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Thermal Decomposition of Poly(methylsilsesquicarbodiimide) to Amorphous Si−C−N Ceramics

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This paper is based on the recent discovery that the thermal decomposition of poly(methylsilsesquicarbodiimide), $[CH_3Si(N{=}C{=}N)_{1.5}]_n$, leads to amorphous silicon carbonitride (SiCN) ceramics. In the present study the polymer-to-ceramic transformation is characterized using analytical and spectroscopic methods. In particular, the structural transition from the molecular precursor to the final amorphous SiCN ceramic was studied by solid-state NMR spectroscopy. The coordination of the silicon atoms changes from $CH_3{-}Si({-}N{=}C{=}N{-})_3$ in the polysilylcarbodiimide precursor at room temperature to $Si({-}N{<})_4$ in the X-ray amorphous reaction product formed at 1200 °C. This result implies the formation of amorphous silicon nitride (Si_3N_4). The remaining weight fraction is analyzed to be elemental carbon. According to bulk chemical analysis, the poly(methylsilsesquicarbodiimide)-derived SiCN is comprised of a mixture of 1 mol amorphous Si_3N_4 with 3 mol amorphous carbon. The molar ratio $Si_3N_4/C = {}^1/_3$ is suitable for the formation of stoichiometric silicon carbide, which is expected thermodynamically at temperatures exceeding 1440 °C in 0.1 MPa N_2. The pyrolysis behavior of the poly(silylcarbodiimide) and the formation of silicon carbonitride ceramics are compared to those of poly(silazanes).

I. Introduction

Commercial silicon-based non-oxide ceramics are produced by the mixing of silicon nitride and/or silicon carbide powders with additives that promote sintering and subsequent densification at elevated temperatures.[1] An alternative route for the production of dense bulk Si−C−N materials is the pyrolysis of organosubstituted polysilazanes.[2] In the latter case, the final materials are completely amorphous up to 1400 °C and form crystalline composites in the Si_3N_4/SiC binary system at $T >$ 1440 °C (0.1 MPa N_2). One interesting property of these materials is their extraordinary oxidation stability at $T <$ 1400 °C due to the absence of sintering additives.[3]

Recently, Riedel et al. developed a novel class of Si−C−N preceramic polymers[4] prepared by the reaction of various chlorosilanes with cyanamide or bis(trimethylsilyl)carbodiimide. In the case of tetrachlorosilane, the reaction led to the discovery of the first two crystalline phases, SiC_2N_4 and Si_2CN_4, in the Si−C−N ternary system.[5]

This approach was extended recently to organically substituted chlorosilanes such as $MeSiCl_3$;[6,7] reaction of methyltrichlorosilane **1** with bis(trimethylsilyl)carbodiimide **2** and pyridine as a catalyst produces a poly(methylsilsesquicarbodiimide) **3** and chlorotrimethylsilane **4** as a liquid byproduct (reaction eq 1).

$$\underset{\mathbf{1}}{nCH_3SiCl_3} + \underset{\mathbf{2}}{1.5n(CH_3)_3Si{-}N{=}C{=}N{-}Si(CH_3)_3} \rightarrow \underset{\mathbf{3}}{[CH_3Si(N{=}C{=}N)_{1.5}]_n} + \underset{\mathbf{4}}{3n(CH_3)_3SiCl} \quad (1)$$

The preparation of polymer **3** can be considered as a non-oxidic sol−gel process[6] that leads to a colorless and transparent xerogel after removal of byproduct **4** and subsequent drying. This sol−gel type of approach was the first to combine sol−gel chemistry with polymer

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pyrolysis for the preparation of oxygen-free silicon-based ceramics.

In this paper, we present a detailed study of the pyrolytic transformation of polymer **3** into the ternary SiCN ceramics. On the basis of an initial thermal gravimetric and in situ mass spectrometric study reported recently,[7] multinuclear (^{29}Si, ^{13}C, and ^{15}N) solid-state NMR spectroscopy was used to characterize the structural transformation from the starting polymer to the final ceramic. The NMR experiments emphasize the use of a cross-polarization (CP) magic angle spinning (MAS) NMR technique coupled with inversion recovery cross polarization (IRCP) to follow the evolution of the Si and C sites during pyrolysis at $T \leq 800$ °C. With these sequences, the response of each site strongly depends on the heteronuclear ^{1}H−X dipolar coupling ($X = {}^{29}$Si, ^{15}N, ^{13}C) and is, therefore, very sensitive to the proton environment of the various sites. These techniques are quite suitable for monitoring the pyrolysis of preceramic polymers, since there are distinct differences in the proton environments of the various constitutive sites. The NMR measurements used in this paper are analogous to those successfully applied to the study of the polysilane−polycarbosilane transformation of poly(methylchlorosilanes).[8] In that study, the ^{29}Si and ^{13}C NMR experiments clearly demonstrated the formation of Si−CH_2−Si moieties that indicate the presence of polycarbosilane backbones. Moreover, the various Si units present in the pyrolysis intermediates were identified quantitatively. Other studies on the pyrolysis process of SiCN preceramic polymers present ^{29}Si and ^{13}C MAS NMR spectra with varying degrees of completeness in their interpretation.[9] In contrast, relatively few reports have shown ^{15}N MAS NMR spectra[10] mainly because of the low sensitivity of this nucleus in natural abundance (even if the CP sequence is used). Recently, the IRCP sequence was successfully extended to this isotope in different reference compounds containing various NH_x sites ($0 \leq x \leq 4$).[11] The application of this sequence to SiCN preceramic polymers could produce new insights concerning changes in the N environment during pyrolysis. However, the weak ^{1}H−^{15}N dipolar coupling in **3** prevented us from performing a detailed study using this IRCP sequence in a reasonable time period. As a result, ^{15}N−CP spectra were recorded at only one contact time.

In the last part of this paper, the preparation of bulk materials from the pyrolysis of green bodies is discussed with respect to the evolution of the gaseous species developed by the polymer-to-ceramic transformation.

