Chem. Mater. 1992, 4, 1263–1271

Thermogravimetric Analysis/Mass Spectrometry Investigation of the Thermal Conversion of Organosilicon Precursors into Ceramics under Argon and Ammonia. 2. Poly(silazanes)

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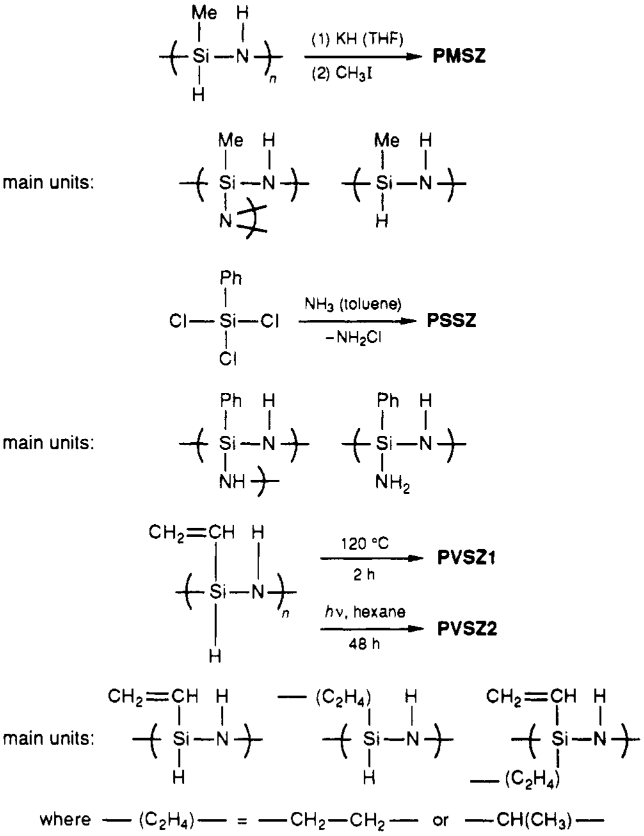
Received May 19, 1992. Revised Manuscript Received September 18, 1992

The pyrolysis under argon and under ammonia of various poly(silazanes) (poly(methylsilazane), poly(phenylsilsesquiazane), and poly(vinylsilazane)) was studied by means of thermogravimetric analysis associated with continuous mass spectrometry of the gases evolved. Under argon the main reactions observed are transamination and dehydrocoupling between N–H and Si–H bonds (if any) followed by homolytic cleavages of Si–H and Si–C bonds and further reactions of the radicals formed. The decomposition under ammonia involves different processes, depending on the nature of the organic groups. The amination of the silicon atoms takes place below 750 °C, before the thermal decomposition of ammonia. The mechanism of this substitution is likely to be nucleophilic in the case of Si–H bonds, whereas homolytic cleavages certainly occur in the case of alkyl or aryl groups. In that case, the possibility of H abstraction from NH_3 molecules prevents cross-linking via combination reactions and favors the escape of hydrocarbons. In the case of poly(vinylsilazane), polyaddition reactions of vinyl groups led to cross-linked carbon atoms which are not completely removed by ammonia and undergo the same radical reactions as under argon, giving unsaturated excess carbon. Above 750 °C, this excess carbon is removed as HCN; this reaction likely involves the pyrolysis products of NH_3.

Introduction

Scheme I



The polymeric route to silicon carbide and silicon nitride ceramics is currently being developed.[1-5] In this process the controlled pyrolysis of suitable organometallic polymers leads to ceramic materials via soluble or fusible intermediates. In fact, industrial interest arises from these processable intermediates, which are required for special applications such as coatings, binders, or fibers. The aim is to obtain (i) a high ceramic yield, that is, a low weight loss throughout the pyrolytic conversion, in order to minimize shrinkage and the destructive effect of the evolution of gases, and (ii) the desired elemental composition of the final ceramic, such as SiC or Si_3N_4 without excess of carbon (or silicon).

A good knowledge of the chemistry involved in each step of this process is necessary in order to choose suitable polymeric precursors,[6,7] as well as to set up the procedures of the curing step and the pyrolysis step, such as the temperature, the heating rate, and the atmosphere. The choice of a reactive gas permits change in the nature of the precursor and of the ceramic material. Thus pyrolysis in an ammonia atmosphere has been widely used;[8-12] it leads to essentially pure Si_3N_4 regardless of the nature of the precursors, poly(carbosilanes) or poly(silazanes). Am-

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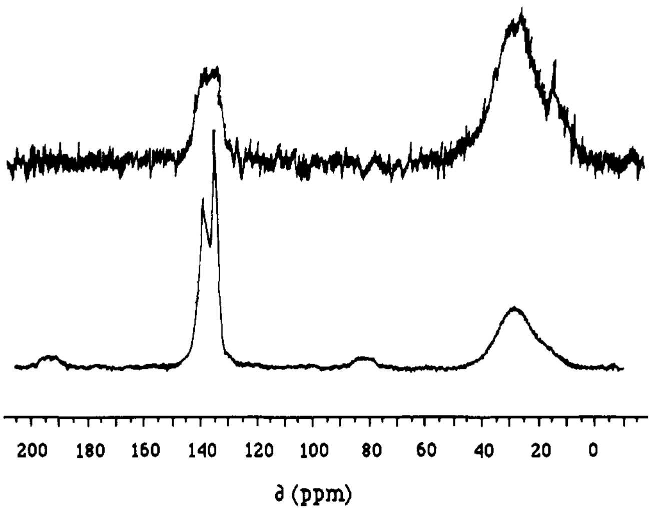

Figure 1. ^{13}C CP MAS NMR spectra of PVSZ1 (a, bottom) and PVSZ2 (b, top).

monia may also be used to remove carbon from ceramic powders, yielding hydrogen cyanide.[13]

To understand the reactions involved in the pyrolysis process, we investigated the thermal degradation of poly(silazanes) under argon and under ammonia by means of thermogravimetric analysis (TGA) associated with the continuous mass spectrometry (MS) of the gases evolved during pyrolysis. We studied three polysilazane samples with quite different structures (Scheme I): poly(methylsilazane) (PMSZ), which was first cross-linked by dehydrocoupling catalyzed by KH according to the method developed by Seyferth et al.;[14] phenylsilsesquiazane (PSSZ), prepared according to Burns et al.;[15] poly(vinylsilazane) (PVSZ),[16] which was cross-linked either by a short thermal treatment (2 h at 120 °C)[16a] (PVSZ1) or by UV irradiation (PVSZ2).

Experimental Section

Materials. PMSZ was prepared according to the literature[14] from oligo(methylsilazane) cross-linked in the presence of KH. The reaction was conducted in tetrahydrofuran, and an insoluble solid was obtained; despite reaction with methyl iodide and washing, the powder obtained still contained 1 wt % potassium, according to elemental analysis. Atomic composition: $SiC_{1,09}H_{4,05}Na_{0,98}O_{0,11}K_{0,015}$.

PSSZ was prepared according to ref 15, by bubbling ammonia into a solution of $PhSiCl_3$ (1 volume) in toluene (10 volumes) cooled to −30 °C. After filtration and evaporation at room temperature, a white solid was obtained, which was characterized by infrared and ^1H NMR spectroscopy. IR spectroscopy showed the presence of NH groups (3362 cm^{-1}) and a small amount of NH_2 groups (3450 and 3362 cm^{-1}).

