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Condensation Polymerization of Tetrakis(ethylamino)silane and Its Thermal Decomposition to Si_3N_4/SiC Ceramics

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The polymer obtained from condensation polymerization of $Si(NHEt)_4$ has been characterized by using ^{29}Si and ^{13}C solid-state NMR spectroscopy, FTIR, and elemental analysis and by analysis of the condensation products. The decomposition of this polymer to ceramic products has been studied by heating the polymer to 500 and 800 °C in vacuo and characterizing the solid products by using ^{29}Si MAS, ^{13}C MAS, and ^{1}H CRAMPS solid-state NMR spectroscopy, FTIR, and elemental analysis. The condensable gaseous products of the decomposition were isolated and analyzed quantitatively by using FTIR. The solid-state NMR studies suggest a predominantly (SiN_4) local environment for the silicon atoms as well as free carbon in the 800 °C product. After heating to 1500 °C for 4 h in an argon atmosphere, β-SiC, α-SiC, and graphite were the eventual crystalline products. Heating at 1600 °C in N_2, however, produced mainly α-Si_3N_4 and graphite.

Introduction

In the context of the continuing search for improved polymeric precursors to silicon nitride and silicon carbide, a number of organosilicon polymers have been prepared and pyrolyzed to ceramics in the past several years.[1] For the most part, however, these efforts have been empirically directed with a strong focus on obtaining and applying precursors for specific applications, such as the preparation of continuous fiber or coatings. There have been relatively few attempts to understand the chemical and structural changes that accompany the pyrolytic conversion of these polymers to ceramic products.[3,4] In this context, the ability to design precursor systems for particular applications or even to control the composition and microstructure of the resulting silicon-containing ceramic products is quite limited at present.

In the specific case of silicon nitride, two main routes to this ceramic product involving the pyrolysis of organosilicon polymeric precursors have been employed. One of these involves the direct pyrolysis, in vacuo or in an inert atmosphere, of polysilazanes.[2] The polysilazanes employed are generally of the type $[SiRR'NR'']_n$, where R, R′, and R″ can be any combination of H, alkyl, or aryl groups. The actual structure of these polymers is generally not known in detail but presumably involves branching and ring formation. In any case, it appears that for most combinations of R, R′, or R″ involving organic groups, on pyrolysis in vacuo or in an inert atmosphere, carbon (as free carbon, silicon carbide, and/or carbonitride) is ultimately retained in the final ceramic product.

Burns and co-workers[3] in their study of the pyrolysis of a series of aryl and alkylsilsesquiazanes have found that unsaturated substituents result in a higher carbon content than saturated substituents, with aryl substituents introducing the greatest amounts of carbon. A detailed characterization of the intermediate and final solid products of pyrolysis was not reported, however. Similarly, Legrow et al.,[4] in the course of their preparation of a ceramic silicon carbonitride fiber from a hydridopolysilazane, characterized the gas products of pyrolysis as well as the composition and microstructure of the final ceramic fiber but apparently obtained little information on the structural changes occurring in the solid during the conversion of the polymer to the final ceramic product.

The second main approach to the preparation of silicon nitride from organosilicon precursors involves pyrolysis in ammonia. In the case of silazanes, transamination presumably plays an important if not dominant role in the conversion to Si_3N_4;[5] however, even in the case of organosilanes that contain no nitrogen initially, ammonia is effective in eliminating organic groups on Si between ca. 400 and 600 °C, leading to a virtually pure Si_3N_4 product.[6]

For certain applications, it would be desirable to be able to effect the direct pyrolytic conversion of the organosilicon precursor to Si_3N_4 without the use of a reactive gas such as ammonia. This can be done by using $[SiH_2NH_2]$,[7] obtained from the reaction of SiH_2Cl_2 and ammonia; however, this polymer is rather unstable and yields a Si-rich product on pyrolysis in vacuo and in argon. Yokoyama and coworkers report reacting SiH_2Cl_2 with pyridine followed by ammonia to give perhydropolysilazane, $[SiH_2NH_2]$.[8] Spinning the polymer into fiber followed by pyrolysis in ammonia resulted in stoichiometric silicon nitride.

A potential alternative source of precursors for this purpose are tetrasilazanes of the type $Si(NRR')_4$, in which the silicon is bonded only to nitrogen in the initial struc-

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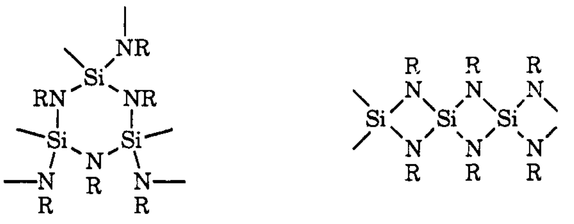

R = Me R = n-propyl, phenyl

Figure 1. Structures proposed by Andrianov for condensation polymers derived from $Si(NHR)_4$ polymers.

ture.[5] Pyrolysis of the simple silazanes of this type in the absence of ammonia are known to lead to a silicon carbonitride product; however, the way in which carbon enters into the ceramic product has apparently not been investigated.

Prior studies of the $Si(NHR)_4$ compounds of this type by Andrianov and co-workers have suggested that polycondensation occurs on heating to form complex polymers containing six- and/or four-membered $(SiN)_n$ rings with a spirocyclic structure at the Si atom.[9] Structural characterization of the polymers was complicated by their insolubility in common organic solvents and was limited to elemental analysis and infrared spectroscopy. Some information was obtained by fractionally distilling and characterizing the oligomeric fraction. Again, structural characterization of these oligomers was based on elemental analysis and infrared spectroscopy. The authors concluded that the structures consisted of six- and/or four-membered silazane rings, depending on the amine group, having a spirocyclic structure at the silicon atom (Figure 1).

Mazaev and co-workers later reported the pyrolysis of the methylsilazane polymer described by Andrianov to a mixture of ceramic products consisting of α- and β-Si_3N_4 and β-SiC.[10] In this study, XRD patterns and elemental analyses of the ceramic chars were monitored as a function of pyrolysis temperature; however, a characterization of the pyrolysis chemistry was not attempted.

We have undertaken a detailed study of the pyrolysis chemistry of this class of silazanes with the initial objective of developing a better understanding of the precursor-to-ceramic conversion process and its dependence on the structure of the initial precursor. A potential outcome of this effort may be a new class of Si_3N_4 precursors that do not require ammonia for their conversion.

Experimental Section

All syntheses and manipulations were carried out in oven-dried glassware under dry N_2 using standard inert atmosphere techniques.[11]

Materials. Silicon tetrachloride and ethylamine were purchased from Aldrich and used as received. Pentane was purchased from Fisher Scientific and dried by refluxing over Na and benzophenone in a N_2 atmosphere.

Physical Measurements and Instrumentation. Solution NMR spectra were obtained on a Varian XL-200 NMR spectrometer equipped with a multinuclear probe. Benzene-d_6 was used as an NMR solvent in all solution NMR spectra. ^{1}H and ^{13}C solution NMR spectra were referenced to benzene-d_6 and are reported with respect to tetramethylsilane (TMS). ^{29}Si solution NMR spectra were referenced to external TMS.

^{29}Si solid-state NMR spectra were acquired on a modified NT-150 spectrometer (observe frequency of 29.81 MHz). Single-pulse excitation (30° pulses) with proton decoupling during data aquisition and magic angle spinning (MAS) at 2.5–4 kHz, using cylindrical rotors,[12] was employed. Typically, 2000–3000 transients (1K data, 10-kHz spectral width) were taken at 15-s intervals. The ^{13}C solid-state NMR spectra were similarly acquired (i.e., with MAS, single-pulse excitation, 2000–3000 scans) on a modified NT-200 spectrometer (observe frequency 50.31 MHz, 1K data, 20-kHz spectral width). A 30° pulse and 10-s recycle delay were employed. All data were Fourier transformed after exponential multiplication using 50-Hz line broadening. Chemical shifts of both silicon and carbon spectra were referenced to TMS. ^{1}H CRAMPS spectra were taken on a highly modified NT-187 spectrometer as described by Bronnimann et al.[13] Solid-state proton chemical shifts were referenced to solid tetrakis(trimethylsilyl)methane (TTMSM) as an external standard and are reported with respect to TMS.

