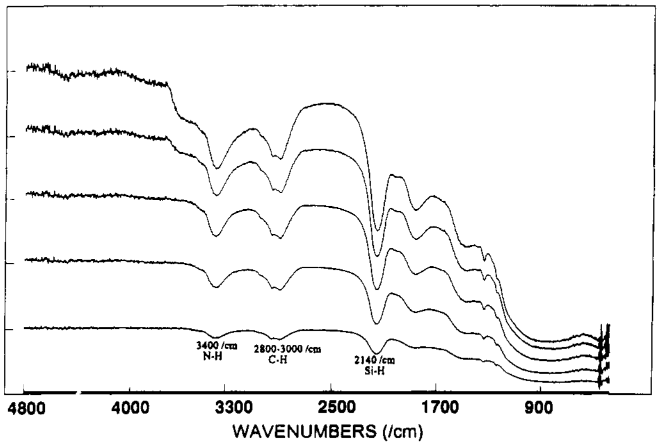

Figure 5. Stacked IR transmission spectra of A residues at 800 (top), 850, 900, 950, and 1000 °C (bottom) pyrolyzed under UHP N_2.

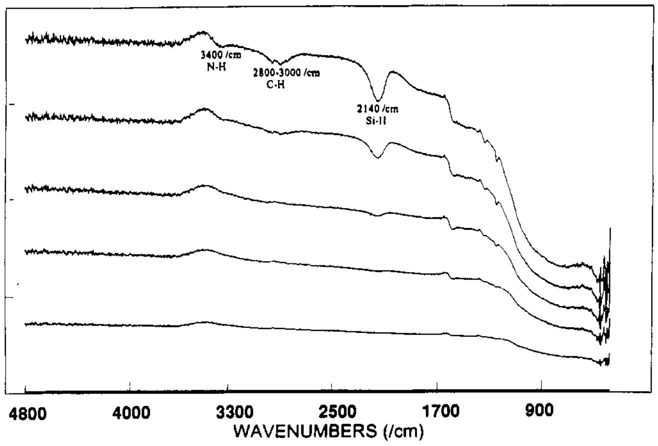

Figure 6. Stacked IR transmission spectra of A residues at 1050 (top), 1100, 1200, 1300, 1400 °C (bottom) pyrolyzed under UHP N_2.

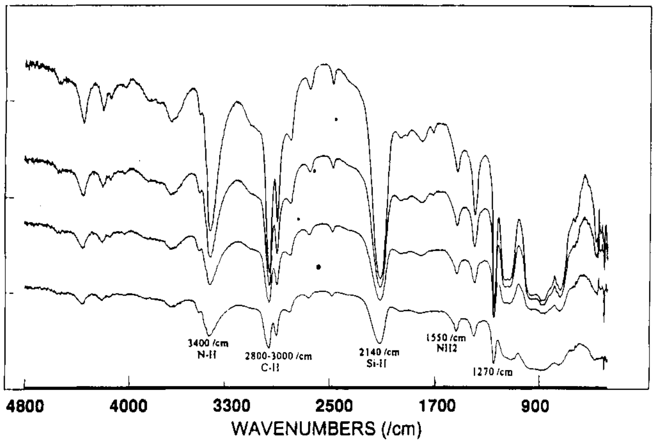

Figure 7. Stacked IR transmission spectra of unpyrolyzed A (top) and A residues at 200, 350, and 550 °C (bottom) pyrolyzed under 99.999% NH_3.

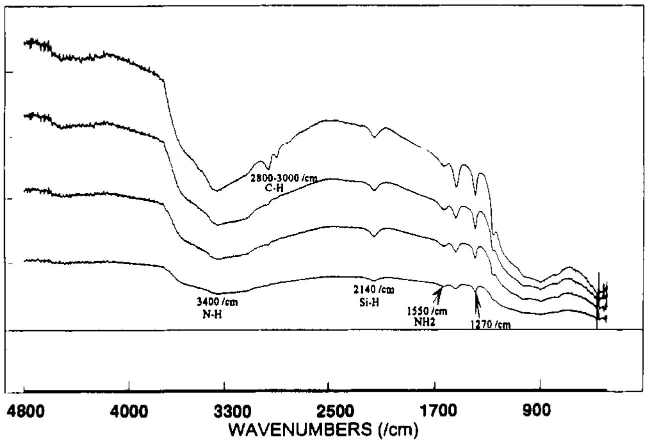

Figure 8. Stacked IR transmission spectra of A residues at 600° (top), 650, 700, and 750 °C (bottom) pyrolyzed under 99.999% NH_3.