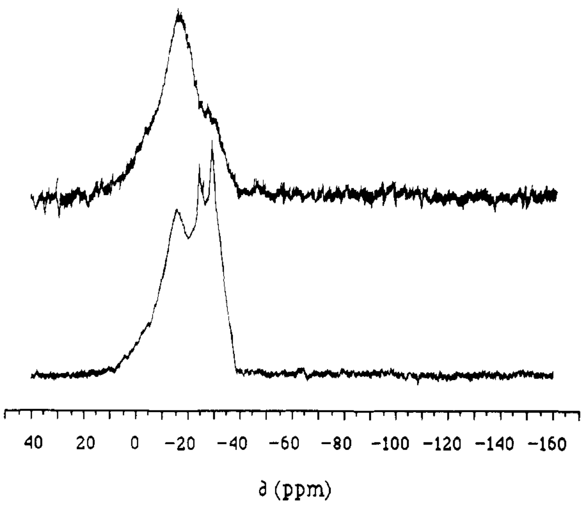

Figure 2. ^{29}Si CP MAS NMR spectra of PVSZ1 (a, bottom) and PVSZ2 (b, top).

PVSZ1 was obtained as an insoluble, elastic solid by heating neat oligovinylsilazane at 120 °C for 2 h. Under these conditions, thermal hydrosilation takes place (i.e., addition of the Si–H bond to the vinylic double bond), leading to the formation of $SiCH_2CH_2Si$ and $SiCH(CH_3)Si$ bridges (Scheme I).[16a] Solid-state ^{29}Si spectroscopy (Figure 2a) indicated the formation of SiC_2N_2, $SiCHN_2$, and $SiCC^{sp^2}N_2$ sites (resonances expected around −6, −15 and −20 ppm, respectively)[16a] in addition to the initial sites $SiC^{sp^2}HN_2$ (resonance around −28 ppm). Solid-state ^{13}C spectroscopy (Figure 1a) showed a broad peak in the range +45 to +5 ppm, corresponding to the resonance of the sp^3 carbons arising from hydrosilation. Atomic composition: $SiC_{1.93}H_{4.65}N_{0.90}O_{0.04}$.

PVSZ2 was prepared as a fine, insoluble, white powder (52% yield) by the following procedure: a solution of oligo(vinylsilazane)[16a] (2.3 g) in dried hexane (150 mL) was irradiated under agitation by a high-pressure mercury lamp for 2 days under a nitrogen atmosphere. The precipitate was washed with anhydrous hexane and dried under vacuum for 2 h at room temperature. The fine white powder obtained was characterized by infrared and NMR spectroscopy.

Solid-state ^{13}C and ^{29}Si spectroscopy (CP/MAS; Figure 1b and 2b) showed the presence of the same sites as in the case of PVSZ1, indicating that the main reaction occurring during the irradiation was also hydrosilation. However the amount of starting sites was much lower, indicating that hydrosilation is more extensive.

Elemental analysis led to the following atomic composition: $SiC_{2.31}H_{5.4}N_{1.1}O_{0.16}$.

The rather large excess of C compound to the theoretical composition (SiC_2H_5N) indicates the presence of ca. 5 wt % of residual hexane despite the drying treatment.

Techniques. *TG/MS Analysis.* Thermogravimetric analysis (TGA) was carried out using a Netzsch STA409 thermobalance. Typically about 20 mg of sample was heated in an alumina crucible from room temperature to 1200 °C at 10 °C/min in a stream of pure argon or ammonia–argon (30/70) mixture (flow rate 50 mL min^{-1}) to avoid the presence of ammonia into the balance part.

The thermogravimetric analyzer was coupled to a Anagaz 200 quadrupole mass spectrometer (ionization energy 75 eV). The volatile products evolved during pyrolysis were taken from the furnace above the sample to the spectrometer by a stainless steel capillary (internal diameter 0.25 mm) heated at 150 °C through a 10-μm molecular leak. One scan from 2 to 150 amu was collected and stored every 30 s throughout the pyrolysis process. This apparatus permits the identification of the different gases evolved during pyrolysis; it is possible either to plot mass spectra obtained at selected temperatures or to plot the evolution of the signal of characteristic ions as a function of temperature. In the absence of standardization only qualitative information may be drawn from these curves. It should be noted that due to the limited range of the mass spectrometer and to condensation in the cold parts of the apparatus only low molecular weight compounds such as gases or volatile liquids (with boiling points lower than ca. 180 °C) are detected by TG/MS. Thus, a release of condensable

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Table I. Ceramic Yields and Elemental Analysis for the Precursors Pyrolyzed at 1350 °C in Argon[a]

precursor	yield (%)	%Si	%C	%H	%N	%O	total %
PMSZ[a]	81	56.7 (1)	13.0 (0.54)	0.5 (0.25)	29.0 (1.02)	0.7 (0.02)	99.9
PSSZ[a]	61	30.2 (1)	45.1 (3.48)	0.4 (0.37)	16.7 (1.11)	4.3 (0.25)	96.7
PVSZ1[a]	83	47.3 (1)	29.9 (1.48)	0.3 (0.18)	21.8 (0.90)	1.1 (0.04)	100.4
PVSZ2[a]	76	46.7 (1)	28.5 (1.42)	0.3 (0.18)	21.6 (0.93)	2.7 (0.10)	99.8

[a] Atomic ratios in parentheses.

Table II. Weight Composition of the Ceramics after Pyrolysis at 1350 °C in Argon, According to the Rule of Mixture Calculations[17]

precursor	%SiO_2	%Si_3N_4	%SiC	%C
PMSZ	1.2	72.9	18.4	7.5
PSSZ	8.4	43.5	1.9	46.2
PVSZ1	2.0	54.3	19.6	24.1
PVSZ2	3.0	54.6	16.9	23.5

compounds such as oligomers may not be detected by MS despite a noticeable weight loss in the TGA curve.

Elemental analyses. Elemental analyses were performed by the Service Central d'Analyse du CNRS. The samples were heated using a temperature program of 10 °C/min until the specified temperature.

NMR. Solid-state high-resolution NMR spectra were recorded on a Brucker AM 300 instrument applying magic angle spinning (MAS, 4.1 kHz spinning rate) and ^1H decoupling techniques (90° pulse). Under cross-polarization conditions (CP), a contact time of 2 ms and a 10-s delay was used for ^{29}Si; a contact time of 5 ms and a 5-s delay was used for ^{13}C. When no CP was done, a 60-s delay was used.

Results and Interpretation

(I) Pyrolysis under Argon. *Elemental Analysis and Ceramic Yield.* The elemental analysis and ceramic yield of the four polysilazanes pyrolyzed at 1350 °C under argon are displayed in Table I. The ceramic yield is high whatever the sample, indicating that the loss of organosilicon species during pyrolysis is negligible, due to the high degree of cross-linking and the thermal reactivity of these precursors.

The composition (neglecting oxygen and hydrogen) of the residues at 1350 °C strongly depends on the nature of the precursor: $SiC_{0.54}N$ for PMSZ, $SiC_{3.48}N_{1.11}$ for PSSZ, and $SiC_{1.42}N_{0.93}$ for PVSZ2. The weight percent composition of the residues, assuming that only equilibrium phases, SiO_2, SiC, Si_3N_4, and C, are present in the final ceramic (rule of mixture calculations[17]) is reported in Table II. These calculations allow the evaluation of the amount of excess carbon in the ceramic, although metastable silicon carbonitride species, SiN_xC_y, are probably present.[17] The amount of excess carbon increases in the order PMSZ < PVSZ < PSSZ.