Infrared spectra were obtained on a Perkin-Elmer Series 1800 FTIR equipped with a Deltech dry air purge assembly using a deuterated triglycine sulfate element detector (DTGS). FTIR solid samples were ground in a glovebox to a fine powder by using a boron carbide mortar and pestle, mixed with potassium bromide in a glovebox, and pressed into pellets for transmission studies. Liquid samples (i.e., $Si(NHEt)_4$) were examined as a thin film between potassium bromide plates. Gas chromatography was done on a Varian 3700 gas chromatograph interfaced with the FTIR via a heated transfer line and a gold-plated light pipe. The mercury cadmium telluride detector was used for all GC-FTIR analyses. Hydrocarbons were separated on an Alltech VZ-10 column (6-ft length, 0.085-in. i.d., stainless steel column, mesh range 60/80), and amines were separated on an Alltech Chromosorb 103 column (6-ft length, 0.085-in. i.d., stainless steel column, mesh range 80/100). Thermal analyses were performed on a Perkin-Elmer 7 Series TGA and 7 Series DSC. A flow of purified N_2 ($\sim$30 mL/min) was maintained during the TGA run. The sample was heated in a platinum pan at a rate of 5 °C/min from 50 to 700 °C and then at a rate of 25 °C/min to 1000 °C. For the DSC study, $Si(NHEt)_4$ was loaded into a stainless steel sealed cell in a glovebox. The sample was heated in the DSC at a rate of 2 °C/min from 40 to 400 °C. X-ray powder diffraction was performed using Cu Kα radiation on a Philips PW 1710 X-ray powder diffractometer equipped with a monochromator. Decomposition studies on samples contained in molybdenum boats were performed up to 800 °C in an evacuated ($\sim$12 μmHg) quartz tube (diameter, 3.2 cm; length, 44 cm; heated length, 22 cm) using a clamshell furnace. High-temperature (to 1600 °C) furnace runs were carried out in a molybdenum-wound, hydrogen-protected alumina furnace under a purified-N_2 or purified-argon flow. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) using inert-atmosphere handling procedures.

Synthesis of $Si(NHEt)_4$ and Polycyclosilazine-Et (PCS-Et). $Si(NHEt)_4$ was synthesized by a modification of the method of Lengfeld.[14] A 1000-mL three-neck flask equipped with a mechanical stirrer, an addition funnel, and a condenser with a N_2 inlet was charged with 500 mL of pentane and cooled to 0 °C. Ethylamine was condensed into a graduated cylinder immersed in ice, and a 16% excess (0.765 mol, 50 mL) was added to the pentane. Silicon tetrachloride (0.0824 mol, 10 mL) was measured by syringe and placed in the addition funnel along with 200 mL of pentane. The silicon tetrachloride solution was added dropwise to the ethylamine solution at 0 °C with stirring over 2 h. The mixture was allowed to stir overnight at room temperature. The product in solution was separated from the solid $EtNH_3Cl$ by using a filter stick attached to a cannula needle. The pentane was removed in vacuo, and the remaining liquid was vacuum distilled (bp 50–53 °C/55 μm). IR 3412.6 (m), 2959.8 (vs), 2926.7 (s), 2864.7 (s), 1470 (w), 1447.9 (m), 1396.0 (s), 1266.6 (m), 1123.9 (vs), 1063.0 (m), 936.8 (s), 826.8 (m), 769.6 (m) cm^{-1}; ^{1}H NMR δ 2.82 (CH_2, quartet superimposed on doublet, shown by decoupling experi-

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ments), 1.03 (CH_3, t), 0.39 (NH, br); ^{13}C NMR [^1H] δ 36.2 (CH_2), 20.7 (CH_3); ^{29}Si NMR [^1H] δ -41.1.

PCS-Et was synthesized by refluxing $Si(NHEt)_4$ in a round-bottom flask equipped with a condenser. The pot temperature was increased gradually from 120° to 180° over 3 days to maintain reflux, since the boiling point of the liquid increased as oligomers were produced. At the end of this period, a white solid remained. Samples were taken for TGA at different stages of the polymerization. At atmospheric pressure, $Si(NHEt)_4$ boils at about 120 °C. Weight loss at 120–150 °C showed the presence of monomeric/oligomeric products. The gases evolved during polymerization were isolated by passing N_2 (~5 mL/min) over the top of the condenser into a trap immersed in liquid N_2. The gases were analyzed by GC-FTIR.

Ethylamine Stability. A Schlenk tube (2.3 cm in diameter) equipped with an inlet tube to carry gas to the bottom of the flask was immersed up to 3 in. in a sand bath and heated to 250 °C. Ethylamine was passed (~5 mL/min) through the tube, and the products were collected in a −196 °C trap. The sample was analyzed by GC-FTIR. GC-FTIR analysis was also performed on ethylamine taken directly from the cylinder.

To determine the stability of ethylamine over the temperature range 400–600 °C, a sample of ethylamine (~1.6×10^{-4} mol) was passed through (dynamic vacuum) an evacuated quartz tube that contained a molybdenum boat in a hot-wall cylindrical furnace held at 400, 500, and 600 °C. The products were collected in −196 °C traps and analyzed by using FTIR. Also, ethylamine at ~17 mmHg was heated in a static vacuum for approximately 1 min at 600 °C in the quartz tube. The products were collected and analyzed by using FTIR.

Pyrolysis to Ceramic Products. This study included two separate decompositions carried out under dynamic vacuum with ca. 1 g of PCS-Et for each experiment. Both decomposition experiments were repeated several times with similar results. In the first experiment PCS-Et was heated from room temperature to 500 °C, and in the second experiment PCS-Et was heated from room temperature to 800 °C. The details of these experiments are given below. At the end of each heat treatment, samples were collected in the glovebox and packaged under N_2 for solid-state NMR, FTIR, and elemental analysis. X-ray powder diffraction was performed on the 800 °C product.

The 800 °C product was then further heated in three separate experiments. One sample was heated to 1500 °C over 4 h and held at this temperature for 4 h in an argon atmosphere (1 atm). A second sample was heated in a N_2 atmosphere (1 atm) to 1500 °C using the same heating schedule. The third sample was heated to 1600 °C in a N_2 atmosphere (1 atm), again using the same heating schedule. All three samples were examined by solid-state NMR, FTIR, X-ray powder diffraction, and elemental analysis.

Decomposition to 500 °C. A sample of PCS-Et in a molybdenum boat was placed inside a quartz tube and transferred to the furnace. After the tube was evacuated for about 2 h, the furnace temperature was increased at about 1 °C/min to 500 °C and held at 500 °C for 4 h. The furnace was allowed to cool for approximately 8 h while the sample was maintained under dynamic vacuum.

Decomposition to 800 °C. A sample of PCS-Et in a molybdenum boat was placed inside a quartz tube and transferred to the furnace. After the tube was evacuated for about 2 h, the furnace temperature was increased at about 1 °C/min to 500 °C and held at 500 °C for approximately 2 h. It was then heated to 600 °C over 4 h and held there for 0.5 h. Heating was continued to 800 °C at 1 °C/min and held there for 13 h. The sample was then cooled in vacuo for 8 h. The polymer was heated at these slow rates because once the pyrolysis temperature reached 500 °C significant amounts of noncondensable gas were generated.

Analysis of Gaseous Products as a Function of Pyrolysis Temperature. A sample of PCS-Et was prepared as above and heated at a rate of 4–5 °C/min to 800 °C under dynamic vacuum. All condensable gaseous products were collected in liquid N_2 traps. At various temperatures (400, 600, and 800 °C), the contents of the traps were transferred to collection vessels and analyzed by GC-FTIR.

Methane was observed by connecting a gas IR cell to the vacuum line downstream from the −196 °C traps, closing the valve leading to the vacuum pump to allow the gas cell to fill with 5 Torr of noncondensable product, and then taking the IR spectrum of the gas in the IR cell. Hydrogen is a likely product of the decomposition of PCS-Et but would not be observed by the methods employed.