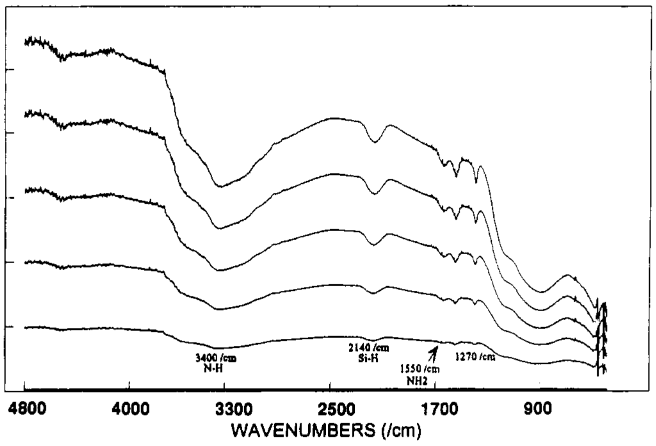

Figure 9. Stacked IR transmission spectra of A residues at 800 (top), 850, 900, 950, and 1000 °C (bottom) pyrolyzed under 99.999% NH_3.

(2 mol %) of CH_3SiCl_3 to solutions of A prior to pyrolysis serves to cure the polymer by increasing the degree of cross-linking. TGA pyrolysis yields of A to 900 °C after such curing are increased from 74% to 79% since the loss of silicon-containing species during firing is suppressed. Polymer A offers a processing advantage due to its increased solubility and the facile means of increasing ceramic yield by addition of methyltrichlorosilane.

Figures 4–6 illustrate the progressive changes in the infrared transmission spectra of the polymer A derived ceramic residue, pyrolyzed under UHP N_2 to 1400 °C with a temperature ramp of 10 °C/min. There was no residence time at any of the different temperature stages of the pyrolysis. It should be noted that the computer program used to construct the stacked spectra in Figures 4–10 increasingly compresses the vertical axis from top to bottom. Peak positions and relative intensities within an individual spectrum are true. The general trend seen in increasing pyrolysis temperatures is a decrease in the intensity of, as well as a broadening of, the absorptions, particularly in the

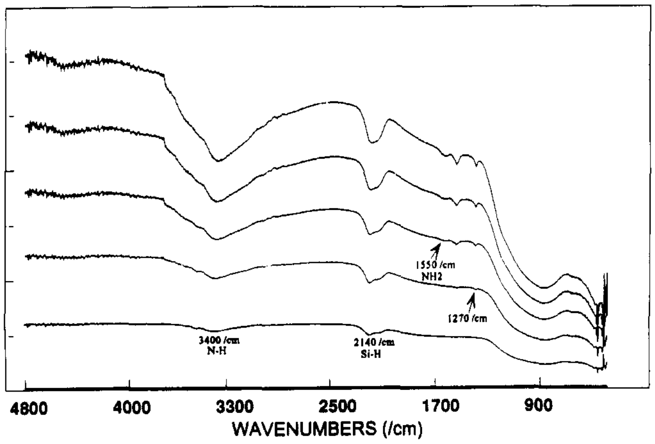

Figure 10. Stacked IR transmission spectra of A residues at 1050 (top), 1100, 1200, 1300, and 1400 °C (bottom) pyrolyzed under 99.999% NH_3.