TG-MS Analysis. PMSZ: The TG-MS analysis of PMSZ is given in Figure 3. The TGA curve shows a small weight loss (2.2%) from 200 to 400 °C which corresponds to the escape of some condensable oligomers; a small amount of ammonia (m/z 16, 17) and hydrogen are also detected in the range 200–300 °C. Three steps may be distinguished in the escape of hydrogen: from 200 to 300 °C, from 300 to 700 °C, and above 700 °C. The escape of methane starts at 400 °C and becomes significant at 500 °C. The major weight loss occurs between 460 and 750 °C with a large release of methane and hydrogen and traces of higher hydrocarbons (ethylene, ethane and propene). The total weight loss is 18.5% at 1100 °C.

PSSZ: The TG-MS analysis of PSSZ is given in Figure 4. The first weight loss (1.7%) below 200 °C corresponds to a loss of residual solvent; from 200 to 500 °C an escape of ammonia (m/z 16, 17) is detected. The major weight loss occurs between 400 and 750 °C and corresponds mainly to a large escape of benzene; hydrogen is evolved above 500 °C. The total weight loss is 39% at 1100 °C.

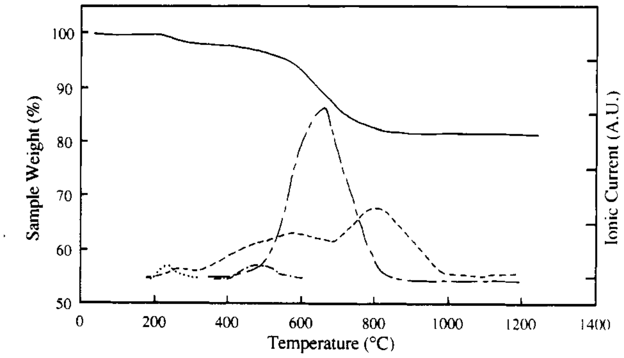

Figure 3. TG/MS analysis under argon of PMSZ: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; m/z 15 (—·—) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (–·–) arises from ethylene and ethane.

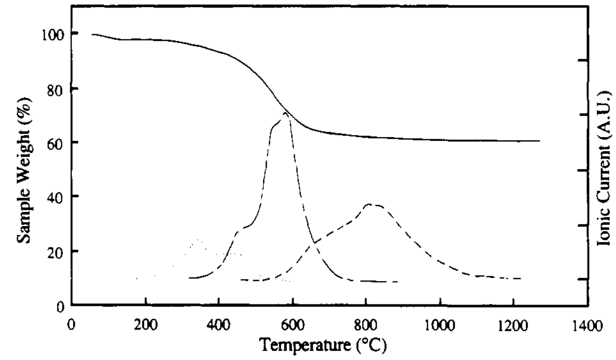

Figure 4. TG/MS analysis under argon of PSSZ: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; m/z 78 (—·—) arises from benzene; m/z 17 (···) arises from ammonia.

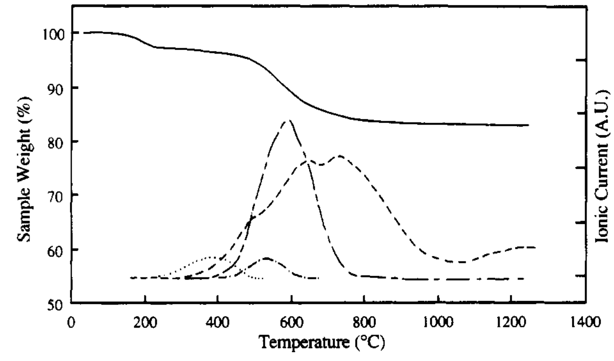

Figure 5. TG/MS analysis under argon of PVSZ1: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; m/z 15 (—·—) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (–·–) arises from ethylene and ethane.

PVSZ1: The TG-MS analysis of PVSZ1 is given in Figure 5. The TGA curve shows a small weight loss (2%) from 140 to 220 °C which corresponds to the escape of a few condensable oligomers. From 250 to 500 °C a small amount of ammonia is detected. Hydrogen is detected only above 300 °C. The loss of methane starts at about 400 °C; in addition, significant amounts of higher hydro-

Table III. Ceramic Yields and Elemental Analysis for the Precursors Pyrolyzed at 750 or 1350 °C in an Ammonia–Argon Mixture (30/70 v/v)

precursor (T_{pyr}, °C)	yield (%)	%Si	%C	%H	%N	%O	total %
PMSZ (750)	82	49.4 (1)	8.5 (0.40)	6.0 (3.4)	31.6 (1.28)	4.4 (0.16)	99.9
PMSZ (1350)	74	56.2 (1)	0.3 (0.01)	0.2 (0.10)	39.8 (1.42)	2.2 (0.07)	98.7
PSSZ (1350)	32	53.8 (1)	0.6 (0.03)	0.5 (0.3)	36.2 (1.35)	4.3 (0.14)	95.6
PVSZ1 (750)	83	46.0 (1)	16.6 (0.84)	2.2 (1.34)	32.6 (1.42)	2.8 (0.11)	100.2
PVSZ1 (1350)	73	52.2 (1)	13.6 (0.61)	0.1 (0.05)	32.9 (1.26)	1.8 (0.06)	100.6
PVSZ2 (1350)	64	55.2 (1)	0.5 (0.02)	0.1 (0.05)	37.9 (1.37)	5.3 (0.17)	99.0

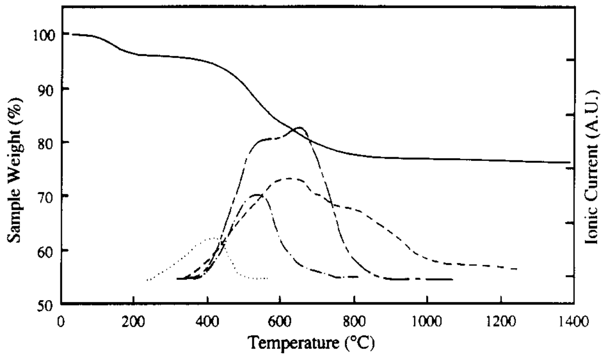

Figure 6. TG/MS analysis under argon of PVSZ2: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; m/z 15 (— - —) arises from methane; m/z 17 (···) arises from ammonia; m/z 27 (- · -) arises from ethylene and ethane.

carbons (ethylene, ethane, propane, ...) are detected in the range 400–650 °C. The total weight loss is 17% at 1100 °C.

PVSZ2: The TG-MS analysis of PVSZ2 is displayed in Figure 6. The TGA curve shows a small weight loss (4%) from 40 to 250 °C, which corresponds mainly to the escape of residual solvent (hexane). From 200 to 500 °C a small amount of ammonia is detected. Hydrogen is detected above 310 °C. The loss of methane takes place from 390 to 820 °C; in addition, ethylene and higher hydrocarbons (propene and butene) are detected in the range 390–700 °C. The total weight loss is 24% at 1100 °C.

(II) Pyrolysis under Ammonia. *Elemental Analysis.* As expected, the compositions of all the samples pyrolyzed at 1350 °C under ammonia (Table III) are close to Si_3N_4 with final carbon contents much lower than under argon and close to 0 except for PVSZ1. The large value still observed for PVSZ1 is at least partly ascribable to the compactness of the sample;[9] as a matter of fact, PVSZ1 is an elastic solid which cannot be ground, contrary to the PVSZ2 sample, which is obtained as a fine powder; it may also be related to the larger amount of free vinyl groups in PVSZ1 (see Discussion). Table III indicates that PVSZ1 is completely aminated at 750 °C (N/Si = 1.42), contrary to PMSZ (N/Si = 1.28). This will be discussed below in connection with the differences observed in the ^{13}C NMR spectra (Figure 7) of PMSZ and PVSZ1 treated at 750 °C under ammonia; actually only unsaturated aromatic (or olefinic) sites (around 135 ppm) remain at 750 °C in PVSZ1, whereas only saturated aliphatic ones (around 10 and 3 ppm) are present in PMSZ.