Table I. Elemental Analysis Data

	% Si	% N	% C	% H	emp formula
$Si(NHEt)_4$	13.60	27.38	47.07	11.78	$SiN_{4.03}C_{8.07}H_{24.25}$
PCS-Et	20.9	25.2	42.5	8.5	$SiN_{2.41}C_{4.75}H_{11.39}$
500 °C	26.01	19.17	30.00	5.95	$SiN_{1.47}C_{2.69}H_{6.4}$
800 °C	39.08	29.16	24.21	<0.5	$SiN_{1.5}C_{1.45}H_{0.36}$
1500 °C, argon	57.31	5.31	36.67	<0.5	$SiN_{0.18}C_{1.49}H_{0.24}$
1500 °C, nitrogen	40.57	27.73	27.20	<0.5	$SiN_{1.36}N_{1.56}H_{0.34}$
1600 °C, nitrogen	54.89	20.15	14.59	<0.5	$SiN_{0.73}C_{0.62}H_{0.26}$

Quantitative Analysis of Gaseous Products. Quantitative analysis of the condensable gaseous pyrolysis products was performed using multiple regression analysis. A classical least-squares calibration using multivariate methods was employed.[15] The infrared spectra of the pure components, ethane, ethylene, propane, propene, acetylene, ammonia, and ethylamine, were taken at five different pressures, ranging from 3 to 39 Torr, depending on the molar absorptivity at the observed frequencies of each compound. The pressure was determined by using a mercury manometer attached to the vacuum line. The uncertainty of the measurement was approximately ±0.1 Torr. The absorbance at 14 different frequencies (730.0, 773.3, 789.6, 912.0, 931.0, 950.0, 965.8, 990.8, 2887.1, 2932.5, 2953.8, 2967.8, 2987.9, and 3309.1 cm^{-1}) was measured for each gas at each of the five pressures. The slope of the line from a plot of absorbance versus pressure is proportional to the molar absorptivity of that component at that frequency. Standard calibration curves were prepared for the 7 different gases by plotting absorbance versus pressure for each of the 14 frequencies. The origin was included as a data point. This resulted in 98 graphs (or molar absorptivities) (14 frequencies × 7 gases) containing six data points (five pressures + origin). The calibration curves were linear with a correlation coefficient of 0.991–1.000 and passed through the origin.

The gases collected after each temperature interval (50–400, 400–600, and 600–800 °C) were transferred to a gas IR cell and analyzed by FTIR. The absorbance at the 14 frequencies was measured for the pyrolysis gas mixture. A multiple regression was performed to solve for P using the series of equations defined by

$$A_{x,\nu} - b = \sum \epsilon_{a,\nu i}(P_a) \qquad (1)$$

where $A_{x,\nu i}$ = absorbance (peak height (cm)) of pyrolysis gas mixture x at frequency i, $\epsilon_{a,\nu i}$ = absorptivity of component a at frequency i (obtained from the calibration curves), P_a = pressure of component a, and b = the average of the y intercepts from the line obtained from a plot of peak height versus pressure for pure component a, b, c, ..., g at frequency i. This resulted in a pressure for each of the seven gaseous components. Values less than 0.5 Torr were considered to be zero.

Results

Synthesis and Characterization of $Si(NHEt)_4$. Reaction of silicon tetrachloride with excess ethylamine gave $Si(NHEt)_4$ in about 90% yield:

$$SiCl_4 + xsH_2NEt \rightarrow Si(NHEt)_4 + 4EtNH_3Cl \qquad (2)$$

The solution ^1H, ^{13}C, and ^{29}Si NMR spectra of $Si(NHEt)_4$ are shown in Figure 2. These are the first reported NMR spectra for this compound. Elemental analysis data are shown in Table I.

Polymerization Studies of $Si(NHEt)_4$. GC-FTIR analysis of the polymerization condensation products resulted in two GC peaks whose IR spectra correspond to ethylamine (~92%) and diethylamine (~8%). Hof-

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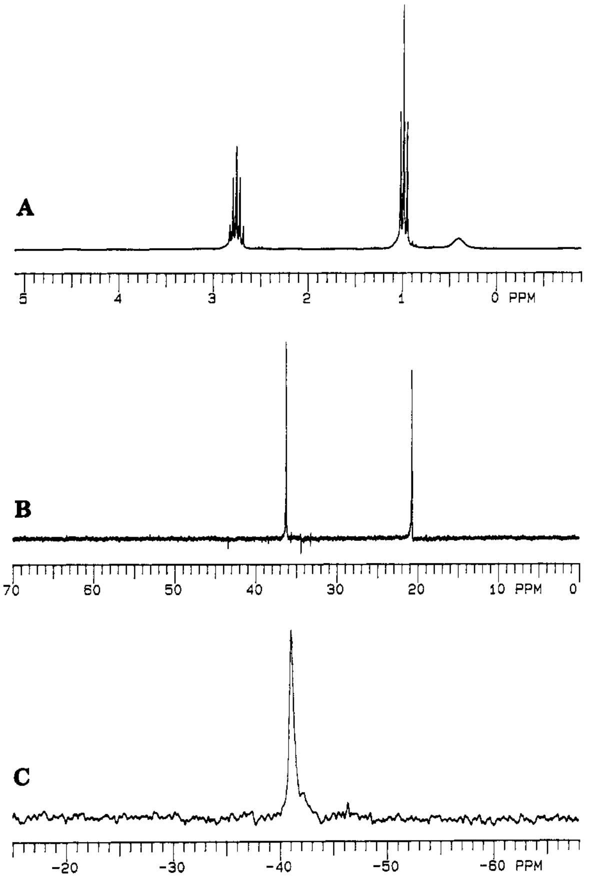

Figure 2. Solution NMR data of $Si(NHEt)_4$: (A) 200-MHz ^1H spectrum, (B) 50-MHz ^{13}C spectrum, (C) 40-MHz ^{29}Si spectrum.

meister and Van Wazer[16] report that the following exchange can occur with methylamine:

$$2H_2NR \xrightarrow{\Delta} HNR_2 + NH_3 \qquad (3)$$

To eliminate the possibility that the ethylamine evolved was undergoing either decomposition or disproportionation during the polymerization to give diethylamine and ammonia, a sample of ethylamine was passed through a Schlenk tube heated at 250 °C. The products observed were only ethylamine and a small quantity of ammonia. Ethylamine obtained from the cylinder showed that ammonia was present as an impurity in the ethylamine. The ratio of the peak areas of $EtNH_2$:NH_3 in the heated and unheated samples were approximately the same. Ethylamine, therefore, appears stable under the conditions of the polymerization, and ethylamine and diethylamine are most likely byproducts of the condensation reaction:

$$Si(NHEt)_4 \xrightarrow{\Delta} H_2NEt + HNEt_2 + \text{PCS-Et} \qquad (4)$$

Furthermore, ethylamine and diethylamine were the only products observed in the polymerization of $Si(NHEt)_4$. If a disproportionation of ethylamine were occuring as in eq 3, ammonia would also be formed.

When $Si(NHEt)_4$ is completely polymerized, the resulting polymer is a white insoluble solid. TGA of the polymer, hitherto referred to as PCS-Et, shows a weight loss of 40% that begins at ~400 °C (Figure 3). DSC shows no endotherms or exotherms at temperatures below 400 °C. The infrared spectra of $Si(NHEt)_4$ and PCS-Et are compared in parts A and B of Figure 5, respectively. ^{13}C and ^{29}Si solid-state NMR spectra of PCS-Et are shown in Figures 6A and 7A, respectively. Elemental analysis

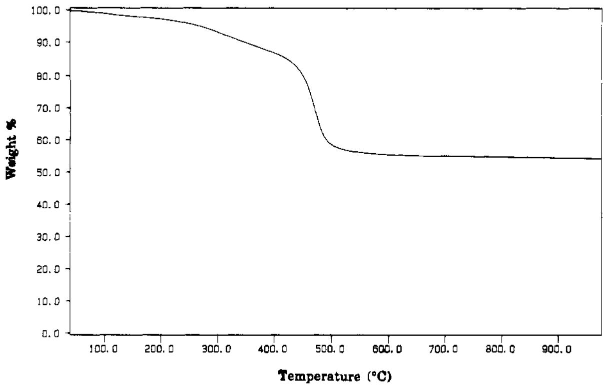

Figure 3. TGA of PCS-Et.