NH stretch (3400 cm^{-1}). The broadening may be attributed to an increase in the number of types of environments for the IR-active groups. At 550 °C, a new peak appears at 1370 cm^{-1}. The intensity of this band is greatest in the 800 °C spectrum (Figure 5, top spectrum) and continues to diminish at higher temperatures. This absorption may be attributed to the formation of a methylene bridge between silicon atoms (Si–CH_2–Si) in the decomposing A polysilazane. The frequency of this low-intensity absorption is the same as the methylene vibration of the molecular compound $H_3SiCH_2SiH_3$[28] and a polycarbosilane (1350 cm^{-1})[29] but is at a somewhat higher wavenumber than is seen in yet another polycarbosilane formed by thermolysis of a polysilane.[14] The appearance of this absorption band at the same temperatures that methane is beginning to evolve suggests the process shown in eq 1. This process may be a step in the formation of silicon carbide.

$$2{\equiv}SiCH_3 \rightarrow {\equiv}SiCH_2Si{\equiv} + CH_4 \qquad (1)$$

CH functionality as observed by IR spectroscopy, remains in the ceramic up to 1200 °C. At 1400 °C, there remains in the IR spectrum of the black ceramic only a very broad absorption band between 600 and 1000 cm^{-1} attributable to SiC and SiN absorptions.[30]

The IR transmission spectra of the solid residues from both polymers A and B fired under 95%/5% N_2/H_2 to 1400 °C are essentially identical to those obtained under N_2 alone. In addition, as mentioned previously, the pyrolyzed solids from A and B all were black after firing under forming gas. Again, the belief that forming gas could be an effective reducing agent for removing carbon functionalities at intermediate temperatures was shown to be unfounded.

Figures 7–10 illustrate the progressive changes in the solids IR transmission spectra of A when it was pyrolyzed in 99.999% NH_3 to 1400 °C. There are significant differences from the spectra of the samples fired in nitrogen and forming gas. Between 200 and 550 °C the NH_2 silylamine peak (1550 cm^{-1}) is of greater intensity than in the forming gas and nitrogen samples and remains present through 1200 °C. This result complements the finding that the ceramic yield below 1000 °C is greater for pyrolyses carried out in ammonia than those effected in a nitrogen atmosphere, presumably due to the persistence of these amine functions. Above 550 °C, the methylene bridge absorption band (1370 cm^{-1}) does not appear (in contrast with the N_2 and forming gas fired samples). There is also a very noticeable increase in the intensity of the NH stretch band (3400 cm^{-1}). After 1400 °C, significant SiH and NH functionality remains, unlike the case of the polymers fired under nitrogen or forming gas. The presence of the 1270-cm^{-1} vibration in the ceramic residues obtained from high-temperature pyrolyses, assigned initially to the $SiCH_3$ stretch in the starting polymer, must be due to another moiety as there are no concomitant CH bands at 2800–3000 cm^{-1} and, in any case, CH_3 groups are unlikely to remain under ammonia pyrolysis. CH functionalities (2800–3000 cm^{-1}) are lost well below 1000 °C under ammonia. This suggests that an ammonia stream is sufficient to remove residual carbon in the polymer at *intermediate temperatures* but is not additionally required at higher temperatures to form carbon-free silicon nitride.

Nitrogen BET surface analysis was performed on the A-derived ceramic residue. After heating under forming gas at 10 °C/min to 1000 °C, the surface area of the unground powder residue was approximately 0.2 m^2/g. This low value indicates that there may exist a large amount of closed porosity in the pyrolysis product. Grinding the sample prior to the surface area measurement must open some of the closed porosity since the surface area of the 1000 °C forming gas residue which was ground using a mortar and pestle prior to the BET measurement was approximately 6.5 m^2/g. The unground A residue fired to 1400 °C also shows a low surface area of 0.2 m^2/g. After grinding the surface area increased to 2.47 m^2/g. More systematic studies are required in order to determine the extent of the closed porosity in the ceramic residues.

Conclusion

It was observed that polymer pyrolyses to 1400 °C under nitrogen as well as forming gas were similar, so forming gas was an ineffective reducing agent for removing the carbon functionalities from the polysilazanes. However, as expected, the pyrolytic transformation under ammonia was significantly different, and this gas was a highly effective reducing agent. Solid IR data supported the formation of methylene bridging functions during nitrogen and forming gas pyrolyses but not during the ammonia pyrolysis.