The compositions of the samples according to the rule of mixture calculations[17] are given in Table IV. The major phase is Si_3N_4 (80–95% of the sample weight). Even in the case of PVSZ1, the amount of SiC is negligible, which indicates that the carbon present after the pyrolysis is present mainly as excess carbon.

TG-MS Analysis under Ammonia. As mentioned above, the pyrolyses were conducted under a flow of argon and ammonia (30/70), at a heating rate of 10 °C/min. These conditions are of course not the most suitable to obtain pure silicon nitride (which is not the aim of this work) but do allow one to get a dynamic picture of the thermal processes occurring during the pyrolysis to be obtained.

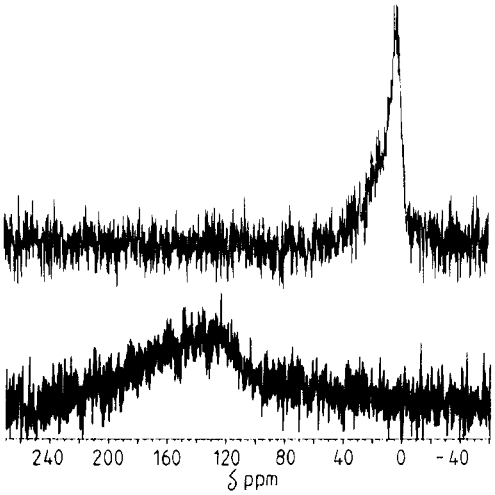

Figure 7. ^{13}C MAS NMR spectra of PMSZ (top) and PVSZ1 (bottom) heated at 800 °C under ammonia/argon (30/70) (heating rate 10 °C/min).

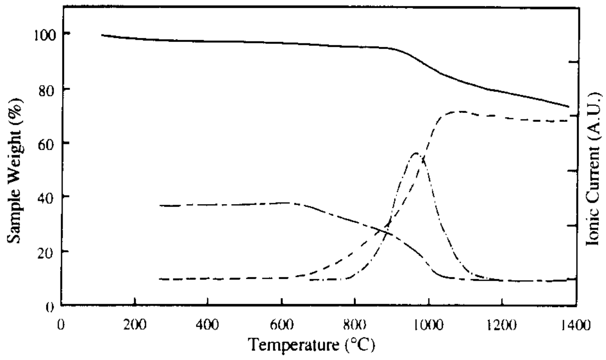

Figure 8. TG/MS analysis under ammonia/argon (30/70) of charcoal, showing the decomposition of ammonia and the escape of HCN: (—) TGA curve; the ion signal at m/z 2 (– – –) corresponds to hydrogen, arising from the thermal decomposition of ammonia; the ion signal at m/z 17 (— - —) arises from ammonia; m/z 27 (- · -) arises from HCN.

Table IV. Weight Composition of the Ceramics after Pyrolysis at 1350 °C in an Ammonia–Argon Mixture (30/70), According to the Rule of Mixture Calculations[17]

precursor	%SiO_2	%Si_3N_4	%SiC	%C
PMSZ	4.4	95.3		0.3
PSSZ	8.8	90.5		0.7
PVSZ1	3	82	2	13
PVSZ2	10.5	89.4		0.1

It was of interest to study the behavior of carbon (here finely ground vegetal charcoal purchased from Prolabo) under the same conditions (Figure 8). Although the carbon used had a high surface area, only 20% of the carbon was removed from 800 °C to 1350 °C. The thermal decomposition of ammonia became significant above 650–700 °C:

$$2NH_3 \rightarrow 3H_2 + 2N_2$$

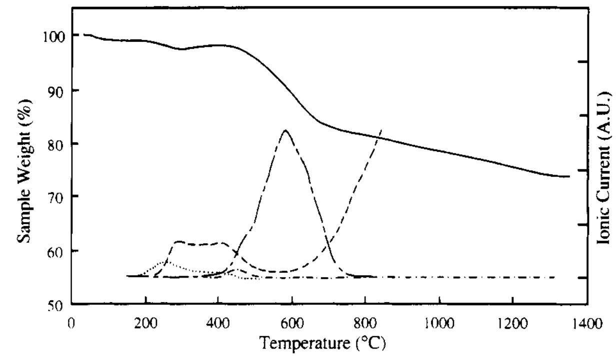

Figure 9. TG/MS analysis under ammonia/argon (30/70) of PMSZ: (—) TGA curve; the ion signal at *m/z* 2 (- - -) arises from hydrogen; *m/z* 13 (— - —) arises from methane; *m/z* 27 (-·-) arises mainly from ethylene and ethane; *m/z* 31 (···) arises from methylamine.

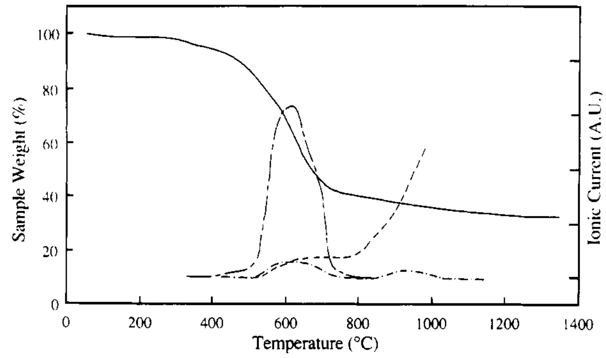

Figure 10. TG/MS analysis under ammonia/argon (30/70) of PSSZ: (—) TGA curve; the ion signal at *m/z* 2 (- - -) arises from hydrogen; *m/z* 27 (-·-) arises from $C_2H_3^+$ coming from ethylene and ethane below 750 °C and arises from HCN^+ coming from HCN above 750 °C; *m/z* 78 (— - —) arises from benzene.

The rate of elimination of carbon was the highest in the range 780–1180 °C (in addition to hydrogen and nitrogen); the main gas detected in that range was hydrogen cyanide (HCN) as shown by the abundant fragments at *m/z* 26 and 27. Above 1200 °C only ammonia, hydrogen, and nitrogen were detected, although the TGA curve showed a continuous weight loss.

Note that, whatever the sample investigated (carbon or precursor), the decomposition of ammonia started roughly at the same temperature (650 °C) and was almost complete above 1100 °C.

PMSZ: In the case of PMSZ (Figure 9), hydrogen is detected above 220 °C. A small amount of methylamine CH_3NH_2 (*m/z* 27–31) is detected from 200 to 500 °C; CH_3NH_2 is likely removed by ammonia from the MeSiHNMe units which arise from the quenching of the amide sites with methyl iodide. It is noteworthy that a weight gain is observed from 300 to 410 °C. The escape of methane, in the range 400–800 °C, is much larger than under argon.

Above 750 °C and up to 1300 °C, the TG curve shows a continuous weight loss (ca. 8%), but no gaseous species are detected in that range except hydrogen and nitrogen arising from the decomposition of ammonia. The total weight loss is 26% at 1350 °C.

PSSZ: In the case of PSSZ (Figure 10), hydrogen is detected above 500 °C; a large escape of benzene takes place in the range 400–750 °C, together with a weak escape of ethylene. Above 800 °C, a small amount of hydrogen cyanide, HCN (*m/z* 26, 27) is detected. The total weight loss is 68% at 1350 °C.