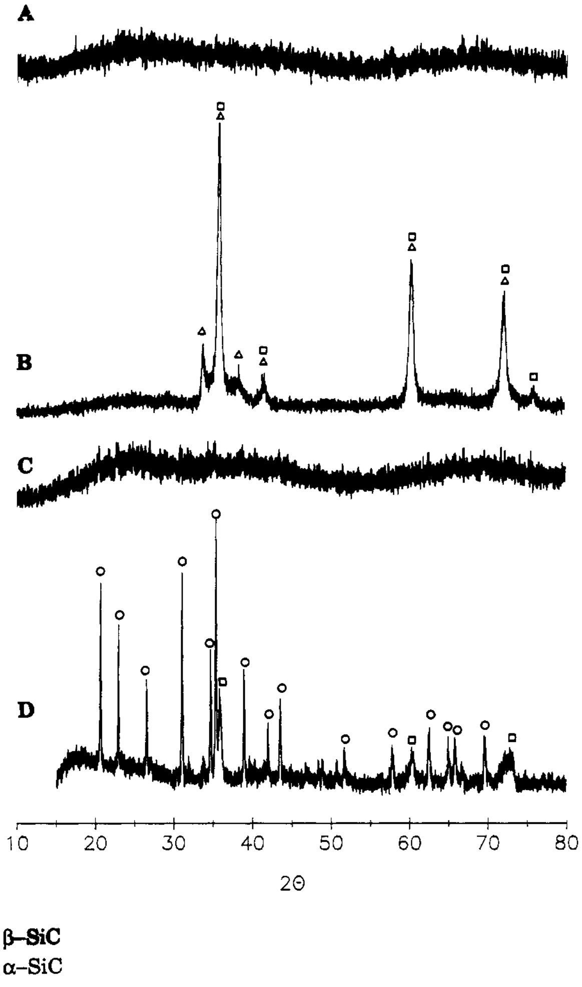

Figure 4. X-ray powder diffraction patterns of (A) 800 °C product, (B) 1500 °C product heated in argon atmosphere, (C) 1500 °C product heated in N_2 atmosphere, (D) 1600 °C product heated in N_2.

results for PCS-Et are given in Table I.

Pyrolysis of PCS-Et to Ceramic Products. In that the TGA of PCS-Et (Figure 3) shows that the major weight loss (decomposition) occurs between 400 and 600 °C; a sample of PCS-Et was pyrolyzed to 500 °C, the midpoint of the decomposition, to determine what structural changes, if any, had occurred to that point. PCS-Et was also pyrolyzed to 800 °C since TGA shows that weight loss is complete at that point. Elemental analysis, FTIR, and ^{29}Si, ^{13}C, and ^1H CRAMPS solid-state NMR data was obtained on both the 500 °C sample and the 800 °C in order to characterize these structural changes.

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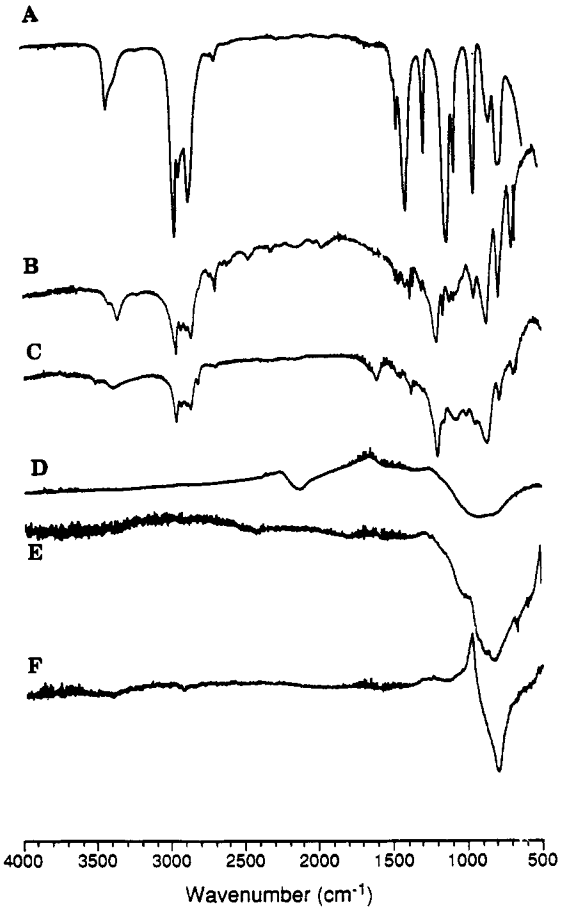

Figure 5. FTIR spectra of (A) $Si(NHEt)_4$, (B) PCS-Et, (C) 500 °C product, (D) 800 °C product, (E) 1500 °C product heated in argon atmosphere, (F) 1600 °C product heated in N_2.

X-ray powder diffraction of the 800 °C material indicated that the solid was amorphous (Figure 4A). The 800 °C product was heated to 1500 °C for 4 h in an argon atmosphere in order to induce crystallization. The X-ray diffraction pattern of the 1500 °C argon atmosphere product is shown in Figure 4B. This is consistent with a combination of the patterns of both β-silicon carbide[17] and α-silicon carbide.[18] A second sample of the 800 °C product was heated in a N_2 atmosphere to 1500 °C for 4 h to compare the effect of environment. This sample is amorphous by XRD (Figure 4C). Heating to 1600 °C for 4 h in a N_2 atmosphere gave an X-ray diffraction pattern that is consistent with the presence of mainly of α-silicon nitride[19] along with a small quantity of β-silicon carbide (Figure 4D).

Analysis of Gases Evolved as a Function of Temperature. The gaseous products of the decomposition of PCS-Et were collected over three temperature regions (50–400, 400–600, and 600–800 °C) in liquid N_2 traps and subsequently analyzed qualitatively by GC-FTIR and quantitatively by FTIR. The gaseous products evolved between 50 and 400 °C were ammonia and ethylamine. Between 400 and 600 °C, methane, ethane, ethylene, propane, propene, acetylene, ethylamine, ammonia, and hydrogen cyanide were produced. Between 600 and 800 °C ammonia, hydrogen cyanide, and methane were formed as decomposition products. Low molecular weight silicon-containing products (Me_xSiH_{4-x}) are separated on the VZ-10 column, but none were observed in the decomposition of PCS-Et. Likewise, volatile silazanes are separated on the Chromosorb 103 column, but none were observed. Table II lists the values obtained from the quantitative study of the decomposition products as a function of pyrolysis temperature as well as the products that were observed qualitatively.

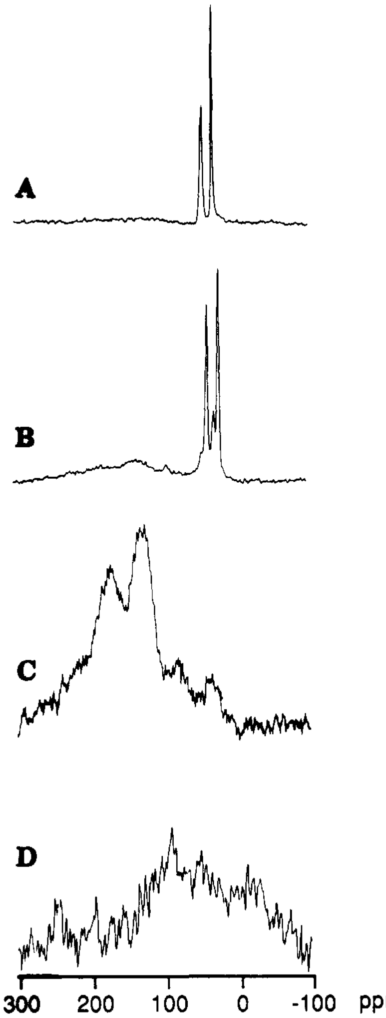

Figure 6. The 50.31-MHz ^{13}C solid-state NMR spectra of (A) PCS-Et, (B) 500 °C product, (C) 800 °C product, (D) 1500 °C product heated in argon atmosphere.