II. Experimental Procedure

The synthesis of poly(methylsilsesquicarbodiimide) **3** has already been described in detail.[6,7] In a reaction flask, 1 mol of methyltrichlorosilane was mixed with 1.5 mol of bis(trimethylsilyl)carbodiimide **2** in the presence of 0.1 mol of pyridine, used as catalyst. The mixture was refluxed for 13.5 h when gelation occurred. After removal of chlorotrimethylsilane **4**, the reaction byproduct, the polymer was obtained in quantitative yield as a colorless and transparent xerogel. Pyrolysis at $T \leq 1200$ °C was performed by inserting a quartz tube equipped with a dried argon gas flow (3 L/min) into a tubular furnace (GERO HTSR 40-200). The heating rate was 2 °C/min. No dwell time was applied at the maximum temperature. The samples were then stored in a glovebox (Braun MB 150G-I SPS; O_2 concentration < 1 ppm; H_2O concentration < 1 ppm) because of their air sensitivity and were handled under inert atmosphere for all characterization measurements.

Thermal analysis in combination with simultaneous mass spectrometry (Netzsch STA 429 and Balzers QMG 420) of the dried poly(methylsilsesquicarbodiimide) was conducted between 20 and 1400 °C with a heating rate of 2 °C/min under flowing He 5.0 (75 cm^3/min).

The MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer operating at 75.47 MHz for ^{13}C, 30.41 MHz for ^{15}N, and 59.63 MHz for ^{29}Si. Samples were spun at 4 kHz for the ^{29}Si NMR experiments and at 5 kHz for the ^{13}C and ^{15}N experiments, using 7 mm ZrO_2 rotors filled up in a glovebox under a dried argon atmosphere. All the CP and IRCP were performed under the same Hartmann−Hahn match condition; both rf channel levels, $\omega_{1S}/(2\pi)$ and $\omega_{1I}/(2\pi)$, were set about 42 kHz. The ^{13}C NMR spectra were measured with a spectral width of 30 kHz, using 3K data points in the time domain. The number of transients per spectra varied from 300 to 1200, depending on the sample. IRCP MAS NMR spectra were recorded with inversion times t_i ranging from 5 μs to 1 ms and a contact time of 5 ms in order to maximize the polarization of the ^{13}C nuclei. The recycle delay between pulses was 6 s. The ^{13}C chemical shifts were determined relative to TMS via solid adamantane ($\delta = 29.4$ and 38.5 ppm). The ^{15}N CP MAS NMR spectra were recorded with a spectral width of 25 kHz, using 2K data points and with 10 ms of contact time. The recycle delays between pulses were 10 s. Chemical shifts were referenced to solid NH_4NO_3 (10% enriched sample, $\delta(^{15}NO_3) = -4.6$ ppm compared to CH_3NO_2 ($\delta = 0$ ppm)). For the ^{29}Si NMR MAS spectra, the following parameters were used for the single-pulse experiment: spectral width of 30 kHz, pulse angle around 30° (2 μs), recycle delay between pulses of 60 s, and 4K data points. The ^{29}Si CP MAS NMR spectra were recorded with recycle delays of 6 s and contact times ranging from 50 μs to 50 ms, while for the ^{29}Si IRCP MAS NMR spectra, the inversion times varied from 5 μs to 4 ms, with an optimized contact time of 10 ms. Chemical shifts were determined relative to TMS ($\delta = 0$). A proton-decoupling power of 42 kHz was always applied during acquisition. A 50 Hz line broadening was applied to the FIDs before Fourier transform. The spectra were simulated with the commercially available WIN-FIT program from Bruker.[12]

The FTIR spectra were measured using the KBr pellet technique, on a Perkin-Elmer FT-IR 1750 equipment with a resolution of 3 cm^{-1}.

The chemical compositions of the pyrolysis intermediates were obtained from the Service Central d'Analyze du CNRS (Vernaison, France).

The thermomechanical analysis (TMA) was performed with a Netzsch TMA 402 to temperatures of 1000 °C. The dried polymer was milled (Fritsch, Planetary Ball Mill, "pulverisette 5") at 150 rpm in a HDPE vessel with use of zirconia balls. The polymer powder was sieved (Retsch, VS 1000) through a 32 μm grid. Cylindrical pellets (ø = 10 mm; length is 8 mm) were processed by cold isostatic pressing (Weber, KIP 100E, 1000 kN) utilizing an india rubber die (ø = 12 mm).

Densification was achieved by hot pressing in a commercial unit (KCE HPW 150/200-220-100-L). An amount of 7.01 g of

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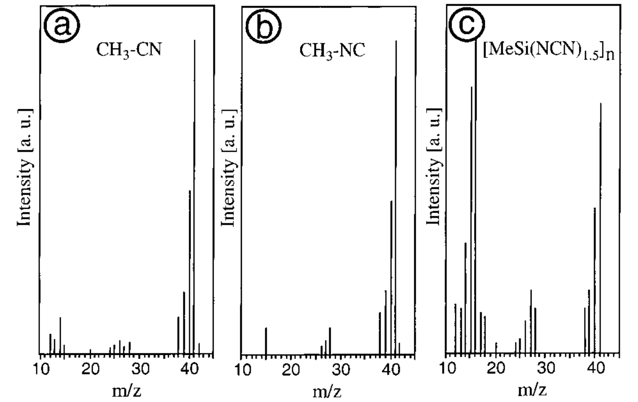

Figure 1. Mass spectrometry fragmentation patterns for (a) acetonitrile,[13] (b) methylisonitrile,[13] and (c) detected gaseous species evolved at 566 °C in He.

the milled and sieved polymer was densified at room temperature in a graphite die (diameter 20 mm) with a load of 3 kN. The heating rate in the hot press was 10 °C/min (in N_2) up to 400 °C and 2 °C/min (in N_2) between 400 and 1300 °C with a constant load of 5 kN.