PVSZ1: The TG curve corresponding to the pyrolysis under ammonia of PVSZ1 shows a weight loss in three steps (Figure 11). The first step, which corresponds to the loss of oligomers, is larger than under argon (5.1% at 300 °C instead of 2.8% under argon). The second weight loss is more significant (about 13% from 400 to 750 °C) and corresponds to an escape of hydrogen and hydrocarbons: methane, ethylene, ethane, and propene mainly. During the third weight loss, above 700 °C, a large escape of hydrogen cyanide (*m/z* 26 and 27) is detected, as in the case of vegetal charcoal (Figure 6). Additional thermogravimetric curves have been recorded at lower heating rates (5 and 2 °C/min), which showed no significant different with the curve obtained at 10 °C/min. The total weight loss is 27% at 1350 °C.

PVSZ2: The TG curve corresponding to the pyrolysis under ammonia of PVSZ2 (Figure 12) is similar to the former one. The first step, below 250 °C, corresponds to the loss of residual hexane and possibly condensable oligomers. The second weight loss (about 19% from 390 to 750 °C) corresponds to an escape of hydrogen and hydrocarbons: methane, ethylene, ethane, and propene mainly. During the third weight loss (12.5% from 750 to 1350 °C), a large escape of hydrogen cyanide (*m/z* 26 and 27) is detected as in the former case. The total weight loss is 36% at 1350 °C.

Discussion

The nature of the gases evolved during pyrolysis of the polymeric precursors strongly depends on their structure (degree of cross-linking, molecular weight, etc.) and their thermal reactivity, which itself depends on the nature of the chemical groups (Me, Ph, vinyl, Si–H, NH, etc.) present in the precursor.

The precursors studied here have been chosen for their quite different chemical structures; in addition, they are highly cross-linked and give high ceramic yields. The main structural units of these precursors are displayed in Scheme I; as mentioned in the Experimental section, the cross-linking of PVSZ1 and PVSZ2 involves the same reaction (hydrosilation); accordingly, the same groups (Si–H, vinyl, $Si–CH_2CH_2Si$, and $SiCH(CH_3)Si$) are present in these samples; on the other hand, the cross-linking degree of PVSZ2 is higher, and it is obtained as a very finely divided powder.

Pyrolysis under Argon. Comparatively few papers have been devoted to the mechanisms of pyrolysis of poly(silazanes) under argon. The decomposition of the precursor was studied by means of gas chromatography combined with MS (GC-MS)[15,18] or Fourier transform infrared spectroscopy (GC-FTIR),[15] TG-MS analysis,[5,16b,c] pyrolysis GC-MS,[15,18] and FTIR[16b,19] in addition to thermogravimetric analysis (TGA) and elemental analysis. These studies indicate that the conversion from the polysilazane to the final inorganic material involves roughly three main steps:

(1) Below 500 °C the precursor undergoes thermal cross-linking which competes with retroversion reactions. Transamination reactions occur also during this step.

(2) At 400–800 °C the thermolysis of the organic groups corresponding to the actual organic–inorganic transition (mineralization) occurs, leading to an escape of hydrocarbons and hydrogen.

(3) Above 800 °C the remaining hydrogen atoms are gradually removed as hydrogen, and the disordered ma-

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(18) Blum, Y. D.; Schwartz, K. B.; Laine, R. M. *J. Mater. Sci.* **1989**, *24*, 1707.

(19) Legrow, G. E.; Lim, T. F.; Lipowitz, J.; Reaoch, R. S. *Am. Ceram. Soc. Bull.* **1987**, *66*, 363.

terial, so-called amorphous covalent ceramic (ACC),[20] gradually converts to a microcrystalline ceramic.

Retroversion Reactions. In the case of poly(silazanes), the main retroversion reaction should be, by analogy with poly(siloxanes), a redistribution reaction of the Si–N bonds,[5,16c,18] leading to an escape of volatile oligosilazanes. Redistribution of Si–N and Si–H bonds has also been proposed in some cases to account for the formation of volatile silanes.[16c,18] This work does not deal with retroversion reactions, as all the precursors studied are highly cross-linked and have high thermal reactivity, so that such reactions are negligible.[1]

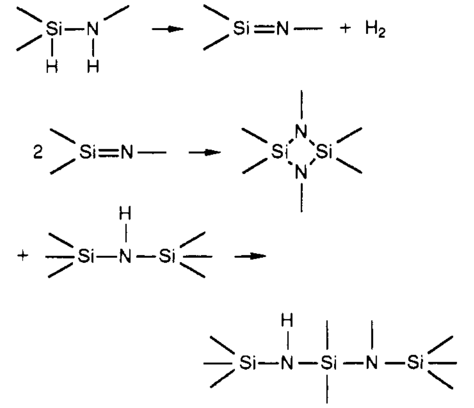
Cross-Linking Reactions. Numerous thermal cross-linking reactions may occur during the first step of the pyrolysis, depending on the functional groups present in the precursor.[5,16c,18,21]

Transamination reactions (reaction 1) take place when N–H bonds are present, which is the case for all the precursors studied here. TG/MS analysis indicates that

$$\begin{array}{l} 2{\equiv}\mathrm{Si{-}NH{-}Si}{\equiv} \rightarrow {\equiv}\mathrm{Si{-}NH_2} + ({\equiv}\mathrm{Si})_3\mathrm{N} \\ \underline{{\equiv}\mathrm{Si{-}NH_2} + {\equiv}\mathrm{Si{-}NH{-}Si}{\equiv} \rightarrow ({\equiv}\mathrm{Si})_3\mathrm{N} + \mathrm{NH_3}} \\ 3{\equiv}\mathrm{Si{-}NH{-}Si}{\equiv} \rightarrow 2({\equiv}\mathrm{Si})_3\mathrm{N} + \mathrm{NH_3} \qquad (1) \end{array}$$

transmination reactions take place in the range 200–500 °C whatever the precursor, as shown by the escape of ammonia. Transamination is quite significant in the case of PSSZ, which has more N–H bonds than the other precursors.

When both Si–H and N–H bonds are present, dehydrogenation reactions may occur, with formation of Si–N bonds. The exact mechanism is not yet known; when hydrogen and N–H groups are borne by the same silicon atom, intermediate formation of silylimine has been proposed,[18] as in the case of catalytic dehydrogenation;[14] silylimine may then dimerize to form a cyclodisilazane (reaction 2a) or more probably insert into a Si-N bond (reaction 2b).[16a,22]

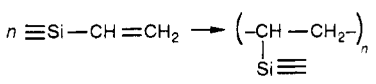


(2a)

(2b)

In the case of PSSZ, which does not possess Si–H bonds, the escape of hydrogen starts at a significantly higher temperature (550 °C) than in the case of PVSZ samples (300 °C) or PMSZ (200 °C). Pyrolysis studies of hydrogenosilsesquioxane, $HSiO_{1.5}$, showed that, under the same conditions, Si–H bonds were cleaved above 450 °C.[23] Thus the escape of hydrogen in the range 200–450 °C may be ascribed to Si-H/N-H dehydrogenations. This reaction is observed above 300 °C for PVSZ samples, as well as for other poly(silazanes) cross-linked thermally;[16c] thus, the lower temperature (200 °C) at which this reaction takes place in the case of PMSZ has probably to be related to catalysis by remaining potassium amide groups. Indeed, elemental analysis indicated the presence of about 1 wt % potassium.