Table II. Quantitative and Qualitative Data for the Volatile Decomposition Products from the PCS-Et Pyrolysis

	pressure, Torr		
component	50–400 °C	400–600 °C	600–800 °C
ethylene	0	20.0	0
ethane	0	6.37	0
propane	0	0.54	0
propene	0	2.53	0
ammonia	1.68	11.7	4.36
acetylene	0	0.98	0
ethylamine	4.56	7.05	0
hydrogen cyanide	no	yes	yes
methane	no	yes	yes
total condensable gas pressure	6.24	49.17	4.36

Because some of the gaseous products observed (ammonia, hydrogen cyanide, methane, ethylene) are known

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(17) *Inorganic Powder Diffraction File*; Berry, L. G., Ed.; Joint Committee on Powder Diffraction Standards: Swarthmore, 1974; JCPDS card number 1-1119.

(18) In ref 17, JCPDS card number 4-0756.

(19) *Inorganic Powder Diffraction File*; Berry, L. G., Ed.; Joint Commitee on Powder Diffraction Standards: Swarthmore, 1967; JCPDS card number 9-250.

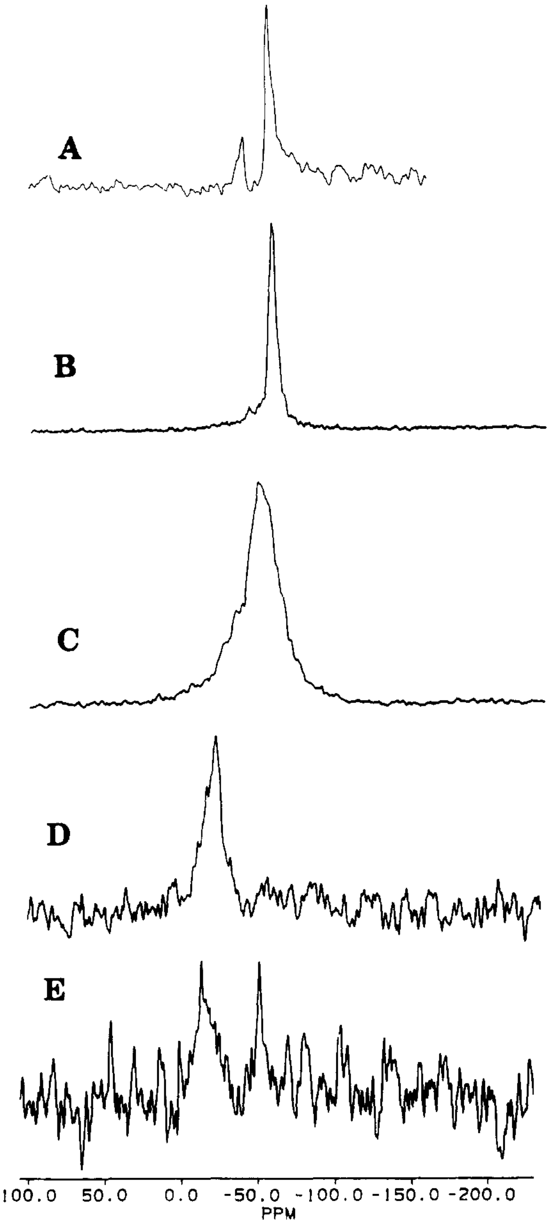


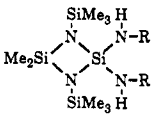
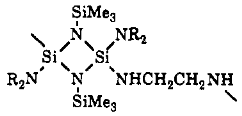
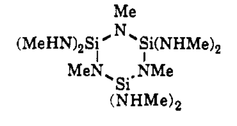
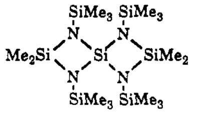
Figure 7. The 29.81-MHz ^{29}Si solid-state NMR spectra of (A) PCS-Et, (B) 500 °C product, (C) 800 °C product, (D) 1500 °C product heated in argon atmosphere, (E) 1600 °C product heated in N_2.

decomposition products of ethylamine,[20] ethylamine was passed through the quartz tube while the furnace was heated to 400, 500, and 600 °C. In all three cases FTIR analysis of the gaseous products showed the presence of ethylamine and a small quantity of ammonia that was present as an impurity. To determine if a more extended residence time in the furnace would cause ethylamine decomposition, a sample was held at 600 °C for 1 min in the quartz tube. Again, FTIR analysis of the gaseous products showed only ethylamine and the small ammonia impurity. Thus, ethylamine appears to be stable over the temperature range 400–600 °C under the polymer decomposition conditions.

Discussion

Polymerization. The condensation polymer derived from $Si(NHEt)_4$ affords an opportunity to study the pyrolytic conversion of an all-nitrogen-bound silicon species to ceramic products. On heating, the silicon tetraamides are known to undergo loss of amine, with resultant condensation of the amides to form insoluble, infusible solids. Andrianov[9] has suggested, on the basis of elemental analysis data and IR spectral studies, that the solid product of this condensation process, in the case of $Si(NHEt)_4$, is a spirocyclic polymer consisting of a chain of interconnected four- and six-membered $(SiN)_{2\,\mathrm{or}\,3}$ rings linked through silicon.

Table III. ^{29}Si Solution NMR Data for Various SiN_4 Structures

structure	SiN_4 ^{29}Si δ	ref
	R = H, −50.63 R = $SiMe_3$, −53.89	42
	R = Et, −53.3	43
	−33.5	43
	−62.91	42

The results of our studies of this system, which have employed ^{13}C and ^{29}Si solid-state NMR spectroscopy in addition to IR spectroscopy, indicate a somewhat more complicated structure involving cyclodisilazane rings linked together by –NEt– bridges between silicon atoms. The ^{29}Si solid-state NMR spectrum of the polymer (Figure 7A) shows a dominant, relatively sharp resonance at −51 ppm, which is shifted considerably upfield relative to the ^{29}Si peak of the starting $Si(NHEt)_4$ (−41.1 ppm, Figure 2C). The position of this peak is consistent with expectations for silicon in an amine-substituted cyclodisilazane environment (∼−52 ppm; Table III) but not with the spirocyclic SiN_4 structure (−62 ppm). The small peak at ca. −35 ppm could be indicative of a small amount of cyclotrisilazane or a highly bridged, acyclic structure; however, this is clearly a minor component of the polymer.

The ^{13}C NMR spectrum of PCS-Et (Figure 6A) is quite similar to that of $Si(NHEt)_4$ (Figure 2C), with peaks at 35.4 and 22.1 ppm, corresponding to the methylene and methyl carbons. Apparently in the case of these peripheral atoms, any difference in chemical shielding between the terminal and bridging NEt groups is insufficient to be resolved.

The IR spectrum of $Si(NHEt)_4$ (Figure 5A) shows a peak at 937 cm^{-1}, which has been attributed to the $Si–N_{asym}$ stretch.[21] This peak is slightly shifted to higher wavenumbers (948 cm^{-1}) in the spectrum of PCS-Et (Figure 5B), and a new peak appears at 864 cm^{-1}. Il'in has assigned peaks in this region to the endocyclic Si–N bond of a cyclodisilazane ring.[22] The band at 3355 cm^{-1} in this spectrum also indicates that an appreciable fraction of the

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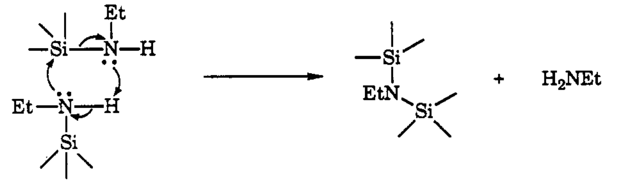
[20] Lovas, F. J.; Clark, F. O.; Tiemann, E. *J. Chem. Phys.* **1975**, *62*, 1925.