III. Results and Discussion

III.1. Thermal Gravimetric Analysis with In Situ Mass Spectrometry. The decomposition behavior of poly(methylsilsesquicarbodiimide) **3** up to 1400 °C as determined by thermal gravimetric analysis and in situ mass spectrometry can be summarized as follows. The mass loss of 10 wt % below 500 °C is due to the evolution of residual chlorotrimethylsilane **4** as characterized by various mass spectroscopic fragments: $m/z = 93$ [$(CH_3)_2Si^{35}Cl^+$], 95 [$(CH_3)_2Si^{37}Cl^+$], 73 [$(CH_3)_3Si^+$], 65 [$Si^{37}Cl^+$], and 63 [$Si^{35}Cl^+$]. A weight loss of about 20% between 500 and 600 °C is due to the evolution of CH_4 (m/z = 16, 15, 14, 13, 12) and $CH_3{-}CN$, acetonitrile (m/z = 41, 40, 39, 38). The formation of methylisonitrile, $CH_3{-}NC$, can be unambiguously excluded by the fragmentation patterns of the two isomers. Acetonitrile is clearly distinguished from methylisonitrile, since the fragment masses with $m/z = 24$ (C_2) and $m/z = 25$ (C_2H) are not found in the mass spectrum of the latter compound (parts a and b of Figure 1).[13] The measured fragmentation pattern of the synthesized polymer **3** at 566 °C is shown in Figure 1c. The presence of characteristic fragments at m/z = 24 and 25 clearly indicates the evolution of acetonitrile.

The outgassing of methane and acetonitrile results from the decomposition of the polymeric backbone and characterizes the onset of the ceramic formation step at $T \approx 570$ °C. The color of the pyrolyzed samples changes from white to black at this temperature, indicating the formation of a free-carbon phase. Moreover, hydrogen (m/z = 2) is detected between 650 and 750 °C. Subsequently, a second ceramic formation step accompanied by a 10% weight loss is found between 800 and 1100 °C. This mass loss is caused by the evolution of nitrogen (m/z = 28) exclusively. No further weight loss is detected up to 1400 °C, and the overall ceramic yield is 60 wt %.

In contrast to the pyrolysis behavior of silicondicarbodiimide $[Si(NCN)_2]_n$,[5] which crystallizes at 400 °C, poly(methylsilsesquicarbodiimide) **3** remains X-ray amorphous up to 1400 °C. The decomposition temperature of **3** is about 350 °C lower than that of silicondicarbodiimide, which is thermally stable up to 920 °C. Moreover, cyanogen, C_2N_2 (m/z = 52), is not detected, as is the case for $[Si(NCN)_2]_n$.[5] These differences in decomposition behavior are likely to be related to the CH_3 groups present in poly(methylsilsesquicarbodiimide) **3**.

Table 1. Chemical Analysis Data and Molar Compositions of Poly(methylsilsesquicarbodiimide), 3, Heat-Treated at Different Temperatures

pyrolysis temp (°C)	element (wt %) Si	N	C	H	empirical formula
100	25.30	36.91	33.06	4.72	$SiN_{2.92}C_{3.05}H_{5.20}$
500	29.75	37.1	30.10	3.02	$SiN_{2.50}C_{2.36}H_{2.84}$
570	27.50	42.60	25.92	2.69	$SiN_{3.05}C_{2.20}H_{2.70}$
600	31.00	37.40	18.41	1.72	$SiN_{2.41}C_{1.38}H_{1.55}$
800	35.60	44.78	18.89	0.47	$SiN_{2.50}C_{1.24}H_{0.36}$
1000	39.10	38.50	18.95	<0.3	$SiN_{1.97}C_{1.13}$
1200	44.25	33.88	18.99	<0.3	$SiN_{1.53}C_{1.00}$

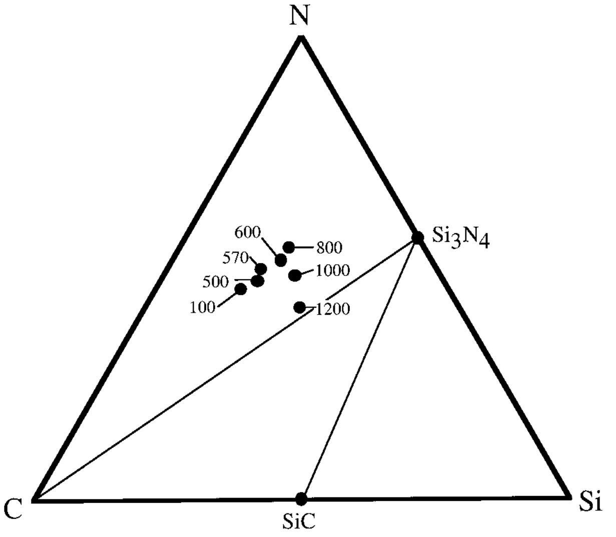

Figure 2. Isothermal section of the ternary Si−C−N phase diagram[14] valid for $T < 1440$ °C and 0.1 MPa N_2. The SiCN compositions obtained by thermal decomposition of poly(methylsilsesquicarbodiimide) **3** at different temperatures are indicated. Compositions are given in atom %.

III.2. Elemental Analysis. The results of the bulk elemental analysis of the samples pyrolyzed at various temperatures are summarized in Table 1.

The chemical composition of each sample listed in Table 1 has been plotted in the Si−C−N ternary phase diagram calculated by Weiss and Lukas[14] (Figure 2) by neglecting hydrogen as a constituent. Table 1 shows that the stoichiometry of the material changes from $SiN_{2.92}C_{3.5}H_{5.20}$ analyzed after annealing of polymer **3** at 100 °C to $SiN_{2.50}C_{1.24}H_{0.36}$ after a heat treatment at 800 °C. The compositional change is in agreement with the TGA/MS study that showed evolution of methane and acetonitrile. Further annealing up to 1200 °C gives an amorphous ceramic with decreased nitrogen content. The analyzed molar composition $Si_3N_4C_3N_{0.74}$ is located close to the C/Si_3N_4 tie-line in the Si−C−N phase diagram (Figure 2), implying the presence of nearly stoichiometric Si_3N_4 and a free-carbon phase. The excess

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[13] NIST/EPA/NIH Mass Spectral Database, version 4.0, 1992.