The presence of vinyl groups as in PVSZ allows a very efficient cross-linking in the range 120–400 °C, via polymerization reactions (reaction 3) and, as Si–H bonds are also present, via hydrosilation (reaction 4).[16,24,25]



$$n\,{\equiv}\mathrm{Si{-}CH{=}CH_2} \rightarrow \big({-}\underset{\underset{\displaystyle \mathrm{Si}{\equiv}}{|}}{\mathrm{C}}\mathrm{H}{-}\mathrm{CH_2}{-}\big)_n$$

$$\begin{array}{l} {\equiv}\mathrm{Si{-}H} + {\equiv}\mathrm{Si{-}CH{=}CH_2} \rightarrow \\ \qquad {\equiv}\mathrm{Si{-}CH_2{-}CH_2{-}Si}{\equiv} + {\equiv}\mathrm{Si{-}CH(CH_3){-}Si}{\equiv} \quad (4) \end{array}$$

These reactions do not lead to the escape of a gas and are therefore not detected by TG/MS analysis, but they have a great influence on both the ceramic yield and the excess of free carbon.[16b]

Formation of Hydrocarbons. The mechanism of mineralization reactions is likely radical, in view of the high temperatures involved (400–800 °C).[26] Burns and coworkers showed that silsequiazanes, $RSi(NH)_{1.5}$, degrade thermally by a two-step radical mechanism rather than by a concerted mechanism. The first step involves Si–C bond cleavage and is followed by β elimination of a hydrogen radical, as exemplified in the case of the ethyl radical in reaction 5:[15]

$$\begin{array}{l} {\equiv}\mathrm{Si{-}CH_2{-}CH_3} \rightarrow {\equiv}\mathrm{Si}^\bullet + {}^\bullet\mathrm{CH_2{-}CH_3} \\ {}^\bullet\mathrm{CH_2{-}CH_3} \rightarrow \mathrm{H}^\bullet + \mathrm{CH_2{=}CH_2} \qquad (5) \end{array}$$

The large escape of methane, in the case of PMSZ, and the escape of benzene, in the case of PSSZ, show that when β elimination is not possible, the most probable reaction is the abstraction of a hydrogen atom from Si–H, N–H, or C–H bonds (reactions 6).

$${\equiv}\mathrm{Si{-}R} \rightarrow {\equiv}\mathrm{Si}^\bullet + \mathrm{R}^\bullet \ (\mathrm{R} = \mathrm{Me, Ph})$$

$$\mathrm{R}^\bullet + {\equiv}\mathrm{Si{-}H} \rightarrow \mathrm{RH} + {\equiv}\mathrm{Si}^\bullet \qquad (6a)$$

$$+ {=}\mathrm{N{-}H} \rightarrow \mathrm{RH} + {=}\mathrm{N}^\bullet \qquad (6b)$$

$$+ {\equiv}\mathrm{C{-}H} \rightarrow \mathrm{RH} + {\equiv}\mathrm{C}^\bullet \qquad (6c)$$

In the case of PVSZ samples, the formation of methane and ethylene points to different degradation pathways. The escape of methane implies that the cleavage of C–C bonds also takes place in the same temperature range, as exemplified in reaction 7 for $Si{-}CH(CH_3){-}Si$ bridges. Such bridges are present in the starting samples and may also be formed during the pyrolysis, either by thermal rearrangement of $Si{-}CH_2CH_2{-}Si$ bridges or by free-radical addition on vinyl groups (reaction 13).

$$\begin{array}{l} {\equiv}\mathrm{Si{-}CH(CH_3)}{-}{\equiv} \rightarrow {\equiv}\mathrm{Si{-}\dot{C}H{-}Si}{\equiv} + {}^\bullet\mathrm{CH_3} \qquad (7) \\ {}^\bullet\mathrm{CH_3} \xrightarrow{\text{H abstraction}} \mathrm{CH_4} \end{array}$$

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(20) Soraru, G. D.; Babonneau, F.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1988**, *106*, 256.

(21) Narsavage, D.; Interrante, L. V.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991**, *3*, 721.

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(24) (a) Schilling, C. L., Jr.; Wesson, J. P.; Williams, T. C. *Am. Ceram. Soc. Bull.* **1983**, *62*, 912. (b) Schilling, C. L., Jr. *Br. Polym. J.* **1986**, *18*, 355.

(25) Schmidt, W. R.; Interrante, L. V.; Doremus, R. H.; Trout, T. K.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991**, *3*, 257.

The large escape of ethylene may arise from the degradation of the SiC_2H_4Si bridges (formed by hydrosilation), in a two-step mechanism: cleavage of the Si–C bond, followed by arrangement of the radical (reaction 8):

$$\equiv Si-CH_2-CH_2-Si\equiv \ (\equiv Si-CH(CH_3)-Si\equiv) \rightarrow \equiv Si^{\bullet} + {}^{\bullet}CH_2-CH_2-Si\equiv$$

$${}^{\bullet}CH_2-CH_2-Si\equiv \ \rightarrow \ \equiv Si^{\bullet} + C_2H_4 \qquad (8)$$

Of course β elimination (reaction 5) may also take place, with formation of a vinyl group:

$${}^{\bullet}CH_2-CH_2-Si\equiv \ \rightarrow \ \equiv Si-CH=CH_2 + H^{\bullet} \qquad (9)$$

Actually, Burns et al.[15] observed the formation of ethylene and vinyl groups in the pyrolysis of $Me_3SiCH_2CH_2Si(NH)_{1,5}$.

The vinyl groups, either unreacted or produced by reaction 9, should lead via Si–C bond cleavage to vinyl radicals; these vinyl radicals would lead to an escape of ethylene (by H abstraction) and acetylene (by β elimination). However, as already noticed by Burns et al.,[15] elemental analysis shows that only a small part of the carbon arising from vinyl groups is lost as hydrocarbons; rather, the vinyl groups are consumed via addition reactions, such as polyaddition or hydrosilation (reactions 3 and 4); above 400 °C, free-radical additions are certainly favored and will be discussed in the next paragraph. The higher hydrocarbons detected would arise from similar degradation reactions of the longer carbon chains formed by polymerization of vinyl groups (reaction 3).

The hydrogen evolved arises (apart from Si–H/N–H dehydrogenation) from the homolytic cleavage of Si–H, N–H, and C–H bonds (reaction 10), leading to hydrogen radicals which may either combine together or abstract hydrogen:

$$X-H \rightarrow X^{\bullet} + H^{\bullet} \quad (X = \ \equiv Si, =N, \equiv C) \qquad (10)$$

$$2H^{\bullet} \rightarrow H_2$$

$$H^{\bullet} \xrightarrow{\text{H abstraction}} H_2$$

In view of their high bond dissociation energy, around 100 kcal mol^{-1}, cleavage of the C–H bonds requires high temperatures, above 650–700 °C; this reaction probably accounts for most of the hydrogen evolved above 800 °C.

Evolution of the Residue. The various free radicals $Si^{\bullet}$, $C^{\bullet}$, and $N^{\bullet}$ formed by the reactions described above may undergo several reactions:

(i) As long as hydrogen atoms are abundant, the most probable reaction is hydrogen abstraction (reactions 6) to give Si–H, C–H, and N–H bonds and new $Si^{\bullet}$, $C^{\bullet}$ and $N^{\bullet}$ radicals.