[21] Andrianov, K. A.; Kopylov, V. M.; Zaitseva, M. G.; Khan, V. S.; Shkol'nik, M. I. *Zh. Obshch. Khim.* **1979**, *49*, 2683.

[22] Il'in, M. M.; Moskovkin, A. S.; Talanov, V. N.; Miroshnichenko, I. V.; Bochkarev, V. N.; Chernyshev, A. E. *Zh. Obshch. Khim.* **1982**, *53*, 110.

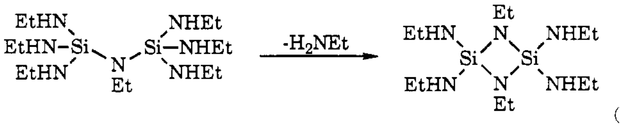
original N–H functionality remains, presumably as terminal Si–NHEt groups.

Ethylamine was found to be the major byproduct of the condensation polymerization of $Si(NHEt)_4$. Ethylamine could be generated by the following mechanism:



(5)

It seems unlikely that the mechanism involves radicals, since the temperature of the polymerization is relatively low (120–220 °C). Further loss of ethylamine by a similar mechanism results in a four-membered ring:



(6)

When multiple condensations occur, a structure such as that shown in Figure 9A could result.

Converting the elemental analysis data for PCS-Et into an empirical formula, $Si_2(NC_{1.97}H_{4.73})_{4.82}$, suggests that there are approximately five NC_2H_5 groups for every two silicon atoms. This is in agreement with the structure proposed in Figure 9A.

Six-membered rings can result in a similar manner, and in the case of the methylamide, structures containing such rings have been assigned to the resulting polymers.[9,10] However, in the case of the ethylamide, the larger size of the ethyl groups may favor the formation of four-membered rings, where steric interactions between the ring substituents are reduced relative to those in the corresponding six-membered ring. The effect of ring substituents on ring size has been investigated in the related $[AlR_2NR'_2]_n$ compounds, where six-membered rings are found when R and R′ are relatively small substituents (e.g., Me and H), whereas four-membered rings result when larger substituents are employed.[23]

Diethylamine was a minor byproduct (~8%) of the condensation polymerization of $Si(NHEt)_4$. Diethylamine forms in the later stages of polymerization, possibly because N–H functionalities become less abundant and more inaccessible because of branching. Structures such as that shown in Figure 9B may form when diethylamine is produced by transfer of an ethyl group.

Pyrolysis to Ceramic Products. Pyrolysis of the PCS-Et polymer leads to structural changes that are evident in the solid-state NMR and infrared spectra of the intermediate decomposition products. The solid-state ^{13}C NMR spectrum of the 500 °C sample (Figure 6B) shows the presence of new sharp peaks at 28.4 and 45.0 ppm, as well as a small, broad pattern in the 100–250 ppm region, which are not present in the solid-state ^{13}C NMR spectrum of the polymer (Figure 6A). The small, sharp peaks are attributed to ethyl groups in a slightly different environment than those of the polymer. The small broad pattern between 100 and 250 ppm is in the region for graphite (see graphite discussion below). The silicon environment in the 500 °C sample, as reflected in Figure 7B, is essentially the same as that of the polymer (Figure 7A), but the major peak at −51 ppm is now slightly broader. The minor peak at −35 ppm in the spectrum of PCS-Et is much weaker in the spectrum of the 500 °C product. We conclude that the structure, from the perspective of the silicon, still consists mainly of SiN_4 units in cyclodisilazane rings, but with increased branching/cyclization leading to a variety of slightly different microenvironments for the individual silicon atoms.

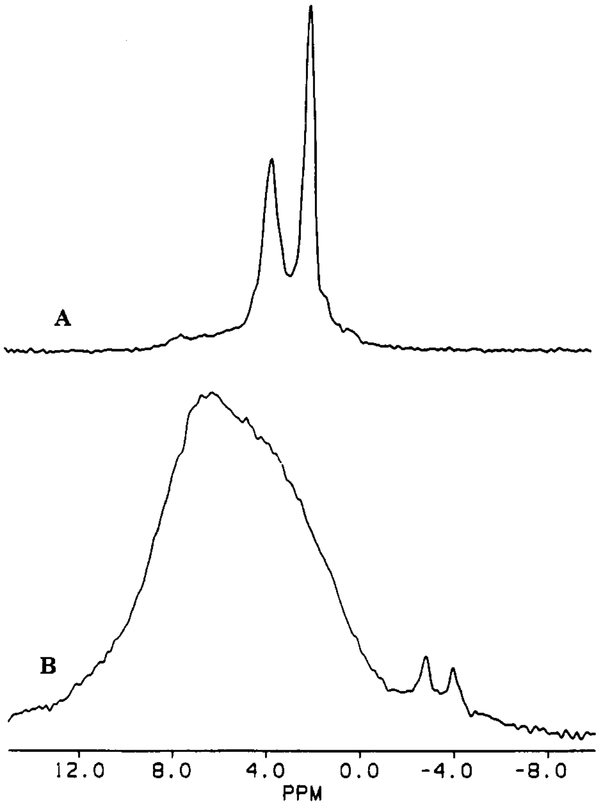
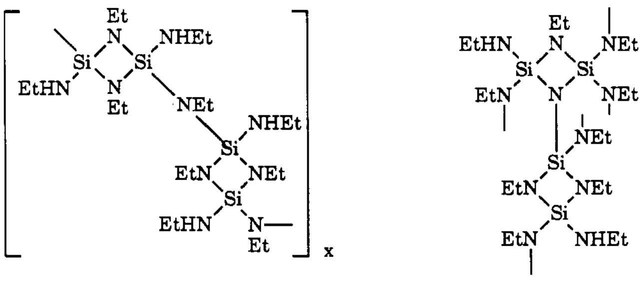


Figure 8. The 187-MHz ^1H CRAMPS solid-state NMR spectra of (A) 500 °C product and (B) 800 °C product. The two small peaks between −2 and −5 ppm are artifacts (rotor lines). Comparison between the peak intensities of Figure 8a and 8b should be done carefully since the amount of sample used to generate Figure 8b was about 5 times that of Figure 8a.



9a 9b

Figure 9. (a) Proposed polymer structure from condensation of four-membered rings. (b) Proposed structure from loss of diethylamine.

The ^1H CRAMPS solid-state NMR spectrum of the 500 °C material (Figure 8A) shows two large peaks at 3.3 and 1.8 ppm, confirming the fact that the ethyl groups are largely intact. Comparison of the frequencies in the C–H stretch region of the IR data for PCS-Et (Figure 5B) and the 500 °C sample (Figure 5C) shows that the frequencies are the same, again suggesting that the ethyl groups are still intact. IR also shows the presence of N–H bonding (3390 cm^{-1}) from the pendant –NHEt groups in the 500 °C sample.

By 800 °C, the organic functionalities are no longer present. The IR spectrum of the 800 °C sample (Figure 5D) indicates the formation of Si–H bonds (2130 cm^{-1})[24]

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[23] Interrante, L. V.; Sigel, G. A.; Hejna, C.; Garbauskas, M. *Inorg. Chem.* **1989**, *28*, 252.

and the disappearance of C–H (2800–3000 cm^{-1}) and N–H (3350–3450 cm^{-1}) and shows a large broad absorption centered at 930 cm^{-1}. Amorphous silicon nitride has a single, broad peak at about 900 cm^{-1}.[25] X-ray diffraction of the 800 °C material (Figure 4A) confirms that it is amorphous.