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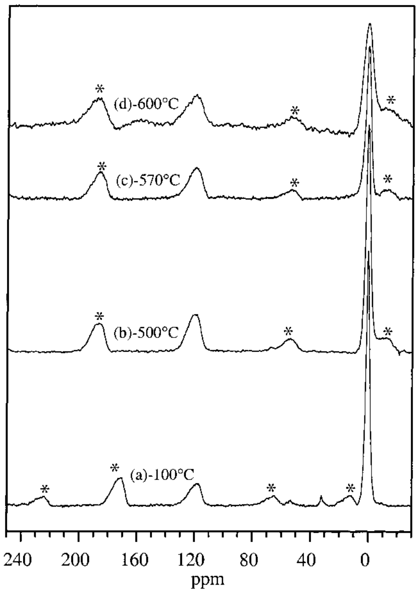

Figure 3. ^{13}C CP MAS NMR spectra of samples heated to (a) 100, (b) 500, (c) 570, and (d) 600 °C (contact time $t_c = 5$ ms). The asterisk (*) marks spinning sidebands.

nitrogen is due to residual carbodiimide groups in the heat-treated product as detected by FT-IR investigations.

III.3. MAS NMR Studies. ^{29}Si, ^{13}C, and ^{15}N NMR spectra were recorded using the cross-polarization (CP) technique, which requires the presence of protons. The use of this technique will thus be limited for samples heat-treated below 800 °C.

III.3.1. ^{13}C MAS NMR. Curve a in Figure 3 represents the ^{13}C CP MAS NMR spectrum of the polymer treated at 100 °C. One peak is present at 1 ppm due to the $Si-CH_3$ groups. A much broader signal centered around 120 ppm and accompanied by spinning sidebands is characteristic of partially averaged chemical shift anisotropy. This signal corresponds to the carbodiimide groups, $-N=C=N-$.[15] The observed asymmetry of the signal could be due to the presence of slightly different groups in the polymeric network but could also reflect the presence of heteronuclear dipolar coupling between ^{13}C and ^{14}N. Asymmetric doublets have been observed for $^{13}C-^{14}N$ and $^{15}N-^{14}N$ spin pairs.[16,17] The splitting has been calculated using first-order perturbation theory for the case of dipolar interaction between a spin $S = ^1/_2$ and a spin $S = 1$, and the values are in good agreement with experimental values.[18] In the case of the nitrile group, the reported values range from 300 to 360 Hz, which is on the order of what is observed in the preceramic polymer. However, it should be noted that in a carbodiimide group, the dipolar coupling of ^{13}C with two equivalent ^{14}N nuclei must be considered. This situation prevents the direct use of the theoretical approach developed for the case of coupling with one $S = 1$ nucleus.

At 500 °C, the spectrum is very similar to that recorded on the polymer (Figure 3, curve b). A quantitative analysis of the CP spectra measured with variable contact times shows that the ratio between the carbodiimide and the methyl signals is 1.4 ± 0.1, which confirms that the C groups are intact at this temperature. After annealing the sample at 570 °C, no change in the peak positions is observed (Figure 3, curve c).

Curve d in Figure 3 exhibits the ^{13}C CP MAS spectrum of polymer **3** annealed at 600 °C. The peak in the aliphatic region at about 2 ppm is broadened. In the C sp^2 region, the signal due to carbodiimide groups is still present, and a broad signal appears around 160 ppm, which is assigned to a free-carbon phase formed during the decomposition of the organic groups.[19] To identify the 2 ppm signal, IRCP experiments with variable inversion times were performed (Figure 4).

In this type of experiment, the dynamics of polarization inversion depend on the proton environment.[20−22] An IRCP experiment was first performed on the 500 °C sample in order to obtain an appropriate reference for a methyl group in such polymeric networks (Figure 4a). The corresponding signal inverts at $\sim$100 μs, in agreement with values reported for methyl groups in poly(methylchlorosilanes).[8] One can note the slower dynamics of the carbodiimide group, due to weaker $^1H-^{13}C$ dipolar coupling. Similar behavior is found in the 600 °C sample (Figure 4b), indicating that the peak at 2 ppm is indeed only due to methyl groups. The presence of CH_2, or even CH groups, would lead to a more rapid signal inversion with an inversion time around 20 ms.[15,16]

The ^{13}C CP MAS study shows that methyl and carbodiimide groups are still present after pyrolysis at 600 °C. No evidence for the formation of CH_2 groups was found, indicating that neither Kumada rearrangement nor condensation between methyl groups occurred. At 600 °C, a free-carbon phase seems to form, as suggested by the presence of weak signals due to aromatic carbon atoms.

III.3.2. ^{15}N MAS NMR. The ^{15}N CP MAS NMR spectrum of the polymer (Figure 5, curve a) shows a unique signal at −323 ppm with a 350 Hz line width, which corresponds to the carbodiimide groups.

Between 570 and 600 °C, the signal is observed with an increasing line width and downfield shift (Figure 5, curves b−d). At 600 °C, the peak is centered at −319 ppm with a line width of 600 Hz. This signal should still arise from carbodiimide groups, but the broadening suggests some changes in the ^{15}N environments. At 800 °C, there is a poor signal/noise ratio despite the rather large number of scans that can be related to the low amount of hydrogen shown by elemental analysis (Table 1). The lack of protons prevents the detection of all the ^{15}N sites. At this temperature, the observed signal is shifted to about −310 ppm, a value close to that reported for silicon nitride phases ($\delta(\alpha\text{-}Si_3N_4) = -309.2$ ppm and

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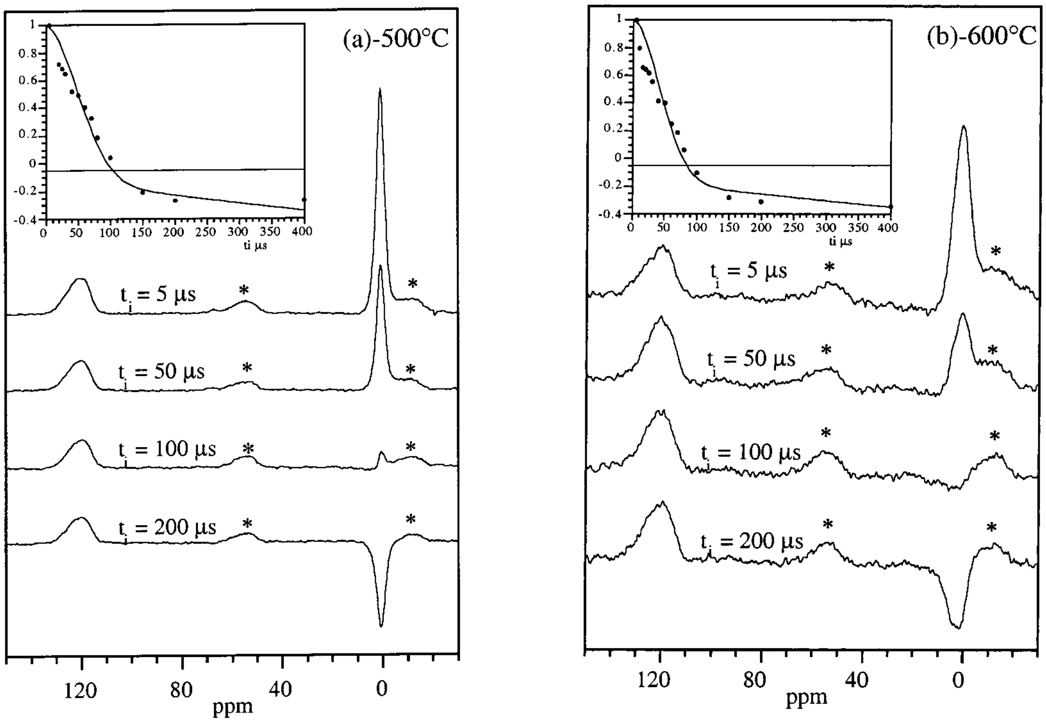