The volatile products of pyrolysis identified in this study are in general agreement with other studies on various silicon- and nitrogen-containing preceramics as described in the Introduction. Silicon and nitrogen losses which occur in these systems are primarily detected at lower thermolysis temperatures. Ceramic yields may be enhanced by suppression of these species if the polymer structure is significantly cross-linked. Conversely, particularly in inert pyrolysis atmospheres, hydrogen and simple hydrocarbons (methane in this case) typically show maximum evolution at significantly higher temperatures. The quantity and temperature range for losses of these latter species are not so easily controlled for the polymers investigated here. For example, mixing the commercial polymer with silicon powder results in a decrease in low temperature volatile species similar to the effect of increased cross-linking as described here; however, the high-temperature losses are unchanged.[31] It is well-known that the presence of organic groups in the preceramic enhances processing properties such as polymer stability and solubility, but their presence necessarily results in de-

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creased ceramic yields. Another fact less emphasized is that pyrolysis gases from these organic groups are evolved primarily at higher temperatures. This becomes a critical issue when fabricating parts from these preceramic polysilazanes. As the temperature increases, the pyrolytic residues become increasingly more rigid and the nondestructive, controlled removal of the gaseous products becomes more difficult.

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Thermogravimetric Mass Spectrometric Investigation of the Thermal Conversion of Organosilicon Precursors into Ceramics under Argon and Ammonia. 1. Poly(carbosilane)

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The pyrolysis under argon and under ammonia of Yajima's poly(carbosilane) (PCS) was studied by means of thermogravimetric analysis associated with continuous mass spectrometry of the gases evolved. The degradation of the polymer skeleton under argon leads to the evolution of methylsilanes and higher linear oligomers; the escape of hydrogen starts simultaneously. Mechanisms of pyrolysis are proposed, which involve in a first step the homolytic cleavage of Si–H and Si–C bonds in the poly(carbosilane) skeleton. Under ammonia, amination and carbon removal (mainly as methane) start well below the thermal decomposition of ammonia. The first step likely corresponds to the nucleophilic substitution of Si–H bonds by ammonia; Si–C bonds are substituted at higher temperature, and homolytic cleavages are probably involved. However, H-abstraction from N–H bonds hinders the cross-linking via Si–Si and Si–C-Si bridges, thus allowing complete nitridation.

Introduction

Since the early work of Verbeek[1] and Yajima,[2] the preparation of silicon carbide and silicon nitride ceramics by pyrolysis of organosilicon polymers has led to numerous publications, which have been reviewed by several authors.[3-5] Insights into the thermolysis chemistry are necessary in order to choose suitable polymeric precursors as well as to set up the procedure of the pyrolysis step, such as the temperature, the heating rate, and the atmosphere (inert or reactive gas, or vacuum). In practice, the use of a reactive atmosphere may drastically modify the nature of the ceramic material for a given precursor.

Thus, the production of SiC Nicalon fiber first developed by Yajima et al.[1,6] was based on the curing of poly(carbosilane) (PCS) fiber by heating in air. This oxidation stage makes the melt-spun PCS fiber infusible before its final conversion into ceramic at higher temperatures under nitrogen. The oxygen introduced during the curing step is still present after the pyrolysis, and the continuous phase in the final fiber is actually an amorphous silicon oxycarbide phase.[7]

Pyrolysis under an ammonia atmosphere has been also used.[8,9] It completely changes the elemental composition of the ceramic material by removing carbon and incorporating nitrogen. Thus, PCS cured either by electron irradiation[8] or thermally[9] is converted to silicon nitride by pyrolysis in ammonia, whereas PCS cured by oxidation leads to silicon oxynitride.[8] The pyrolysis in ammonia may also be used to remove the excess carbon from SiC or Si_3N_4 ceramic powders.[10] Many papers have been devoted to the thermal conversion of PCS under argon. The structural evolution of the materials during the pyrolysis was investigated by IR, NMR, and X-ray absorption spectroscopy,[11-14] while the analysis of the volatile products was

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