The ^{13}C solid-state NMR spectrum of the 800 °C PCS-Et (Figure 6C) shows two major, broad peaks at 176 and 130 ppm and two minor broad peaks at 83 and 35 ppm. Wilkie and co-workers[26] analyzed different samples of graphite by ^{13}C solid-state NMR and report a large, broad peak centered at about 170 ppm. In an earlier publication, Haworth and Wilkie[27] report a peak at about 155 ppm for graphite. Nikonorov and Zhuzhgov[28] report positions at 191 and 85 ppm for graphite. The low-shielding pair is assigned to aromatic type environments, and the high-shielding peaks are assigned to carbon in a tetrahedral bonding arrangement. In the spectrum of 800 °C PCS-Et the peaks at 176, 130, and 83 ppm are very close to those reported in the literature and can be assigned to graphite. ^{13}C solid-state MAS NMR spectrum of β-silicon carbide shows a single peak in the region between 18 and 24 ppm depending on the crystallite size.[29] The small peak at 35 ppm in the ^{13}C solid-state NMR spectrum of the 800 °C sample may arise from a silicon carbide type structure in which there are SiN_xC_{4-x} environments, thus causing a shift to lower shielding in the ^{13}C peak position.

The ^{29}Si solid-state NMR spectrum (Figure 7C) of the 800 °C product shows a broad peak centered at −45.0 ppm, indicative of amorphous Si_3N_4.[30] β-SiC has a single peak between −16 and −20 ppm, again depending on the crystallite size, in the ^{29}Si MAS NMR spectrum.[29-31] Since there is only a slight rise in the baseline in this region, not much silicon carbide or SiC_4 functionality is present. The peak at −45.0 ppm tails out into the low-shielding direction, however, suggesting SiN_xC_{4-x} formation.

The ^{1}H CRAMPS solid-state NMR spectrum of the 800 °C sample (Figure 8B) shows a major asymmetric broad peak at ~6 ppm, which is in the region for the Si–H functionality.[24] No literature was found for the ^{1}H CRAMPS spectrum of the residual hydrogen in graphite, but considerable work has been done on the ^{1}H CRAMPS of coal. Comparison of the ^{1}H CRAMPS spectrum of coal with the ^{1}H CRAMPS spectrum for the 800 °C product shows some similarities. The ^{1}H CRAMPS spectrum of coal has two broad resonances centered at ~6.5 and ~1 ppm,[32] corresponding to the aromatic region and the aliphatic region, respectively. The large broad resonance centered at ~6 ppm in the ^{1}H CRAMPS spectrum of the 800 °C product most likely contains aromatic C–H environments from the free carbon in addition to some Si–H bonding, which was shown to be present by infrared spectroscopy.

After heating the 800 °C product to 1500 °C in an argon atmosphere, X-ray powder diffraction showed that crystalline β-SiC and a small quantity of α-SiC were present (Figure 4B). Solid-state ^{29}Si NMR (Figure 7D) shows a single resonance at −19.1 ppm, which is consistent with that of β-SiC. The peak at −45 ppm present in the 800 °C material (Figure 7C) and attributed to SiN_4 is not present in the 1500 °C sample heated in argon. The FTIR spectrum of this product (Figure 5E) has a sharp peak centered at 800 cm^{-1}, which is consistent with the spectrum of silicon carbide.[33] Thus, whereas both the infrared spectrum and ^{29}Si MAS NMR spectrum showed that amorphous silicon nitride was present and little silicon–carbon bonding was present relative to silicon–nitrogen bonding in the 800 °C sample, the main product obtained after heating to 1500 °C in argon was silicon carbide. Previous workers have reported that when α-silicon nitride is heated in the presence of carbon to 1500 °C, β-silicon carbide is formed by reaction 7.[34]

$$Si_3N_4(s) + 3C(s) \rightarrow 3SiC(s) + 2N_2(g) \qquad (7)$$

Solid-state ^{13}C NMR (Figure 6D) shows no resonances for either graphitic or carbidic type carbon. A reduction in the intensity of the graphitic peaks is expected since this is the source of carbon for the reaction with silicon nitride. Excess carbon is still present, however, since the empirical formula obtained from the elemental analysis (Table I) of the 1500 °C argon sample shows that the ratio of carbon to silicon is 1.49. Although a graphite spectrum was obtained on the 800 °C spectrum, it may be more difficult to obtain a graphite spectrum of the 1500 °C sample because of the reduction in the concentration of graphite in the sample and the reduction in the quantity of residual hydrogen present in heating from 800 to 1500 °C. A loss of hydrogen would result in longer relaxation times for the ^{13}C NMR of the graphite. No spectrum of β-SiC was obtained despite use of long relaxation times (up to 0.5 h) and/or cross polarization techniques. Previous workers have reported having the same difficulty in obtaining a ^{13}C spectrum of β-SiC.[29,35,36]

Since heating the 800 °C product at 1500 °C for 4 h in N_2 was not sufficient to crystallize the sample, the 800 °C product was heated at 1600 °C in N_2 for 4 h. The X-ray diffraction pattern (Figure 4D) is consistent with that of α-Si_3N_4 but also shows some peaks for β-SiC. FTIR of the 1600 °C product (Figure 5F) shows peaks characteristic of α-Si_3N_4.[25] Assigning an absorption for silicon carbide in the infrared spectrum of the 1600 °C material is difficult, since it absorbs in the same region as silicon nitride. Solid-state ^{29}Si NMR (Figure 7E) shows two resonances at −13.2 and −50.8 ppm. There are consistent with β-SiC and crystalline Si_3N_4, respectively. Elemental analysis shows that 16.6% carbon is present in the sample after heating to 1600 °C in N_2.

These data show the importance of the environment in determining the crystalline end product of the high-temperature anneal. In a N_2 environment, most of the SiN_4 species are retained while in an argon environment the

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(25) Luongo, J. P. *Appl. Spectrosc.* **1984**, *38*, 195. Wada, N.; Solin, S. A.; Wong, J.; Prochazka, S. *J. Non-Cryst. Solids* **1981**, *43*, 7. Trout, T. K.; Bellama, J. M.; Brinkman, F. E.; Faltynek, R. A. *J. Mater. Res.* **1989**, *4*, 399.

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(35) Hartman, J. S.; Richardson, M. F.; Sheriff, B. L.; Winsborrow, B. G. *J. Am. Chem. Soc.* **1987**, *109*, 6059.

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SiN_4 species lose N_2 and react with the available carbon to produce SiC_4 species.

Pathway for PCS-Et Decomposition. Table II summarizes the qualitative and quantitative results on the analysis of the volatile products of PCS-Et decomposition. These data agree quite well with the TGA data, which show that the major decomposition occurs between 400 and 600 °C. These data will be discussed first with respect to the nitrogen-containing volatile products, ethylamine, ammonia, and hydrogen cyanide, and then with respect to the hydrocarbon species.

The evolution of ethylamine is attributed to continuing condensation of the polymer, leading to a network of —NEt— and —N= bridged silicon atoms. Ethylamine is known to decompose at temperatures as low as 500–600 °C in a quartz tube if sufficient surface area is provided.[37] The quantitative analysis data for the volatile products show that the ratio of ethylamine to ammonia, formed in the temperature range 50–400 °C, is 2.71, whereas the ratio for the temperature range 400–600 °C is 0.60. Additionally, hydrogen cyanide is observed between 400 and 600 °C. Within the 600–800 °C temperature interval, ethylamine is no longer observed, only ammonia and hydrogen cyanide. The changing ratios of ethylamine to ammonia and the presence of hydrogen cyanide suggest the decomposition of ethylamine. Ethylamine was not observed to decompose, however, in the quartz tube containing the molybdenum boat within the temperature range 400–600 °C. The only difference between the conditions of ethylamine furnace stability studies and the polymer decomposition was the presence of the polymer. It is possible that the polymer provides the additional surface area to catalyze decomposition of the evolved ethylamine. Alternatively, ammonia and hydrogen cyanide may be direct decomposition products of PCS-Et. The NHEt and NEt groups attached to silicon may decompose in a manner similar to the decomposition of ethylamine and, thus, result in the same products. It is difficult to say conclusively which of the two processes actually occurs.