Figure 4. ^{13}C IRCP MAS NMR spectra of samples annealed at (a) 500 and (b) 600 °C (inversion times are indicated for each spectrum). The inset shows the inversion time dependence of the signal intensities for the peak at 1 ppm assigned to Si−CH$_3$ groups.

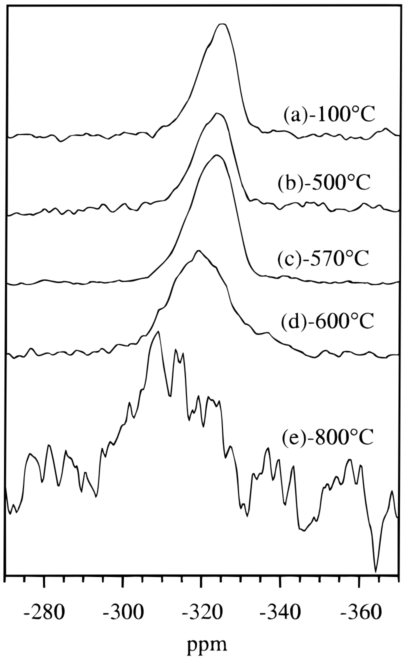

Figure 5. ^{15}N CP MAS NMR spectra of samples heated to (a) 100, (b) 500, (c) 570, (d) 600, and (e) 800 °C.

δ(β-Si$_3$N$_4$) = −306.7 ppm).[23] This behavior suggests the transformation of some carbodiimide groups into tertiary −N< sites.

III.3.3. *^{29}Si MAS NMR.* Figure 6 shows a series of ^{29}Si MAS NMR spectra recorded on samples pyrolyzed at temperatures up to 1200 °C. The polymer is characterized by a main peak at −59 ppm due to Me*Si*(N=C=N)$_3$ sites. A less intense signal is also present at −43 ppm, whose assignment is discussed later. The end groups, Me$_3$*Si*(N=C=N), are characterized by a peak at 1 ppm that disappears at 500 °C because of completion of the condensation reactions. At this temperature, the polymeric backbone remains unchanged, since the two resonance peaks at −43 and −59 ppm have the same relative intensities. Above 570 °C, new resonance signals appear, suggesting a large distribution of Si sites, especially at 600 °C. The number of sites then

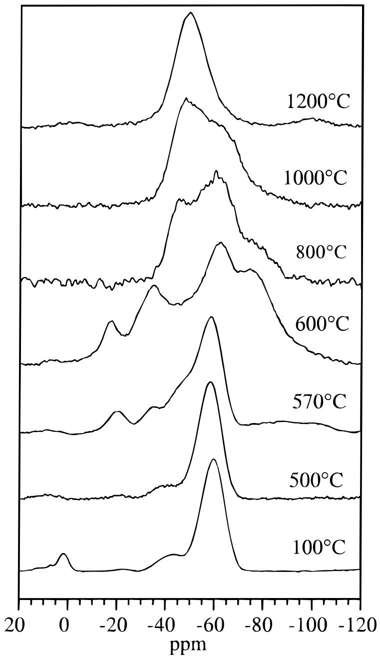

Figure 6. ^{29}Si MAS NMR spectra of samples heated at various temperatures (spectra of the samples heat treated at 100, 500, 570, and 600 °C were recorded with the CP sequence).

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decreases with increasing temperature so that at 1200 °C there is a unique signal at −49 ppm that is characteristic of $Si(-N<)_4$ sites such as those found in silicon nitride phases. The line width suggests that this phase is amorphous.

The temperature dependence of the NMR peak pattern suggests the formation of $-N<$ sites, with complete removal of the carbodiimide and methyl groups. Since the ^{13}C NMR results have only shown the presence of Me groups as aliphatic C in the pyrolyzed samples, it is proposed that the polymer-to-ceramic transformation results in a distribution of $Me_xSi(N{=}C{=}N)_y(-N<)_{(4-x-y)}$ sites (with $x = 0, 1$). IRCP experiments were performed in order to distinguish between sites with $x = 0$ and $x = 1$, since the presence of a methyl group directly attached to the Si site should strongly influence the dynamics of $^1H \rightarrow {}^{29}Si$ polarization transfer. Experimental and simulated spectra are shown in Figure 7 for samples heated from 500 to 800 °C. It is evident from this figure that the IRCP spectra are quite dependent on temperature.

In the 500 °C sample, all the signals are negative for an inversion time of 4 ms, as expected for Si sites bearing one methyl group.[8] In contrast, all the detected signals are positive for the 800 °C samples, which strongly suggests the presence of only $Si(N{=}C{=}N)_y(-N<)_{(4-y)}$ sites. In the 600 °C sample, both sites (with or without Me groups) are present. Identification and quantification of the various Si sites have been accomplished using a previously reported approach.[16] A series of IRCP spectra recorded with variable inversion times (a total of 17 spectra for each temperature) have been simulated by a single set of peaks with given positions and line widths but variable amplitudes. This procedure allows us to distinguish the various sites from the strongly overlapping peaks. A total of eight signals have been obtained and labeled from A to H with their chemical shifts summarized in Table 2. The peak labeling is shown in Figure 7. The proposed peak assignment is based on the IRCP behavior and the previously reported chemical shift values for $Si(N{=}C{=}N)_y(-N<)_{(4-y)}$ sites[5] (summarized in Table 3). The values for $y = 2$ and 3 have been extrapolated.