(ii) At high temperature, when H atoms become less and less abundant and the probability of bond cleavage increases, the concentration of radicals increases and combination reactions become significant, leading to the formation of Si–Si, Si–C, Si–N, C–C, etc., bonds (reaction 11).

$$R^{1\bullet} + R^{2\bullet} \rightarrow R^1R^2 \qquad (11)$$

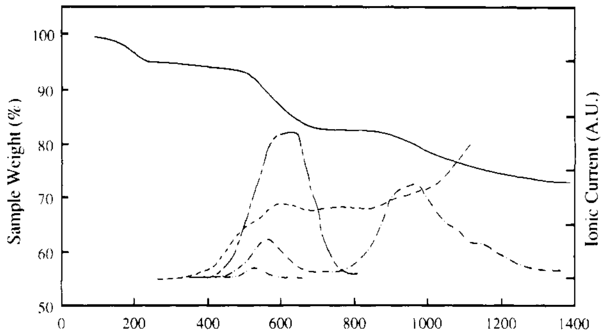


Figure 11. TG/MS analysis under ammonia/argon (30/70) of PVSZ1 cured at 120 °C: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; the ion signal at m/z 13 (— - —) arises from CH^+ coming from methane below 750 °C and from HCN above 750 °C; m/z 27 (–·–) arises from $C_2H_3^+$ coming from ethylene and ethane below 750 °C and arises from HCN^+ coming from HCN above 750 °C; m/z 41 (–··–) arises from propylene.

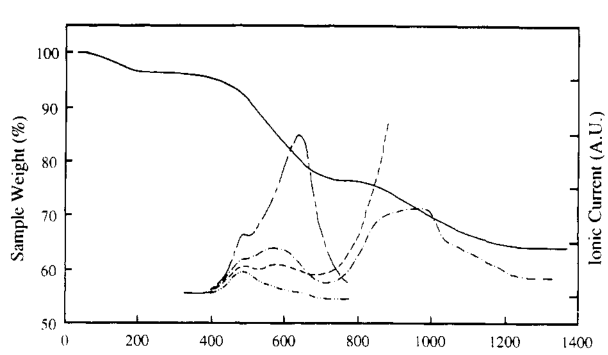
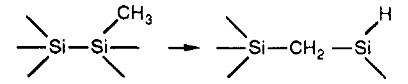


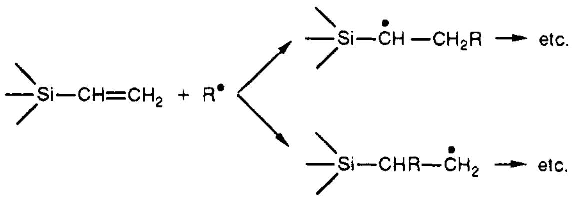
Figure 12. TG/MS analysis under ammonia/argon (30/70) of PVSZ2: (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; the ion signal at m/z 13 (— - —) arises from CH^+ coming from methane below 750 °C and from HCN above 750 °C; m/z 27 (–·–) arises from $C_2H_3^+$ coming from ethylene and ethane below 750 °C and arises from HCN^+ coming from HCN above 750 °C; m/z 41 (–··–) arises from propylene.

It is noteworthy that only Si–C, Si–N, aromatic carbon bonds are stable at high temperature, as shown by the structure of the final silicon carbonitride residue at 1200 °C;[17] the other bonds either give back the radicals, or rearrange, as for instance the Si–Si bonds, which give more stable Si–C–Si bonds via a methylene insertion[26c] (Kumada's rearrangement)[27] (reaction 12).



(12)

(iii) When unsaturated carbon groups are present, other reactions may compete with H abstractions and combinations: radical additions to the vinyl group in the case of PVSZ samples (reactions 13), and aromatic radical substitutions of the phenyl group in the case of PSSZ (reactions 14).



(R = ≡Si, ≡CH) (13)

These reactions lead to a cross-linking of the carbon atoms, which hinders the formation of volatile hydrocarbons and favors the formation of pyrolytic carbon (excess carbon)

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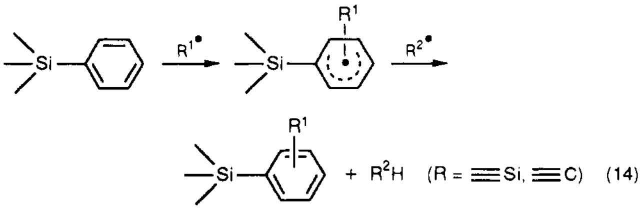
(26) (a) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**, *13*, 2569. (b) Hasegawa, Y.; Iimura, M.; Yajima, S. *Ibid.* **1980**, *15*, 720. (c) Hasegawa, Y.; Okamura, K. *Ibid.* **1983**, *18*, 3633.

(27) Shiina, K.; Kumada, M. *J. Org. Chem.* **1958**, *23*, 139.



(14)

at higher temperature. Thus, Burns et al. observed that only 21% of the carbon atoms of vinylsilsesquiazane are lost during pyrolysis at 1200 °C in argon, compared to 67% for ethylsilsesquiazane.[15] In the same way, only 27% of the carbon atoms of PVSZ samples are lost during the pyrolysis.

Pyrolysis under Ammonia. *Amination Mechanisms.* It is well-known that the pyrolysis of poly(silazanes) in an ammonia atmosphere yields essentially pure Si_3N_4,[4,9] independently of the nature of the organic groups (methyl, ethyl, phenyl, etc.);[9] both amination and carbon removal have been reported to occur between 400 and 700 °C for poly(carbosilane) and poly(silazane) precursors.[9,28]

Three different mechanisms may be considered for the amination of silicon atoms.

First, it was suggested that this reaction could involve ammonia thermolysis products, such as NH_2 radicals or nitrenes;[4,9] however, our results indicate that, whatever the precursor, the thermal decomposition of ammonia is negligible below 650–700 °C. Thus, this mechanism may be discarded below these temperatures.

The second possibility would be nucleophilic substitution by ammonia,[4,5,28] which well account for the formation of hydrogen, methane, or benzene:

$$\equiv Si—X + NH_3 \rightarrow \equiv Si—NH_2 + HX \qquad (15)$$

$$X = H, CH_3, C_6H_5, \text{etc.} \qquad (15a)$$

The third possible mechanism would be a free-radical substitution initiated by bond cleavage around silicon:[28]

$$\equiv Si—X \rightarrow \equiv Si^{\bullet} + X^{\bullet} \quad (X = Me, Ph, \text{etc.}) \qquad (16a)$$

$$X^{\bullet} + NH_3 \rightarrow XH + NH_2^{\bullet} \qquad (16b)$$

$$\equiv Si^{\bullet} + NH_2^{\bullet} \rightarrow \equiv SiNH_2 \qquad (16c)$$

In the case of Si–H bonds, which are sensitive to nucleophilic substitution,[29] amination via nucleophilic substitution by ammonia certainly predominates, at least below 500 °C.[28]

In the case of methyl or phenyl groups, nucleophilic substitution is much less favorable. Moreover, our experiments show that the escape of methane and benzene starts at the same temperature as under argon and therefore homolytic cleavages of the Si–C bonds certainly occur. Thus, free-radical substitution (reactions 16) appears as the most probable mechanism. However, the same radical reactions as under argon should compete with reactions 16, with two results: cross-linking of the precursor, which should prevent a complete amination;[9] formation of excess carbon.

Actually, amination is almost complete at 700 °C whatever the precursor, and comparison of the excess carbon under argon and ammonia (Tables II and IV) well illustrates the efficiency of carbon removal under ammonia, particularly in the case of PSSZ. Thus, the presence of ammonia hinders the radical cross-linking reactions which occur under argon and facilitates carbon removal; this may be ascribed to the possibility of abstraction of hydrogen from ammonia molecules (reaction 16b) which is favored in view of the high concentration and the accessibility of hydrogen atoms provided by ammonia. This reaction apparently competes efficiently with the radical reactions observed under argon, and the formation of hydrocarbons (reaction 16b) is favored, as was previously noted;[28,12b] thus, the carbon atoms of PMSZ and PSSZ are nearly quantitatively removed as methane and benzene, respectively.