Among the condensable hydrocarbon products, ethylene is the most abundant. Our solid-state ^{13}C NMR data showed that carbon was present in the polymer in the form of ethyl groups bound to nitrogen. Cleavage of the ethyl group from nitrogen would result in an ethyl radical. Purnell and Quinn, in their study of the decomposition of *n*-butane, discuss the decomposition of the ethyl radical.[38] They observed that both ethane and ethylene were produced in decomposing *n*-butane and determined that at low pressures (<50 mmHg) and high temperatures (~500 °C) ethylene was formed at the expense of ethane. On the basis of Purnell and Quinn's results, one would expect ethylene to be the major hydrocarbon product of the decomposition of PCS-Et followed by ethane. The remaining hydrocarbon products—propene, acetylene, and propane—are reported products in the decomposition of ethylene and/or ethane[39] and, therefore, are most likely secondary decomposition products. The decomposition of hydrocarbons to carbon has been extensively studied and shown to yield graphite upon pyrolysis.[39b,40]

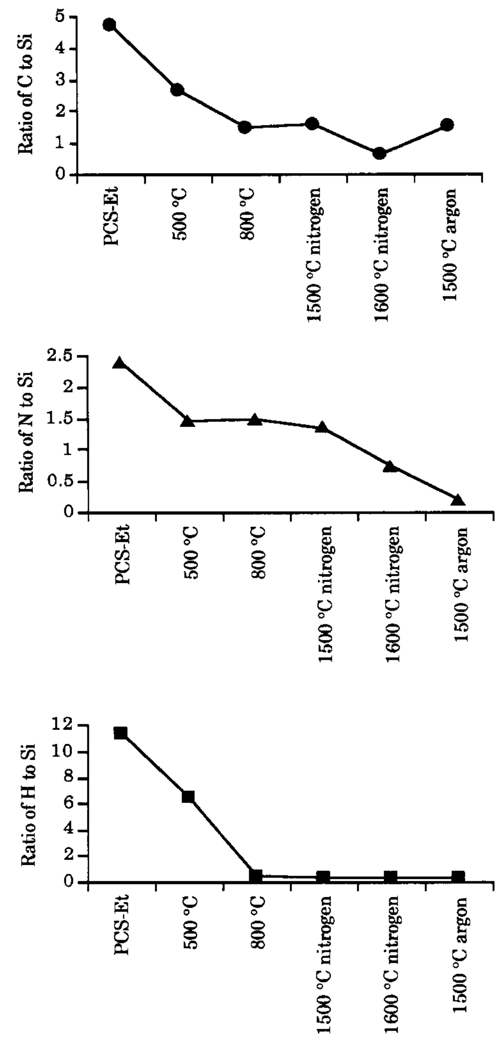

Figure 10. Comparison plots of the loss of (a, top) carbon, (b, middle) nitrogen, and (c, bottom) hydrogen in heating PCS-Et from room temperature to 1600 °C.

The elemental analysis data in Table I have been converted to an empirical formula normalized to the respective silicon values. The loss of carbon, nitrogen, and hydrogen at each of the intermediate steps of the pyrolysis is represented graphically in Figure 10. Elemental analysis shows that carbon is lost at a steady rate in heating PCS-Et up to 800 °C. This is consistent with the gaseous analysis, which shows loss of both amines and hydrocarbons over this temperature range. Between 800 and 1500 °C the loss of carbon stabilizes. The 1600 °C sample that was heated in N_2 shows additional loss of carbon as compared with the 1500 °C sample heated in N_2. Loss of carbon may be due to an oxygen impurity in the N_2 source, since at 1600 °C even a small amount of oxygen in the gas flow is likely to promote loss of carbon as CO or CO_2. The 1500 °C argon sample contains approximately the same amount of carbon as the 800 °C product, but as was shown by the solid-state NMR data and FTIR data, it is present primarily in a carbidic form rather than the graphitic form of the 800 °C product.

The elemental analysis shows that nitrogen is lost up to 500 °C and levels off between 500 and 800 °C. This is consistent with the gaseous analysis data, which shows loss of ethylamine and ammonia in both the 50–400 and the

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(37) Private communication with Frank J. Lovas, N.I.S.T.

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Chem. Mater. **1991**, *3*, 730–737

400–600 °C temperature ranges. In going from 800 to 1500 °C in N_2, a small amount of nitrogen is lost, while in going from 800 to 1600 °C, an even greater amount of nitrogen is lost. Schmidt et al. have shown that precursor-derived silicon nitride begins to decompose in 1 atm of helium at approximately 1000 °C with major decomposition beginning at 1500 °C.[41] Thus, the loss of nitrogen in the sample heated to 1500 °C in N_2 and the sample heated to 1600 °C in N_2 can be attributed to decomposition of silicon nitride. As is shown by the elemental analysis data obtained after heating to 1500 °C in argon, this loss of nitrogen is increased substantially when N_2 is excluded from the gas phase. This substantiates the solid-state NMR and IR data showing the reaction of silicon nitride and carbon to give silicon carbide and N_2.

The analytical data also show steady loss of hydrogen in heating PCS-Et to 500–800 °C. This is consistent with the gaseous analysis showing loss of hydrocarbons, ammonia, and amines over this temperature interval. In addition, molecular hydrogen may be produced; it was not specifically investigated. By 800 °C the amount of hydrogen left is less than 0.5%.

Conclusions

PCS-Et has been shown to decompose to either silicon nitride or silicon carbide, depending on the atmosphere used when heating above 800 °C. Heating PCS-Et to 500 °C results mostly in further cyclization and/or branching of the polymer with little decomposition of the hydrocarbon substituents. For a sample heated to 800 °C, FTIR and ^{29}Si MAS NMR reveal that the product contains amorphous silicon nitride and little silicon–carbon functionality. Elemental analysis shows the presence of carbon in the sample, and ^{13}C MAS NMR suggests that it is, at least in part, in the form of graphite. Heating the 800 °C product to 1500 °C in argon results in mostly β-SiC and carbon with some α-SiC, and heating to 1600 °C in N_2 results in mostly α-Si_3N_4 and carbon with a minor amount of β-SiC.

The most notable observation is the retention of the SiN_4 structural environment for Si throughout the conversion of the polymeric silazane to the amorphous ceramic product at 800 °C, albeit with the formation of a considerable amount of free carbon as a byproduct of hydrocarbon (or hydrocarbon radical) decomposition. This carbon byproduct is then available for reaction with the amorphous Si_3N_4, leading to the production of crystalline SiC observed on heating to 1500 °C. The loss of nitrogen that accompanies this latter process is inhibited by the presence of this gas in the pyrolysis environment, resulting in the formation of crystalline Si_3N_4 on heating to 1600 °C in 1 atm of N_2.

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Synthesis of Amide- and Ester-Functionalized Zirconium Phosphonates

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The syntheses of layered amide and ester derivatives of $Zr(O_3PCH_2CH_2COOH)_2$ are described. These new materials, $Zr(O_3PCH_2CH_2COXC_nH_{2n}H)_2$ ($X = NH$, $n = 0$–18; $X = O$, $n = 2$–6), are prepared via amine and alcohol intercalation reactions of layered $Zr(O_3PCH_2CH_2COCl)_2$. They are characterized by powder X-ray diffraction, IR, and ^{13}C CP MAS NMR spectroscopies as well as by thermogravimetric analysis. The interlayer separation in these materials is directly related to the length (n) of the amide or ester alkyl chain. For amides, the interlayer distance varies from 13.8 to 53 Å and is consistent with an angle of 59° between the the alkyl chain and the surface of the inorganic layer. The layered amide compounds have greater thermal and chemical stabilities than analogous compounds prepared by Brønsted acid/base reactions. A bridging ester derivative, $Zr(O_3PCH_2CH_2COOCH_2CH_2CH_2PO_3)$, has also been prepared by the reaction of $Zr(O_3PCH_2CH_2COCl)_2$ with $HSn(C_4H_9)_3$.

Introduction

The intercalation of organic molecules into layered inorganic compounds has been studied by a number groups over the past 25 years.[1] In this reaction inorganic host layers separate to accommodate interaction with organic guest molecules. A fully intercalated material consists of regularly alternating organic and inorganic layers as shown schematically in Figure 1. Intercalation can significantly alter both the physical nature and chemical reactivity of a host. For example, intercalation has been used to modify a host's optical properties, superconducting critical temperature, and interlayer magnetic coupling.[1,2] Applications of intercalation compounds include materials design,[3] ion exchange,[4] and catalysis.[5] Some recent and very inter-

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