The chemical shift data have been used to simulate the spectra recorded for a single-pulse experiment and used to quantify the various $Me_xSi(N{=}C{=}N)_y(-N<)_{(4-x-y)}$ sites. Figure 8 shows the variation in the number of Si−Me, Si−N=C=N−, and Si−N< bonds per Si atom as a function of pyrolysis temperature. Three temperature ranges can be distinguished that are in perfect agreement with the TG/MS results. For $T \leq 500$ °C, the polymer network, mainly formed by $Me_xSi(N{=}C{=}N)_3$ sites, is thermally stable. The peak at −43 ppm might suggest the presence of some $Me_xSi(N{=}C{=}N)_2(-N<)$ sites. Between 500 and 700 °C, most of the methyl groups and some of the carbodiimide groups are consumed to form nitridic $-N<$ groups. When the temperature exceeds 700 °C, the residual carbodiimide groups also transform to $-N<$ sites with loss of N_2, as detected by mass spectrometry. Simultaneously, free carbon is formed according to ^{13}C NMR and bulk analysis studies.

III.4. Proposed Pyrolysis Mechanism. The analytical and spectroscopic results indicate that the process of forming a ceramic material from poly(methylsilsesquicarbodiimide) **3** can be divided into two principal stages.

(1) Between 550 and 600 °C methane is one of the two gases that have been detected. This evolution is characteristic of the cleavage of $Si-CH_3$ bonds and has already been reported for the pyrolysis of poly(methylsilazanes),[24] polycarbosilanes,[25] and polysiloxanes.[26] In contrast with the previous systems, some of the methyl groups originally bonded to silicon in **3** migrate to the carbon of the N=C=N unit and form acetonitrile, which is the second gaseous species detected in this temperature range. This mechanism leads to a complete rearrangement of the Si−N=C=N−Si backbone. The formation of nitridic Si−N bonds has been clearly identified by the ^{29}Si NMR study. The stoichiometric change from $SiC_{2.5}N_3(H_3)$ in polymer **3** to $SiC_{1.24}N_{2.50}$ (residual hydrogen is neglected for clarity) after annealing at 800 °C can be summarized by the following equation:

$$4[CH_3Si(N{=}C{=}N)_{1.5}]_n \xrightarrow{570-800\ °C} 4Si_{1.00}C_{1.25}N_{2.50} + 2CH_3{-}CN + CH_4 + H_2 \quad (2)$$

The theoretical weight loss corresponding to eq 2 is calculated to be 24 wt % and is in good agreement with the 22 wt % measured between 500 and 800 °C. The decrease in nitrogen content is only due to the formation of acetonitrile, CH_3CN. Therefore, 50% of the methyl groups bonded to Si must react with the carbodiimide group to give acetonitrile. Following eq 2, a 1:2 molar ratio of methane/acetonitrile is formed, implying that 25% of the remaining methyl groups form methane. Finally, the remaining 25% methyl groups give free carbon with the simultaneous evolution of hydrogen as detected by the TG/MS measurement. The formation of a free-carbon phase has been suggested by FT-IR and ^{13}C NMR spectroscopy of samples annealed at $T > 600$ °C.

Since the methyl/carbodiimide ratio is 1:1.5, $^2/_3$ of the carbodiimide groups remain unchanged in the polymer after the first ceramic formation step. This finding is consistent with the ^{29}Si MAS NMR spectrum that shows the presence of three different Si sites assigned to $Si(-N<)_{4-x}(N{=}C{=}N)_x$ $(0 \leq x \leq 2)$ in samples annealed at $T = 800$ °C.

(2) In the second ceramic transformation step between 800 and 1200 °C, only N_2 is detected, which is related to the decomposition of the residual carbodiimide units. According to elemental analysis, a significant part of the nitrogen content remains in the ceramic. The weight fraction of nitrogen decreases from 44.8 wt % at 800 °C to 33.8 wt % at 1200 °C, corresponding to the 10 wt % loss measured by TGA. As confirmed by ^{29}Si NMR spectroscopy, the material annealed at 1200 °C exhibits the presence of silicon atoms coordinated to four nitrogen atoms as in silicon nitride. Silicon attached to carbon can be excluded unambiguously from these measurements. Consequently, the amorphous Si−C−N obtained by the pyrolysis of poly(methylsilsesquicarbodiimide) **3** at 1200 °C in Ar may be considered as a