In addition, combinations of $Si^{\bullet}$ and $NH_2^{\bullet}$ radicals (reaction 16c)[28] also competes with other combination reactions (reaction 11), and hinders the formation of Si–Si or Si–C–Si cross-links.

It is noteworthy that the formation of silanes via H abstraction from NH_3 by silyl radicals (reaction 17) should also be favored; thus, an alternative amination mechanism may be considered:[28]

$$\equiv SiX \rightarrow \equiv Si^{\bullet} + X^{\bullet} \quad (X = Me, Ph, \text{etc.}) \qquad (16d)$$

$$\equiv Si^{\bullet} + NH_3 \rightarrow \equiv SiH + NH_2^{\bullet} \qquad (17)$$

$$\equiv Si—H + NH_3 \rightarrow \equiv Si—NH_2 + H_2 \qquad (15)$$

In the case of PMSZ, the small escape of methylamine detected around 450 °C likely arises from the substitution by ammonia of the Si–N bonds[30] in the –Si(Me,H)N(Me)– units resulting from the quenching of the amide sites with methyl iodide:

$$\equiv Si—NMe—Si\equiv + NH_3 \rightarrow \equiv Si—NH_2 + \equiv Si—NMeH$$

$$\equiv Si—NMeH + NH_3 \rightarrow \equiv Si—NH_2 + MeNH_2 \qquad (18)$$

The formation of the trisilylated nitrogen atoms present in the final silicon nitride phase requires the condensation of NH_2 and NH groups. Above 700 °C, the mechanism of these condensations likely involves radical intermediates.

Excess Carbon Removal. Although the removal of carbon atoms as hydrocarbons is favored under ammonia, excess carbon still forms in the case of the two PVSZ samples, as shown by elemental analysis and the large escape of hydrogen cyanide detected above 750 °C. ^{13}C solid-state NMR (Figure 5) shows that this excess carbon corresponds to unsaturated units, which prefigure the polyaromatic structures expected at higher temperature.[17] The formation of this excess carbon may be accounted for by the fact that the cross-linked carbon atoms arising from polyaddition of vinyl groups (reaction 3) are much less easily removed by ammonia than methyl or phenyl groups.

This excess carbon reacts with ammonia above 750 °C in the same way as elemental carbon[31,13] or carbon arising from thermal polymerization of diacetylenic units,[32] according to

$$C + NH_3 \rightarrow HCN + H_2 \qquad (19)$$

This reaction, which does not entail any nitrogen incorporation, starts after the thermal decomposition of ammonia; it likely involves radicals such as $^{\bullet}NH_2$ and :NH.[33] As shown by the TGA curves in Figure 8, the rate of this reaction decreases markedly above 1000 °C, possibly as the radicals $^{\bullet}NH_2$ and :NH arising from the decomposition of ammonia are less abundant in the steady state. In addition, above 1200 °C, HCN is no longer detected although

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[28] Corriu, R.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1992**, *4*, 711.

[29] Bassindale, A. R.; Taylor, P. G. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, p 838.

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[31] Badger, R. M. *J. Am. Chem. Soc.* **1924**, *46*, 2166.

[32] Corriu, R.; Gerbier, P.; Guérin, C.; Henner, B.; Jean, A.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507.

[33] Ovsyannikov, A. A.; Oliver, D. KH. *Khim. Vys. Energ.* **1978**, *12*, 62.

the weight loss still goes on; this may possibly be ascribed to the thermal decomposition of HCN itself. These results show that the elimination of excess carbon under ammonia is optimum at about 1000 °C. Reaction 19, like any solid–gas reaction, is highly sensitive to the surface area of the sample,[9] and the large excess carbon still present after the pyrolysis of PVSZ1 in ammonia is certainly related to the compactness of this sample; in addition, the larger amount of vinyl groups in PVSZ1 compared to PVSZ2 leads to the formation of a larger amount of excess carbon.

In the case of PMSZ, elemental analysis indicates the presence of 8.5 wt % carbon at 750 °C, whereas no HCN is detected. The ^{13}C solid-state NMR (Figure 7) shows that, after heating at 750 °C under ammonia, the remaining carbon atoms are still in the sp^3 hybridization state; in addition, the nitrogen content of the pyrolysate increases from 750 to 1350 °C. Thus the amination stage of the precursor is not complete at 750 °C (probably due to the high heating rate used), and ammonia continues to substitute the Si–C bonds above 750 °C.

Conclusion

The thermal reactions occurring during the pyrolysis of preceramic polysilazanes depend on the nature of the functional groups of the precursors.

In an inert atmosphere, mineralization involves mainly free-radical reactions; large amounts of excess carbon are observed when the precursors possess unsaturated carbon groups, probably due to their reactivity toward free radicals.

Under ammonia, different mechanisms may be distinguished depending on the nature of the groups borne by the silicon atoms.

In all cases, complete amination of silicon occurs between 300 and 750 °C, before the thermal decomposition of ammonia. The mechanism of this substitution is likely nucleophilic in the case of Si–H bonds, whereas homolytic cleavages of Si–C bonds certainly occur in the case of carbon substituents.

The possibility of hydrogen abstraction from ammonia favors the escape of hydrocarbons: thus, methyl and phenyl groups are quantitatively removed as methane and benzene, respectively, and amination and carbon removal coincide. On the other hand, vinyl groups are not completely displaced by ammonia and lead to the formation of unsaturated excess carbon; above 750 °C, this excess carbon reacts with ammonia decomposition products, leading to an escape of hydrogen cyanide.

Registry No. PMSZ, 105009-41-4; PSSZ, 144043-04-9; PVSZ, 144043-05-0; Ar, 7440-37-1; NH_3, 7664-41-7.

Plasma-Enhanced Chemical Vapor Deposition of Bulk Organosilicon Solids Using Hexamethyldisilane Precursor

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Received May 20, 1992. Revised Manuscript Received July 27, 1992

Plasma polymerization of hexamethyldisilane ($[CH_3]_3SiSi[CH_3]_3$) at low radio frequency powers results in the formation of a fine brown powder. On prolonged exposure to air, this deposit changes in appearance to bright yellow. Freshly collected organosilicon material and its subsequent ageing have been investigated by XPS, FTIR, XRD, and solid-state NMR. A high proportion of $(CH_3)_xSi$ (x = 1, 2,3) linkages and trapped reactive centers are identified in the gathered material; these species readily undergo oxidation and cross-linking on standing in the laboratory atmosphere.

Introduction

Molecules injected into a glow discharge may undergo activation and fragmentation while subjected to the influence of electrons, metastables, radicals, ions, and photons. Under optimum conditions, successive dissociation and recombination of the reactive components within a plasma can yield extended molecules in the gas phase, with concurrent attachment of fragments to an adjacent substrate.

Plasma-deposited organosilicon materials are reported to possess high dielectric strengths.[1] Tetramethylsilane ($Si[CH_3]_4$),[2,3] phenylsilane ($[C_6H_5]SiH_3$),[4] and trimethylvinylsilane ($[CH_3]_3Si[CHCH_2]$)[5,6] are among some of the carbosilane monomers previously used. Silylmethyl groups, $(CH_3)_xSi$ (x = 1, 2, 3) have been invoked to play a major role during the plasma polymerization of organosilanes.[7] However, none of the above-mentioned precursors are reported to readily yield vast amounts of solid product. In this study we have chosen hexamethyldisilane ($[CH_3]_3SiSi[CH_3]_3$) as the monomer. This molecule contains a weak Si–Si linkage which should make it much more susceptible toward plasma-enhanced chemical vapor deposition (PECVD) relative to monosilicon-based pre-

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