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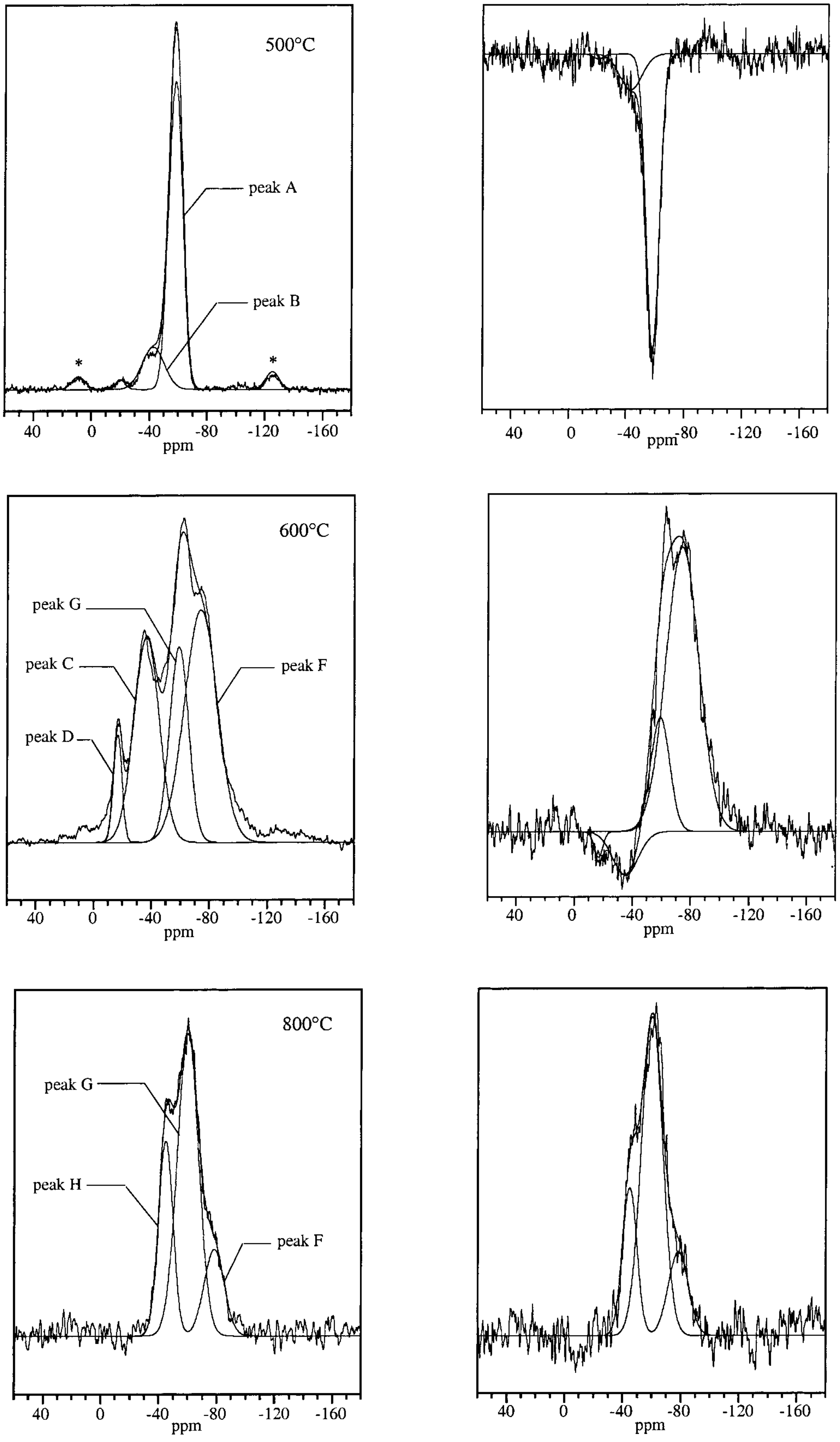

Figure 7. Experimental and simulated ^{29}Si IRCP MAS NMR spectra of samples heated to 500, 600, and 800 °C with $t_c = 6$ ms and $t_i = 5$ μs (left) and $t_c = 6$ ms and $t_i = 4$ ms (right).

mixture consisting of amorphous silicon nitride and carbon phases. The thermally induced transition between 800 and 1200 °C produces a composition that is close to 1 mol Si_3N_4 and 3 mol C (Table 1, Figure 2).

In contrast to the behavior of the poly(methylsilsesquicarbodiimide) system, the polymer-to-ceramic transformation of poly(methylsilazanes) leads to silicon carbonitride phases comprised of Si−C and Si−N bonds.[27]

Table 2. Assignments for the ^{29}Si Chemical Shift Data of Poly(methylsilsesquicarbodiimide), 3, Annealed at 600 °C in Ar

peak	chemical shift range (ppm)	assignment
A	−59	$\mathrm{Me}\mathbf{Si}(\mathrm{N{=}C{=}N})_3$
B	−48 to −43	$\mathrm{Me}\mathbf{Si}(-\mathrm{N}<)(\mathrm{N{=}C{=}N})_2$
C	−36 to −33	$\mathrm{Me}\mathbf{Si}(-\mathrm{N}<)_2(\mathrm{N{=}C{=}N})$
D	−20 to −17	$\mathrm{Me}\mathbf{Si}(-\mathrm{N}<)_3$
E	−88	$\mathbf{Si}(-\mathrm{N}<)(\mathrm{N{=}C{=}N})_3$
F	−78 to −71	$\mathbf{Si}(-\mathrm{N}<)_2(\mathrm{N{=}C{=}N})_2$
G	−60	$\mathbf{Si}(-\mathrm{N}<)_3(\mathrm{N{=}C{=}N})$
H	−49 to −45	$\mathbf{Si}(-\mathrm{N}<)_4$

Table 3. ^{29}Si Chemical Shift Values for $Si(\mathrm{N{=}C{=}N})_x(-\mathrm{N}<)_{4-x}$ Sites

$\mathrm{Si}(-\mathrm{N}<)_{4-x}(\mathrm{N{=}C{=}N})_x$	^{29}Si chemical shift (ppm)	ref
$\mathbf{Si}(-\mathrm{N}<)_4$	−49	17
$\mathbf{Si}(-\mathrm{N}<)_3(\mathrm{N{=}C{=}N})$	−67	5
$\mathbf{Si}(-\mathrm{N}<)_2(\mathrm{N{=}C{=}N})_2$	−80	*a*
$\mathbf{Si}(-\mathrm{N}<)(\mathrm{N{=}C{=}N})_3$	−90	*a*
$\mathbf{Si}(\mathrm{N{=}C{=}N})_4$	−104	5

[a] This work.

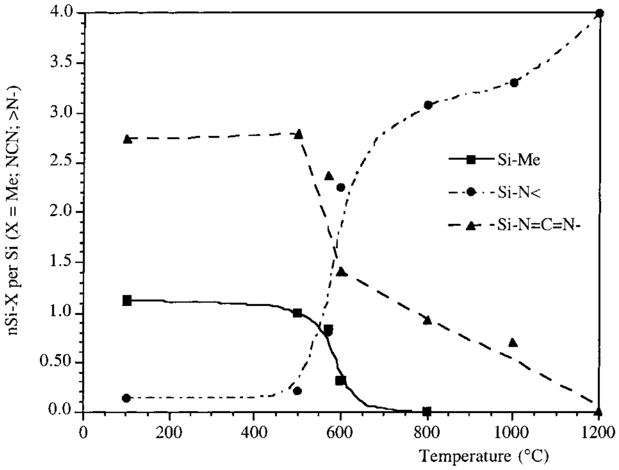

Figure 8. Variation of the number of Si−X bonds with X = Me, N=C=N, and >N− per Si atom as a function of the pyrolysis temperature. The data were derived from the ^{29}Si NMR study.

Accordingly, the pyrolysis process of poly(methylsilsesquicarbodiimide) **3** clearly differs from that of poly(methylsilazane). This behavior is mainly related to the specific reaction between the methyl and the carbodiimide group during the thermal decomposition.

III.5. Thermomechanical Analysis (TMA) and Hot Pressing of Compacted Poly(methylsilsesquicarbodiimide) Powders. The pyrolysis mechanism of poly(methylsilsesquicarbodiimide) can be of great significance for the preparation of bulk SiCN ceramics. Figure 9a shows the TMA study of a compacted poly(methylsilsesquicarbodiimide) **3** powder measured between room temperature and 1000 °C.

It is evident that up to 550 °C the sample shrinks in length, which is explained by a partial softening of the material. According to the proposed pyrolysis mechanism, the polymeric backbone is being rearranged with release of acetonitrile. The evolution of acetonitrile and methane at $T > 550$ °C causes foaming of the sample, with the result being the large expansion detected by TMA. Subsequently, densification is observed between 600 and 1000 °C. The pronounced expansion of the compacted green body could be utilized to produce ceramic foams.

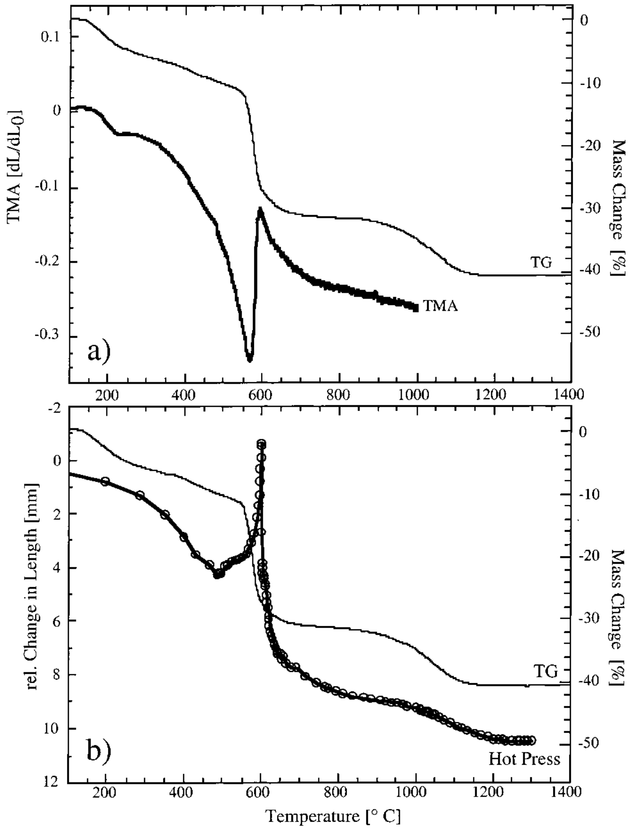

Figure 9. (a) Thermomechanical analysis (TMA) of poly(methylsilylcarbodiimide) **3** in comparison to the thermal gravimetric analysis (TGA), with heating rate of 2 °C/min in Ar. (b) Relative length change of compacted poly(methylsilsesquicarbodiimide) **3** powder during hot-pressing, with heating rate of 2 °C/min in N_2. The length change is not corrected for the expansion of the carbon piston.

The same behavior is found when densification is performed under hot pressing conditions with a constant load of 5 kN (Figure 9b). Up to 500 °C a shrinkage of the material is detected. In the range between 500 and 600 °C, the sample expands. Densification occurs at temperatures above 600 °C. After hot pressing, the resulting silicon carbonitride sample has a foamy consistence with a low mechanical stability. Consequently, the intermediate foaming of poly(methylsilsesquicarbodiimide) **3** during the polymer-to-ceramic transformation provides porous rather than dense silicon carbonitride matrices.

Once again this behavior contrasts with that found for poly(methyl(vinyl)silazanes), which can be processed to form dense SiCN ceramic monoliths with an open porosity below 3 vol %.[28] The polymer-to-ceramic transformation and densification processes of polysilazanes were also investigated by thermomechanical analysis (TMA).[28,29] In contrast to the thermal behavior of poly(methylsilsesquicarbodiimide) **3,** which is characterized

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by a stepwise weight loss up to about 1200 °C as shown in Figure 1, the mass loss of poly(methylsilazane) caused by the exclusive evolution of methane and hydrogen is completed at 800 °C. The [Si−N−] backbone of polysilazanes is similar to that found in the resulting silicon nitride matrix. Therefore, the rearrangement of the polymeric network such as that described for poly(methylsilsesquicarbodiimide) **3** is less pronounced for the polymer-to-ceramic conversion of polysilazanes.

IV. Conclusions and Outlook

The polymer-to-ceramic transformation of poly(methylsilsesquicarbodiimide) **3** in Ar up to 1200 °C gives an amorphous SiCN ceramic. The pyrolytic product is comprised of a mixture of amorphous Si_3N_4 and carbon. This result was derived from several spectroscopic (IR, NMR, TGA/MS) and analytical studies. In particular, the application of solid-state NMR spectroscopy details the significant changes occurring in Si-, C-, and N-coordination from pyrolysis of poly(methylsilsesquicarbodiimide) **3**. One principal result is that the silicon coordination changes from $CH_3{-}Si({-}N{=}C{=}N{-})_3$ at room temperature to $Si({-}N{<})_4$ at 1200 °C. A fraction of the carbon atoms present in the starting polymer remain as free carbon after decomposition.

The molar fraction of elemental carbon analyzed by chemical bulk analysis is 3 times higher than that of the amorphous Si_3N_4 formed. From thermodynamic considerations (eq 3), crystallization of the $Si_3N_4/3C$ reaction mixture at $T > 1440$ °C is expected to give stoichiometric SiC.

$$Si_3N_4 + 3C \rightarrow 3SiC + 2N_2 \tag{3}$$

The formation of polycrystalline SiC by this particular route is of great interest, since poly(methylsilsesquicarbodiimide) **3** can be processed by the sol−gel technique.[6,7]

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